16th International Conference on Plasma Surface Engineering

PSE 2018

Garmisch-Partenkirchen
September, 17 – 21, 2018

Abstracts

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Poster – Properties of technological plasmas (PO4072 - PO4094)
Beyond charge currents: spin and ion currents for future computing Technologies

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The era of computing technologies based on charge currents is coming to an end after more than 40 years of exponential increases in computing power that have been largely based on shrinking devices in two dimensions. A new era of “Beyond charge!” will evolve over the next decade that will likely be based on several new concepts. Firstly, devices whose innate properties are derived not from the electron’s charge but from spin currents and from ion currents. In some cases new functionality will arise that can extend charge based devices but in other case fundamentally new computing paradigms will evolve. Secondly, devices will inevitably become three-dimensional: novel means of constructing devices, both from bottom-up and top-down, will become increasingly important. Thirdly, bio-inspired devices that may mimic the extremely energy efficient computation systems in the biological world are compelling. In this talk I will discuss possible spintronic and ionitronic devices and how they may lead to novel computing technologies.

Keywords
Future Computing Technology
spin current
ion current
Plenary Lecture

Monday, September 17, 2018

PL0001

Plasma-based greenhouse gas conversion: Modeling the plasma chemistry and plasma reactor design to improve the application

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Plasma-based greenhouse gas conversion (mainly CO₂ and CH₄) is gaining increasing interest. To improve this application in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. We try to obtain this by computer modelling, supported by experiments. We simulate both the plasma chemistry as well as the optimum reactor design, in the three types of plasma reactors most commonly used for gas conversion, i.e., dielectric barrier discharges (DBDs), gliding arc (GA) discharges and microwave (MW) plasmas. For the plasma reactor design, we use 2D or 3D computational fluid dynamics modelling. For the plasma chemistry, we make use of zero-dimensional chemical kinetics modeling, which solves continuity equations for the various plasma species, based on production and loss terms, as defined by the chemical reactions. We focus especially on the role of vibrationally excited CO₂ levels, which are the key species for enhanced energy efficiency of the CO₂ conversion. Our model reveals the relative importance of various processes, responsible for the CO₂ conversion, in a range of different conditions, and this is linked to the energy efficiency in the various types of plasma reactors. We have also studied the plasma chemistry in CO₂/CH₄ and in CO₂/H₂O mixtures, with the purpose of producing value-added chemicals. The main products formed are a mixture of H₂ and CO, or syngas, with a tuneable H₂/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds, such as methanol, formaldehyde, etc, is very limited, showing the need for combining with a catalyst. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to further improve the formation of value-added products.

Keywords
CO₂
plasma chemistry
plasma reactor design
chemical kinetics modeling
fluid dynamics modeling
Nonthermal biocompatible plasma (NBP) sources and their applications to plasma medicine, agriculture and food technologies

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Nonthermal biocompatible plasma (NBP) sources and their characteristics operating at atmospheric pressure have been introduced for plasma medicine, agriculture, and food technologies, especially developed and used in Plasma Bioscience Research Center (PBRC). The electron temperatures and plasma densities are characterized to be 0.8 ~ 2.1 eV and 3×10¹⁴ ~ 5×10¹⁵ cm⁻³, respectively, for the NBP soft jet and micro-DBD sources [1]. Here, the various applications of these NBP sources to plasma medicine including rescue vehicle sterilizer, plant growth, agriculture, and food technologies will be discussed by RONS generation mechanism inside the liquid, so called synergistic action of plasma initiated UV photolysis [2] and molecular-transport diffusion processes.

We have investigated neural differentiation [3] for degenerate neural diseases and enhanced anticancer effect of monocytes and macrophages activated by NBP which act as immune-modulator on these immune cells. Recently, we also apply DBD plasma and PEG-coated gold nano particles synergistically in-vivo on the solid cancer cells to enhance apoptosis of lung cancer efficiently. High voltage nanosecond pulsed arc-plasma and DBD plasma devices could be also applied to rice, spinach (Spinacia oleracea) and coriander (Coriander sativum) in both air and N₂ environments for inactivation of fungi, enhancement of germination and seeding growth rate along with enhancement of disease resistance and beneficial bacteria. The cylindrical DBD plasma with underwater bubbler could also be used as an environmentally friendly food disinfection device in cleaning processes of the food industry by lipid peroxidation of cell membranes.


Keywords
Nonthermal biocompatible plasma (NBP) plasma medicine and agriculture food technologies plasma initiated UV photolysis and molecular-transport diffusion process
Nanogenerator for self-powered systems, robotics, artificial intelligence and blue energy

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Self-powered system is a system that can sustainably operate without an external power supply for sensing, detection, data processing and data transmission. Nanogenerators (NG) were first developed for self-powered systems based on piezoelectric effect and triboelectrification effect for converting tiny mechanical energy into electricity, which have applications in internet of things, environmental/infrastructural monitoring, medical science, environmental science and security. Here, we first present the fundamental theory of the NGs starting from the Maxwell equations. In the Maxwell’s displacement current, the term related to time variation of electric field gives the birth of electromagnetic wave, which is the foundation of wireless communication, radar and later the information technology. Our study indicates that, owing to the presence of surface polarization charges present on the surfaces of the dielectric media in NG, an additional term related to time variation of surface polarization density should be added in the Maxwell’s displacement current, which is the output electric current of the NG. Therefore, our NGs are the applications of Maxwell’s displacement current in energy and sensors. NGs have three major application fields: micro/nano-power source, self-powered sensors and blue energy. We will present the applications of the NGs for harvesting all kind mechanical energy that is available but wasted in our daily life, such as human motion, walking, vibration, mechanical triggering, rotating tire, wind, flowing water and more. Then, we will illustrate the networks based on triboelectric NGs for harvesting ocean water wave energy, for exploring its possibility as a sustainable large-scale power supply. Lastly, we will show that NGs as self-powered sensors for actively detecting the static and dynamic processes arising from mechanical agitation using the voltage and current output signals.

Keywords
Nanogenerators
Organic materials
self-powered system
blue energy
For nearly all engineering products, it is their surfaces which define their functionality and practical performance, including their operating lifetime. Coatings are therefore critical to the enhancement and optimisation of products in all application sectors. Usually these coatings have to fulfil several requirements simultaneously. This is especially true of tribological coatings which often have to resist different wear mechanisms whilst also providing protection in different operating environments. A suitable approach to the design and selection of coatings is to categorise the types of contact occurring and to base the selection around design rules for each type of contact. This then allows combined contact types to be considered. The concept can be extended to the testing procedures for coatings. The presentation discusses 7 typical contact types (static, sliding, contact fatigue, fretting, abrasive, impact and corrosive) and the design rules pertinent to each one, emphasising the property requirements from a coating in each case (such as toughness, hardness elastic modulus and elastic strain limit). The implications for coating selection and development are outlined, emphasising the benefit of nanocomposite coatings and duplex systems. The use of this selection approach in industrial coating development is discussed, mentioning the different requirements that can be placed on the mechanical properties of coatings- not only wear resistance, but other factors such as the ability to remain bonded even under severe substrate deformation, or even to permit a controlled degree of wear, for example to assist with maintaining a seal or to enable “running in” and to accommodate part misalignments or defections. We have moved on a long way from the days when it was thought that increasing hardness should be the main aim of those developing tribological coatings, and the talk will illustrate that fact.

**Keywords**
Tribology
Coatings
Selection
Bio-functionalized surfaces are of great interest for a wide range of applications, particularly in biomedical diagnostics and implantable medical devices. We have shown that radicals embedded in polymeric surfaces facilitate simple, one-step surface-functionalisation [1]. The radicals are created by energetic ion bombardment of the surfaces. Covalent immobilisation of functional molecules is achieved by immersion or spotting / painting of the biomolecule-containing solutions onto the activated surfaces. This strategy simplifies covalent functionalisation of surfaces enormously, eliminating the need for wet-chemistry and the associated solvent disposal and yield problems. This approach has been used to immobilise bioactive peptides, antibodies, enzymes, single stranded DNA, and extra-cellular matrix proteins [2] onto many materials, including polymers, metals and ceramics.

This presentation will expound the fundamental science underpinning these new approaches. Process adaptions that extend the application of these techniques to functionalisation of the internal surfaces of complex, porous materials and structures will be explored. New applications enabling biological studies of the response of individual cells to proteins on a sub-cellular scale [3], and the preparation of multi-functionalisable nanoparticles for theranostics [4] will be elucidated. Finally, we describe recent work which shows that spontaneous covalent immobilisation enabled by surface embedded radicals allows control of the density and orientation of surface-immobilised bioactive peptides [5]. This is achieved by tuning electric fields in the double layer at the surface during the immobilization through pH variations and/or the application of external electric fields as delivered by a simple battery.


Keywords
radical enabled functionalisation
Advancements and perspectives on plasma-deposited polymer coatings in the legacy of Riccardo d’Agostino

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Riccardo d’Agostino has left us a few months ago, after 40 years and more of a bright career at the University of Bari mostly devoted in investigating plasma deposition, treatment and etching processes, and in developing their applications in Material Science and Technology. This talk is intended to highlight in brief the main achievements obtained in the group of Prof. d’Agostino in years, in the contest of the international Plasma Science and Technology community, as well as to describe Low Pressure and Atmospheric Pressure plasma deposition processes recently developed in Bari for several applications, including nano/bio-composite coatings and free-standing “nano-films”.

Keywords
PE-CVD
applications of plasma deposited polymers
nano/bio composite coatings
nano films
PL0007

**Plasma/target interactions in biomedical applications of cold atmospheric pressure plasmas**

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The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature plasmas, especially with plasma sources working at atmospheric pressure. In this new trend, beside decontamination/sterilization and surface treatment which have already a quite long story through low pressure plasma research and developments, medical applications are tacking an increasing place underlined by the actual numerous clinical trials. Medical applications of low temperature plasmas now concern a very wide range of domains, including primary hemostasis and blood coagulation, dental care, skin decontamination and hygiene, wound and ulcer treatment, dermatology, cancer treatment. Biological applications are also now extended to agriculture and, more recently, to cosmetic. Despite the huge number of in vitro and in vivo experiments there are still numerous challenges to overcome linked to the nature of the encountered target (biological tissues and materials, organs and their direct environment, liquids) that have a direct effect on the produced plasma itself and on the generated species.

In this talk, after a presentation of the context, the plasma devices, and the main applications, we will focus on the different problems linked to the plasma/target interaction, including treatments of tissues and liquids. Beside the induced changes in gas flow, the radical production and the potential role of the strong electric field generated around the plasma plume of atmospheric plasma jet systems, we will discuss possible changes induced in microenvironment of living targets. Throughout this presentation, we will emphasize on the fact that plasma diagnostics must be performed in real treatment conditions. We will also tackle the main issues, challenges and opportunities linked to the control of these multimodal action of non-equilibrium cold plasmas on living organisms.

**Keywords**
Atmospheric pressure plasma
plasma medicine
biological applications
plasma tissue interactions
plasma liquid interactions
Plasma Physics of Sputtering Magnetrons Revisited

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Sputtering magnetrons are widely used to make thin films and are generally considered a mature technology. Over the last years it has become known that magnetrons show surprisingly rich physics based on plasma instabilities. Without these instabilities, magnetrons would generally not work. Key to a magnetron’s operation is the generation a magnetically enhanced glow discharge plasma with closed electron drift. The energy needed to produce plasma, i.e. to ionize atoms of the process gas and those sputtered or outgassed from the target, is delivered by sufficiently energetic “hot” electrons. Key to a functioning magnetron is thus the electron heating mechanism and the presence of atoms to be ionized, which in the case of HiPIMS, may primarily come from the target, not the background gas. Both electron heating and atom density are generally not uniform. Recent theoretical [1], spectroscopic [2], and probe data [3] prove that most of the electrons’ energy comes from the presheath, and is provided by localized electric fields concentrated at the edge of “ionization zones” or “spokes” [4, 5]. This is closely related to self-organization and turbulence as visualized in interesting images of magnetron plasmas.

Most experimental work reported here was done at Lawrence Berkeley National Laboratory, Berkeley, CA, in collaboration with Yuchen Yang, Matjaz Panjan, and others, whose contributions are gratefully acknowledged.


Keywords
magnetron sputtering
plasma diagnostics
electron heating
plasma instabilities
spokes
Benefits and challenges for atomic layer deposition in organo-metal halide perovskite solar cells

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Within the class of emerging photovoltaic technologies, organo-metal halide perovskite solar cells have exhibited a sky-rocketing conversion efficiency above 20% in just a few years. In this contribution I will address the opportunities which atomic layer deposition (ALD) offers to perovskite solar cells by highlighting the following merits: film growth conformality, engineering of charge transport layer/perovskite interfaces and compatibility with low-temperature processing. Specifically, two case studies will be presented:

- Extremely thin ALD Al₂O₃ layers (< 1 nm) conformally decorate the hybrid perovskite crystals and improve the environmental stability of the absorber, and well as lead to an increase in perovskite cell efficiency up to 18% (with respect to the pristine device of 15% efficiency).

- Plasma-assisted ALD TiO₂ is adopted in mesoscopic perovskite solar cells, with the purpose of suppressing charge recombination processes at the ITO/mesoscopic scaffold/perovskite interface. The superior performance of 10 nm thick ALD TiO₂ layers with respect to conventionally adopted spray pyrolysis TiO₂, is explained by a lower reverse dark current measured for ALD TiO₂. Electrochemical analysis points out a lower level of defects (i.e. pinholes) in ALD TiO₂, with respect to spray pyrolysis TiO₂, as key to suppress shunting paths leading to electron-hole recombination. Since ALD TiO₂ is carried out at temperatures below 150°C, flexible perovskite solar cells are tested, exhibiting a conversion efficiency of 10.8% under indoor illumination, comparable to the performance of flexible dye-sensitized solar cells.

This contribution will end by discussing the challenges yet to be met by ALD processing directly on the perovskite absorber, without affecting the opto-chemical and morphological perovskite properties.

Keywords
plasma
ALD
interface engineering
perovskite solar cells
Diagnostics and Monitoring of Thermal and Plasma Enhanced Atomic Layer Deposition of Titanium Nitride

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Atomic Layer Deposition (ALD) is a rapidly evolving technique allowing one to produce films for optoelectronic, microelectronic and other nanotechnology applications with unprecedented quality and precision. Further development and optimization of the ALD processes requires novel approaches and diagnostic tools for the process control and monitoring. In the present work, we study the deposition process of TiN films obtained from TiCl₄ as a precursor for Ti, and NH₃ vapor or Ar/N₂/H₂ plasma as a reducing agent in thermal and plasma-enhanced (PE) ALD modes. High sampling rate in-situ spectroscopic ellipsometry was used to provide the insight into the TiN growth kinetics, specifically the thickness and the optical and electrical properties. Chemical reactions were assessed by optical emission spectroscopy directly in the reaction zone as well as in the downstream pumping line. In the latter case we used a remote plasma spectroscopy concept in which secondary plasma was generated within the sensor head, and its emission was analyzed by a spectrometer. We found that the high-voltage Penning-type discharge gives rise to an intensity enhancement of the N₂⁺ first negative band head at 391.4 nm, making it possible to follow the relatively small changes in the downstream concentration of nitrogen in relation to its consumption by the ALD reaction. In addition, mass spectrometry measurements were performed to obtain complementary information about the reaction dynamics.

Films obtained in both configurations are compared for their stoichiometry, concentration of contaminants (oxygen and chlorine), resistivity, and growth rate per cycle. Based on the results, we discuss the capabilities and limitations of the different diagnostics techniques in thermal ALD and PEALD configurations. Appropriate use of such techniques allows for rapid optimization of the ALD process, better reproducibility, and improved properties of the deposited films.

Keywords
PEALD
Titanium nitride
Plasma diagnostics
Optical emission spectroscopy
**Plasma enhanced atomic layer deposition of metal thin films**

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Copper and aluminum thin films were deposited by plasma enhanced atomic layer deposition at low temperature, using copper(I)-N,N′-di-sec-butylacetamidinate ([Cu^{I}Bu-Me-amd])_2 and trimethylaluminum (Al(CH_3)_3) as precursor, respectively, and hydrogen as reductive gas for both deposition. Influence of temperature, plasma power, mode of plasma and pulse time on deposition rate of thin film, purity of film and step coverage were studied, feasibility of copper film deposition on inner wall of carbon fiber reinforced plastic waveguide with high aspect ratio was also studied. Morphology and composition of thin film were studied by atomic force microscope and X-ray photoelectron spectroscopy, respectively. Square resistance of thin film was also tested by four probe technique. On the basis of on-line diagnosis, a growth mechanism of thin films was put forward, it was considered that surface functional group play an important role in the process of nucleation and determined property of thin film. High density of plasma and high content of free radical were helpful for deposition of metal thin films. Copper film with high purity required by waveguides can be deposited on the inner wall of waveguides by ALD, with some contaminants of oxygen and carbon only on the surface of thin films.

**Keywords**

Atomic layer deposition
Copper
Aluminum
Thin film
Plasma
OR0103

Plasma Activation and Plasma-assisted ALD Surface Modification of Polymers for Improved Bonding and Adhesive Strength

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Bonding strength is crucial on polymers of low surface energy, for clean surfaces limited to 0.5, 1, and 2 MPa for PTFE, PP, and PE. Plasma treatment may improve bonding strength by a factor of 2 (PTFE) or 5 (PP and PE). The efficiency of treatment is usually 10% as both low pressure and atmospheric pressure processes show low topographic conformity. Besides, lifetime of activation/modification is rather short. Hence, bonding has to be carried out immediately after plasma treatment.

The concept of plasma-assisted ALD (atomic layer deposition) interlayers was introduced in the project HARFE of SENTECH (modification/deposition/in-situ monitoring) and BAM (bonding, characterization, testing). ALD deposition has a high surface conformity and for dielectric films of Al₂O₃ also a good long-term stability given that the films are dense enough. Based on TMA and O₂/O₃ precursors, ALD layer stacks from 60 to 375 monolayers were prepared under different conditions. For a transfer time of 24 hours from deposition to measurement, bonding strength could be increased up to 5 MPa (PTFE) respectively 10 MPa (PP, PE). The huge potential of ALD layers as adhesive interlayers was demonstrated for Al₂O₃ on stainless steel with bonding strength beyond 15 MPa, i.e. interface strength within the ALD stack is also in this range.

This is a prerequisite for subsequent PVD/CVD-deposition in hybrid systems. By means of the SI ALD LL system of SENTECH thermal and plasma-supported ALD processes can be alternatively realized. Ellipsometric in-situ monitoring provides monolayer sensitivity and reveals that the efficient bonding of the lower ALD layers on the polymer has to be further improved. Testing of bonding strength was realized by CAT (centrifugal adhesion testing) technology. It was shown that ALD modification correlates with the increase of surface energy and bonding strength.

Keywords
plasma activation
plasma-assisted ALD modification
adhesive ALD interlayer
bonding strength
adhesive strength
Substrate effect on the dielectric constant of TiN films grown by plasma enhanced atomic layer deposition

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TiN films have gained much interest because of its low resistivity and compatibility with the materials used in semiconductor fabrication. TiN thin films have been applied to electrodes for DRAM capacitor and diffusion barrier for metalization. In recent, plasma enhanced atomic layer deposition (PEALD) has been employed to deposit the TiN films due to its excellent conformality, precise thickness control of nm, and reproducibility. The common method determining the thickness of TiN is measuring the sheet resistance with a 4-point probe. In addition to 4-point probe, spectroscopic ellipsometry (SE) is an effective and nondestructive method which is commonly used to measure the thickness and dielectric constant of thin films. As TiN film grown with an ALD is very sensitive to the substrate material, the dielectric properties of TiN varies with substrate. In this work, the optical properties of TiN were investigated with several substrates of oxide films.

A 20-nm TiN films were deposited on Si and ultra-thin SiO2, Al2O3, HfO2, and SiN substrates using TiCl4 and NH3 as precursors in the PEALD chamber. To get the precise dielectric constant, at first, the film thickness were evaluated with 4-point probe and high resolution TEM images. The dielectric constant were fitted with the combination of Lorentz oscillator and Drude model in the range of 1.5-5.0 eV. The dielectric function of TiN is varied with the substrate material, especially near 2.5 eV with a different peak feature. This difference is discussed with the physical and chemical properties of TiN and substrate: the surface roughness of both substrate and TiN film itself analyzed by AFM, the crystalline status of TiN measured by XRD, and the chemical state of TiN measured by XPS.

Keywords
PEALD
TIN
Dielectric function
Substrate
Pathways for the preparation of technologically important metal oxides

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The growth of metal oxide thin films is studied by molecular dynamics (MD) simulations. The overall aim is to define pathways for the low-temperature preparation of desired crystalline phases. Because the success and reliability of classical MD in general and growth simulations in particular strongly depends on the interaction potential (force field), the first part of the contribution presents an algorithm for the development of interaction potentials optimized for the growth simulations. Most importantly, and contrary to most of the literature, the newly developed potentials correctly reproduce the preferred coordination number of individual elements. The second part of the contribution uses the reliable interaction potentials in order to investigate the relationships between the (i) process parameters such as energy delivered into the growing films (E), energy distribution function of the particle flux (EDF), temperature (T) and growth template and (ii) film characteristics such as densification, crystal nucleation, uninterrupted crystal growth and its dependence on the crystal orientation. The results show that and how the characteristics of individual phases depend not only on E (i) per fast atom (ion) or (ii) per any atom, but especially on the (iii) EDF (particularly the fraction of fast atoms in the particle flux) and (iv) mass (momentum) of fast atoms. There is a difference between conditions for crystal nucleation (often difficult, T-dependent) and for uninterrupted growth of existing crystals (for some phases and orientations much easier and almost T-independent). Optimum EDFs which allow uninterrupted growth of densified difficult-to-prepare phases at as low T and/or E as possible are characterized by (i) narrow EDF around a material-dependent optimum value and (ii) high momentum delivered into the growing films.

Keywords
molecular dynamics
crystal nucleation
crystal growth
metal oxides
Thickness prediction and uniformity optimization of films deposited by PVD on complex substrates in motion

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Plasma thin film (≤10 µm) deposition nowadays state-of-the-art technology is used to provide added value to 2D and 3D complex substrates. Nevertheless, the deposition of films with uniform thickness on 3D complex shapes is still a challenge for various deposition systems. In the case of magnetron sputtering, concavities and different substrate orientations lead to macroscopic shadowing and affect the thickness uniformity. Also, the thickness uniformity for each part may be strongly affected by the load ratio of the chamber. The aim of this work is to present the current state of the implementation of multiple algorithms to tackle the challenge: the prediction and optimization of films thickness deposited by PVD technics on complex shapes in rotation.

First, we use oriented meshed objects to describe the complex shape of the substrate. This meshing is performed with a Delaunay triangulation to minimize the triangular meshes angles. Secondly, we compute the start positions, directions and energies of the particles. Thirdly, these are transported through the gas phase by a combination of a 3D Monte-Carlo simulation describing the transport and a “Pseudo-Verlet-linked-cells-list” algorithm used to speed-up the simulation. For the detection of the atoms on the meshes, we use techniques of back-faces culling which take automatically into account the shadowing from the substrate itself or from other substrates in the chamber. This combination of algorithms allow us to predict the films thickness on a high amount of substrates in motion (multiple rotations) in a chamber whatever the cathode shape, position and the metal sputtered. Finally, a genetic algorithm is combined to the transport code to obtain the best experimental parameters leading to the maximum of uniformity. Experimental chrome deposition with a bipolar pulsed system on high shadowed substrates installed on planetary rotation axis has been performed to validate the code. Experimental and simulation results presents a general good accordance.

Keywords
PVD
Simulation
Uniformity Optimization
Complex substrates
Particle Impact Induced Point Defect Structure of Titanium Nitride

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Physical vapor deposition (PVD) of titanium nitride (TiN) thin films in case of highly ionized discharges (e.g., HPPMS, cathodic arc) are inherently dependent on particle bombardment at the respective surface site (atop Ti, atop N, Ti-N bridge). In particular, the redistribution of the kinetic energy of the impinging titanium particles (i.e., 100 eV and onward at the target) and the implied structural changes at the atomic scale need to be understood, both qualitatively as well as quantitatively. In the literature fundamental TiN surface and large-scale film growth dynamics have been investigated extensively by D. Sangiovanni and coworkers for low energetic particles [1], whereas a supplementary study of small-scale growth processes has been published as well [2]. A complementary analysis of sputtering by highly energetic ion bombardment has not been reported yet. In this study, a more unified perspective is attained with the aim to cover the complete energy range from growth to sputtering conditions. Hence, for a wide range of kinetic energies deposited at the surface sites (specifically, from 20 to 200 eV) the collisional generation, the evolution, and the relaxation of point defects are investigated. A twofold simulation approach is pursued: Classical molecular dynamics (MD) simulations of the particle impingement on TiN(001) are compared with the outcome of ab initio MD computations. The latter are based on effective thermal spike simulations for which the generation of Frenkel pairs is taken to model the impact of energetic ions (i.e., for energies $\varepsilon > 45$ eV) [3,4]. Together, the development of the titanium nitride point defect structure induced by energetic particle bombardment is discussed in terms of changes in the potential energy surface.

This work is supported by the German Research Foundation (DFG) in the frame of the transregional collaborative research centre SFB-TR 87.


Keywords
Physical vapor deposition
Molecular dynamics
Instabilities in magnetron plasma and electron transport

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Magnetron plasma presents common features with other magnetized plasmas such as Hall thrusters, and in both, localized density structures – so called spokes – have been reported. Spokes are present in the direct current discharges as well as in high power impulse magnetron sputtering (HiPIMS) and they can be at the origin of the abnormal electron transport.

Recently, LPGP (Orsay) modeling team has developed a particular approach called Pseudo-3D [1] as an extension of the PIC-MCC (Particle-in-Cell Monte Carlo Collision) approach, called OHiPIC (Orsay High Density Particle-In-Cell). It models the plasma behavior in the azimuthal direction in the magnetized trap, just above the target either in DC or in HiPIMS mode. The results undoubtedly show high frequency instabilities lying in the range of MHz, in addition to centimetric space structured plasma as previously observed by other groups by fast camera, for instance.

The coherent Thompson scattering experiments performed with the Praxis diagnostic platform (ICARE) can record the electron instabilities in the plasma, and especially in the magnetized region. The measurements found the same MHz fluctuations of the electrons, compatible with the electron cyclotron drift instabilities [2].

Very recently, ICARE team has developed a complementary incoherent Thompson scattering platform THETIS (THomson scattering Experiments for low Temperature Ion Sources). Hence, for the first time it was possible to measure the electron density and temperature in front (few mm) of the magnetron target, in DC and HiPIMS without disturbing the plasma.

Experimental and modeling results are in good agreement and they are compared and commented.


Keywords
Magnetron Plasma
Magnetron Sputtering Depositions at Oblique Angles on Seeded Substrates for the Development of sub-Micron Structural and Chemical Patterns

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Thin films grown at oblique geometries by magnetron sputtering are well known for their high porosity and the formation of quasi-periodic tilted nanocolumnar arrays, whose morphology depends on the deposition conditions. We demonstrate that the existence of periodic or quasi-periodic patterns on the film substrate previous to the deposition originate a vast phenomenology of novel nano- and microstructured layers, whose chemical composition may also vary in the same spatial scale range. The result of numerous depositions of SiO\textsubscript{2} and SiO\textsubscript{x} thin films on laser-patterned and ion-induced rippled substrates will be shown, supported by numerical simulations. It is found that the morphological patterns follow similar wavelength than that defining the distribution of seeds on the substrate for thicknesses in the order of 1 micron. For higher thicknesses, the substrate information is progressively lost and a fast convergence to typical morphologies of films grown on flat substrates. In addition, under certain conditions, surface protuberances may induce the appearance of compositional patterns in the same scale length as that of the seeds. Overall, an overview of a new variety of porous micro and nanostructures available by magnetron sputtering will be given, as well as the main principles governing the formation of such structures. The results of numerous experiments and numerical simulations will be presented and insights on the potential applications of these nanostructured layers given.

Keywords
Magnetron Sputtering
Seeded Substrates
Porous Thin Films
Monte Carlo Simulation
Fundamental Atomistic Processes
Microstructural study of antibacterial Zr-Cu, Zr-Ag and Zr-Cu-Ag thin films

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The controlled synthesis of metallic thin films (TFs) is crucial in many applications. Zr-, Cu- and Ag-based TFs may be suitable candidates for infrared reflector, decorative, antibacterial or electronic applications. In this context, the development of thin film metallic glasses (TFMGs) has also received an active interest due to promising mechanical and physicochemical properties. On the other hand, combinatorial thin film approach has been widely used to study composition-structure-property relationships and to discover new functional materials. Films representing a large chemical composition range are deposited in a single synthesis step, which is particularly convenient for the study of phase diagrams, compared to the traditional one-alloy-at-a-time method.

In the present work, Zr-Cu, Zr-Ag and Zr-Cu-Ag alloy systems are investigated by combinatorial thin film approach using PVD magnetron co-sputtering. Detailed structural, microstructural and chemical investigation is performed using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Zr-rich TFs can be described by three distinct structures, depending on pressure and temperature. In this context, the influence of copper content on the formation of hexagonal metastable structure (ω-Zr) is firstly studied. On the other hand, binary Zr-Cu films, deposited by magnetron sputtering, is known to exhibit a glassy-like microstructure in a wide composition range. The Zr-Cu TF microstructure is secondly discussed with regard to deposition parameters, such as oxygen content and sputtering method. Finally, ternary Zr-Cu-Ag TFMGs deposition is investigated in relation to the development of antibacterial coatings.

Keywords
Thin film metallic glasses
Sputtering
Antibacterial
High performance antibacterial thin films for titanium biomedical components

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Titanium and Ti alloys are extensively used in biomedical market due to their excellent biocompatibility and high corrosion resistance in the human body fluids. However, they exhibit poor mechanical properties and inadequate antibacterial properties. Currently, one of the main concerns in biomedical market, is the microbial infection of the components which leads to their failure after long time exposure due to bacterial colonization. Particularly, microorganisms are abundant in the oral environment where dental implant failure can be a direct consequence of serious microbial attack and hence, new Ti based biomaterials with the desirable antibacterial properties are essential for high quality implant performance.

In this study, high durability coatings with antibacterial properties are investigated to be applied of Ti dental implants. Tantalum nitride thin films deposited by High Power Pulsed Magnetron Sputtering (HPPMS) technique incorporating antibacterial agents are developed. TaN is well known as high corrosion and wear resistance thin film in biological environment. To provide to the TaN thin film the antibacterial property, silver (Ag) is incorporated into the matrix by co-sputtering of Ta and Ag in N$_2$/Ar reactive atmosphere. Although the benefits of Ag to attack bacterial colonization are well documented, the Ag dose needs to be accurately controlled to avoid Ag from becoming cytotoxic.

Different composition and microstructure TaN _Ag films are grown in this work. Tribocorrosion performance of TaN _Ag films with different Ag atomic contents in oral environment was investigated to evaluate the durability of these surface treatments. Cytotoxicity (cell viability) tests and antibacterial tests against different bacteria were performed on TaN _Ag films with different Ag contents.

Keywords
Implants
TaN
Silver
Antibacterial
Plasma polymer based coatings with tailor-made antibacterial action

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Bacterial infection is a frequent complication associated with the use of medical implants. Onset of such implant-related infections is commonly connected with a biofilm formation on their surfaces. Once formed, a biofilm is extremely difficult to eliminate even with vigorous use of antibiotic treatments as the biofilm populations are less susceptible to most of known antibiotics. This often results in a necessity to increase the dosage of antibiotics and with it connected possible undesirable side-effects. An alternative strategy that gains increasing attention is to prevent biofilm formation on implanted devices that may be achieved by their coating with thin antibacterial films. In this study we investigated two possible approaches for production of such antibacterial coatings. The first one is based on the impregnation of nitrogen-rich plasma polymer film (magnetron sputtered nylon 66) with bioactive molecules (antibiotics in this study). It is shown that the amount of bactericidal agents released from the impregnated films as well their release kinetics may be controlled in the wide range either by the amount of impregnated bioactive molecules or by the additional barrier plasma polymer film deposited on the top of the antibiotics-loaded coatings. The second followed strategy was based on the use of plasma polymer/Cu NPs/plasma polymer sandwich structures that were prepared by combination of gas aggregation source of Cu NPs and magnetron sputtering of polymeric targets. The antibacterial efficiency of such nanocomposites was found to be again tailorable by the amount of Cu NPs or by the thickness of the top-most film of plasma polymer. Finally, it was proved that both strategies can be combined that may offer the possibility to design coatings with desired course of their antibacterial action.

This work was supported by grant GACR 16-14024S (Grant Agency of the Czech Republic) and grant GAUK 1394217 (Grant Agency of Charles University).

Keywords
antibiotics
nanoparticles
Implant-related bacterial infections remain a serious problem that is not solved yet. Herein we combined several antibacterial agents to achieve synergistic effects and broader protection of widely used metallic implants. Various strategies for development of bioactive and bactericidal films with various antibacterial components (Ag nanoparticles, antibiotics) that can rapidly inhibit infection and provide long-lasting antibacterial effect are considered. Approaches to the fabrication of bactericidal surface included doping with bactericidal elements, loading of antibiotic into specially formed surface cavities, and a combination of these methods. Surface modification to produce a specific surface relief can also be utilized to control bactericide metal ion release. The obtained results show that under optimal surface chemistry and topography conditions the material can be biocompatible, bioactive and bactericidal. Different types of synergistic effects are discussed: (a) dependence of Ag$^+$ ion release versus Ag content in the film and surface roughness and (b) enhanced antibacterial activity of Ag$^+$ ions and antibiotics. It is demonstrated that silver can be successfully coupled with different types of antibiotics to provide innovative hybrid metal-ceramic bioconstructions that are able to deliver precise doses of bactericide agents within a certain period of time and are equally effective against gram-negative and gram-positive bacteria and fungus. In addition, crosslinking reaction between gentamicin and TiCaPCON film resulted in the formation of a relatively stable drug/film conjugate preventing rapid dissolution of gentamicin and ensuring its long-term (for 72 h) antibacterial protection. These results open up new possibilities for the production of cost-effective, scalable, and biologically safe implants with pronounced antibacterial characteristics for future applications in orthopedic field.

**Keywords**
- Films
- Bactericide release
- Biocompatibility
- Bioactivity
OR0304

**Assembly of vancomycin containing nano-capsules by means of aerosol-assisted atmospheric-pressure plasma**

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We optimized a one-step process to assembly vancomycin-containing nano-capsules for drug delivery applications by means of aerosol-assisted atmospheric-pressure plasma. Nano-capsules are nanometric vescicular systems with a core-shell structure consisting of a cavity and a surrounding polymeric membrane or a coating. A Dielectric Barrier Discharge (DBD) reactor was used: it is very easy to handle and it is suitable for plasma processing thermolabile substrates, as well as for feeding discharges with thermo-degradable biomolecules, due to its very mild operational conditions. This system allows an aerosol of a solution containing a bioactive molecule to be sprayed directly inside the reactor chamber. The droplets of the solvent act as a shield for the dissolved biomolecule, which maintains its structure undamaged in the discharge. The very interesting and unexpected morphology obtained demanded some further investigations. After the immersion in water these spheres become hollow or collapsed upon themselves suggesting a core-shell structure where the core is released in water. A fluorescein solution was sprayed inside the chamber and the coating obtained was observed by means of confocal microscopy; the fluorescence is originated mainly from the spheres therefore it could be hypothesized that the spherical shape derives from the polymerization of the monomer fragments on the surface of the droplets (with structure retaining) in the plasma zone. XPS and FT-IR proved that the Vancomycin drug is present in the coating but not on the surface, more likely inside the spheres. Various discharge parameters and aerosol solutions containing molecules with different molecular weight, ionic groups and polar moieties content were tested and it pointed out that an ionic molecule is necessary to obtain this peculiar morphology and that the discharge parameters can affect the characteristics of the coating obtained.

**Keywords**

Nano-capsules  
DBD  
Aerosol  
Drug-delivery
Continuous Atmospheric Pressure Plasma Enhanced CVD for the Large Area Deposition of TiO$_{2-x}$ Electron Transport Layers for PV Applications

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In recent years, perovskite solar cells have emerged as an attractive technology for next generation solar modules, combining high power conversion efficiencies with relatively low cost and abundant materials. However the component layers are typically produced by spin coating or vacuum processes, which precludes or adds significant cost to large area application. To this end, we describe the production of highly effective TiO$_{2-x}$ electron transport layers (ETL) via a continuous atmospheric pressure, plasma enhanced CVD (APPECVD) process. The films are evaluated in mesoporous perovskite cells and demonstrate cell performance matching or exceeding that achieved by an optimised sputtering process (13.57 vs 13.15 % Maximum Power Point for 1 cm$^2$ cells), suggesting significant potential for continuous large area production. Whilst operation at atmospheric pressure may be expected to result in compromised film properties compared to vacuum processes, these films, deposited on a 10 x 10 cm substrate, are shown to be sufficiently thin (lower 100 nm) to facilitate electron transport and minimise series resistance whilst being sufficiently dense and pinhole free to provide a hole blocking function, essential to prevent recombination with electrons from the TCO electrode. The production of device quality films represents a significant step forward, with the demonstrator unit clearly showing the potential for scale up. It is envisaged this approach could be particularly advantageous if used on-line in combination with the APCVD process used to produce the transparent conducting oxide (TCO) electrode.

Keywords
atmospheric pressure
plasma-enhanced chemical vapour deposition (PECVD)
perovskite
titania
roll to roll
Plasma-technological barrier layers for flexible thin film solar modules

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The aggressive pricing on the world market opposes the production of photovoltaic (PV) applications in Europe - and especially in Germany – facing the challenge of producing cheaper products. Novel PV concepts based on solar modules with copper indium gallium di-selenide (CIGS) technology manufactured on flexible and cost effective substrates such as metal foils with functional barriers can withstand the pressure of the market due to the technological lead. Plasma-technological processes for cleaning, activation and coating in particular contribute to this success. Nonetheless, the need to stay ahead of the competition by continuous innovations is evident.

A plasma-technological high-rate coating process of insulating SiO$_x$ layers on metal foils is presented. This incremental step in CIGS solar module production could be an important contribution for further cost reduction. The challenge of the plasma-based layer is to electrically insulate the metal foil, and to protect the sensitive CIGS absorber layer against the diffusion of iron from the substrate, while maintaining the full flexibility of the solar module. In addition, the layers must withstand process temperatures of up to 650 °C during the subsequent CIGS deposition. Finally, the dielectric should not be affected by the laser scribes needed to fabricate monolithically integrated modules.

The insulating SiO$_x$ layers are deposited from hexamethyldisiloxane (HMDSO) via a low-pressure chemical vapour deposition process fed by a microwave plasma (MW-PECVD). The plasma source used is the Duo-Plasmaline which generates a homogeneous plasma within an array configuration. The high rate deposition of up to 60 µm/min keeps the process times very short and is therefore suited for industrial applications.

Efficient insulation layers on steel foils of an area of 7 x 9 cm² were already deposited and a monolithically integrated CIGS module with a conversion efficiency of up to 10.2 % could be achieved so far.

Keywords
high rate deposition
microwave plasma
Duo-Plasmaline
Thin film solar modules (CIGS technology) on insulated steel substrate in R2R production for their integration into roofing elements

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In the frame of LIFE-PHOSTER project, which aims at developing new solar technologies and products with low environmental impact, we develop thin film solar modules (CuInGaSe2 or CIGS technology) on insulated steel substrate for their integration into roofing elements. To do so, we have designed and built roll-to-roll pilot lines, dedicated to wet and vacuum dry coatings in a clean room environment, constituting a unique combination of pilot lines for the functionalization of steel substrate.

Thin-film CIGS solar cells are diodes composed of two semiconductors: p-type CuInGaSe2 absorber layer and n-type buffer layer (such as ZnMgO), sandwiched in between Mo-based back electrode and ZnO:Al top transparent electrode. Moreover, when laser-patterned, these cells can be directly assembled into mini-modules with tunable voltage and current. This technology, already industrialized onto glass substrates, has been implemented onto functionalized steel substrate in the frame of the PHOSTER project.

The functionalization of steel substrate is done through wet deposition techniques while the completion of solar cells is a succession of vacuum based-dry coatings. These prototypes present similar features, making their combination quite unique:
- Possibility to treat steel coils up to 200 mm in width and with thicknesses ranging from 0.05 mm to 0.4 mm
- Speeds ranging from few mm/minute up to several m/min
- Modularity in the implementation of the processes, making possible to realize depositions in any order

These two prototypes are combined with a third one called SELENIZATION line, enabling to thermally treat the deposited layers under selenium atmosphere in order to turn them into a photoactive CIGS one. Significant achievements have been obtained on the prototypes with the completion of solar cells and mini-modules.

Keywords
GIGS
R2R pilot
insulated steel
Reactive magnetron sputtering of Ta-doped SnO2 at low temperatures: carrier transport and role of negative ion bombardment

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The benefits of SnO2 compared to the often used tin-doped indium oxide (ITO) are its significantly lower costs and its higher chemical stability. In principle, low resistivities of doped SnO2 are possible, caused by its conduction band, composed of isotropic 5s orbitals, advantageous for good transport properties [1]. Recently, Toyosaki et al. [2] achieved resistivities as low as $1 \cdot 10^{-4}$ Ωcm by pulsed laser deposition at 800 °C on sc-TiO2. Low temperature deposition of TCO films are often required for temperature sensitive devices. Magnetron sputtering is accompanied by the possible formation of negative ions as soon as electronegative elements are present, which is the case for oxygen [3]. In this work we give a comparative study of the radial distribution of ion density in the magnetron discharge and of the electrical film properties. The SnO2:Ta films were deposited at low substrate temperatures by reactive dc and rf magnetron sputtering from a ceramic target (Sn98at%Ta2at%O2) in Ar/O2, Ar/N2O, and Ar/H2O gas mixtures. The as deposited films were X-ray amorphous for substrate temperatures below about 200 °C. While the amorphous films are remarkably conductive ($\approx 5 \cdot 10^{-3}$ Ωcm), the crystallized films exhibit higher resistivities, probably owing to the grain boundary scattering. The width of the process window is wider for N2O and H2O compared with O2. Therefore, using N2O and H2O improves process stability and transparency of the films. A prospective application of such amorphous SnO2:Ta films are low temperature transparent and conductive protection layers, e.g. to protect semiconducting photoelectrodes for water splitting.


Keywords
transparent conductive oxide
magnetron sputtering
thin film
Production of Photocatalytic Materials for Use in Plasma Methane Reforming

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Plasma catalysis can allow chemical reactions to occur at temperatures otherwise insufficient when using catalyst alone. Hydrogen is a zero emission fuel that can be obtained by plasma catalysis and is one of the most promising forthcoming fuel sources. This research focuses on combining catalysts and plasma generated in a packed bed dielectric barrier discharge reactor (PBR) to break down waste gases such as methane and carbon dioxide into hydrogen and carbon monoxide. Photocatalysts are employed due to their activation by UV light, which is naturally produced by plasma further enhancing the synergistic effect of the combined non-thermal plasma and catalyst. Magnetron sputtering is used to produce the photocatalysts in a novel way onto the surface of particulate substrates, prior to using the catalysts in the PBR to assess their use in plasma catalysis. Thin films of titania, tungsten doped titania and bismuth tungstate have been coated using unbalanced type II magnetrons onto various beads. The titania, doped titania and bismuth tungstate thin films were annealed in air in order to obtain their photocatalytic phase. These thin films were characterised by X-ray powder diffraction, Raman spectroscopy and scanning electron microscopy with EDX. The beads were also characterised through surface area measurements. Characterisation concluded that the thin films were amorphous following sputtering, and upon annealing photocatalytic anatase titania, anatase doped titania and russellite bismuth tungstate were produced. Photocatalytic testing using the acetone degradation method in a reaction cell where the irradiation of UV-visible light was used in order to investigate the effect of the photocatalytic films and substrates, which determined titania to be the most active. Finally testing of the coated beads within the PBR was undertaken to investigate the effect of the photocatalyst on the degradation of methane and the products produced.

Keywords
Non-thermal plasma
magnetron sputtering
plasma catalysis
Pulsed PECVD of vertically aligned SnS nanowalls for solar cell applications

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The electric performance of a solar cell is mostly determined by the quality of the absorbing layer. Besides environmental harmlessness, a high absorption coefficient and a high charge carrier mobility are desirable. Since orthorhombic tin sulfide (SnS) fulfills most of the required criteria, it is regarded as a promising candidate for solar cell applications. Nevertheless, by now, the highest reported efficiency for SnS-based solar cells does not exceed 5%. Since orthorhombic SnS is naturally a layered structure, charge transport is anisotropic along the [001] direction. The performance of tin sulfide as absorber material in solar cells might be significantly improved by using aligned nanostructured SnS, namely SnS nanowalls. We report on a novel synthesis of phase-pure, crystalline SnS nanowalls via plasma-enhanced chemical vapor deposition (PECVD) using a single-source precursor. The precursor was fully characterized via, e.g., TGA, MAS-\textsuperscript{119}Sn-NMR, and single-crystal diffraction. In a home-built setup, the metal-organic complex is evaporated and then transported into a pulsed 13.56 MHz capacitively-coupled RF plasma. Silicon wafers and ITO-covered glass slides are used as substrates. After PECVD, the homogeneously deposited nanowalls turned the substrate surface to be dull, black, and non-reflecting. Structure characterization was done via, e.g., SEM, XRD, electron diffraction, and conductivity measurements. We prove the nanowalls to be phase-pure, with their growth direction along [001], which would advantageously minimize recombination processes and improve charge transport in devices with conventional top and bottom electrodes, e.g., solar cells.

Besides the characterization of the readily grown SnS samples, we also intensively investigated the plasma processes via spatially resolved optical emission spectroscopy (OES). The gained two-dimensional plasma maps were translated into electron-temperature maps via a convenient semi-empirical approach. Hence, a detailed in-situ monitoring of the plasma processes is enabled.

Keywords
PECVD
Nanowalls
Plasma-mapping
In-situ X-ray diffraction measurements following the details of ion nitriding of stainless steel has been developed during the last 5 years. Nevertheless, the amount of local information is limited as diffusion and relaxation processes due to the elevated temperature during the process will lead to dynamic processes difficult to be resolved as a function of depth. At the same time, samples produced by plasma nitriding or PIII cannot be analyzed. Here, we propose to use low energy ion beam etching coupled with in-situ XRD to obtain detailed, depth-resolved data. Limiting the ion energy to 1 keV or less will lead to minor modifications of material, avoiding potential plastic or elastic deformation during mechanical removal, restricted to the immediate surface zone of only up to 10 nm. At the same time, the XRD information depth is between 2 and 200 µm, conditional on the specific materials system. With a current density near 100 µA/cm², a depth resolution of 15 – 25 nm per spectrum can be realized. The analysis of the results can be performed using the intensity of reflections from the layer system as well from an underlying substrate. As the experimental setup is constrained to Bragg-Brentano geometry, surface roughening may result in a continuously degrading depth sensitivity. As one example, the ion beam sputtering of expanded austenite formed on austenite using PIII is compared to samples formed by low energy ion nitriding. Several interesting points have been identified here: (i) orientation dependent sputtering (but not orientation dependent diffusion), (ii) the XRD peak shape and position does not follow the nitrogen depth profiles of the expanded phase as obtained by SIMS, (iii) PIII samples show consistently broader peaks not confined to the surface zone affected by the ion implantation, and (iv) by adjusting the ion energy, beam induced surface roughening can be minimized. A further experiment to demonstrate the versatility of the system was performed using a thin magnesium foil fixed on a substrate for a determination of the relative sputter yield for the surface oxide and the bulk foil.

Keywords
in-situ XRD
depth profiling
ion etching
Hyperspectral Imaging  a novel inline-capable tool for spatially resolved inspection of thin films

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The reliable knowledge of surface and thin film properties is essential in the development of thin film processes as well as in the quality assurance in their industrial production and applications. Beside common single point measurements the need of a 100% inspection of the whole sample area is nowadays increasingly important. Hyperspectral imaging (HSI) opens the easy and fast access to spatial resolved large area measurement of a variety of properties of thin film samples. The optical and therefore contactless approach enables furthermore the inline application of the HSI technology.

Versatile applications can be addressed by a broad spectral range, which covered UV, VIS and NIR. Depending of the target objectives of the measurement, dedicated strategies of data analysis are used. Hard-modelling approaches based on fundamental physical laws enable the imaging of thin film thickness, the imaging of optical properties or imaging of the sheet resistance. Soft-modelling approaches like multivariate data analysis leads to the fast detection of surface impurities e.g. contaminations like particles or of target sample properties e.g. the adhesion strength of plasma treated surfaces. The flexibility in system setup by hardware (detector, optics, and lighting) and software (data analysis algorithms) enables tailored solutions for dedicated inspection tasks.

The technology of Hyperspectral Imaging will be illustrated by means of certain examples from the thin film sectors: Thickness imaging of ALD thin films, Sheet resistance imaging of TCO coated substrates, Imaging of adhesive strength of plasma treated surfaces, Contamination detection on surfaces, Evaluation of decoating processes (laser scribing).

Finally, the possibility of an inline inspection by HSI will be demonstrated exemplary by the continuous quality control of an alumina layer in electrode manufactory.

Keywords
thin film analytics
in-line inspection
hyperspectral imaging
multivariate data analysis
Optical monitoring of sputtered ultrathin TiN films

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The plasmonic applications require search for novel materials with metal-like optical properties and low optical losses. Transition metal nitrides exhibit metallic properties depending on a concentration of free-carriers of charge. Their plasmonic properties can be controlled by the film structure and the stoichiometry. In this work, we deal with the study of the growth process of TiN films. The films are grown by RF magnetron sputtering on fused silica, silicon and MgO substrates at a substrate temperature ranging from 20°C to 500°C. The growth process is monitored using in-situ spectral ellipsometer in a spectral range from 245 to 1690 nm. The ellipsometric data are analysed using mathematical models based on Drude-Lorentz oscillators describing the interband transitions and free-electron behaviour. The number of physical parameters such as free-electron concentration, Drude relaxation time and electrical conductivity is estimated at each stage of the deposition process by analysis of dielectric functions. Special attention is devoted to the initial nucleation stage when the free-electron behaviour is significantly influenced by the interface between the substrate and the TiN film. The prepared TiN coatings are analyzed using infrared ellipsometer operating in the spectral range from 1.7μm to 30μm where the optical functions are the most significantly influenced by free-electron behaviour. The obtained results are compared with those obtained by Van der Pauw and Hall effect measurement. The TiN film structure, chemical bonding and composition are analysed by X-ray Photoemission Spectroscopy and Energy Dispersive Spectroscopy, respectively. The surface morphology is studied using Atomic Force Microscopy and Scanning Electron Microscopy.

Keywords
titanium nitride
spectral ellipsometry
optical monitoring
A remote plasma spectroscopy based method for monitoring of Atomic Layer Deposition processes

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Atomic layer deposition (ALD) is an exciting emerging technology in the deposition of many functional thin films. Effective monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique. Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is rarely undertaken.

An alternative gas sensing technique that operates directly at pressures above $1 \times 10^{-4}$ mbar has been built around plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor’s plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Photomultiplier and CCD spectroscopy based methods were investigated for analysing the plasma emission. It was found that by synchronising the spectrum acquisition with the precursor injection, it was possible to consistently capture the fast gas dynamics of the ALD process. Sensitivity limitations of the technique are also investigated, in particular the effectiveness of plasma emission monitoring in being able to distinguish between similar precursors.

Examples of this sensing technique’s practical uses for ALD processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption.

Keywords
ALD
RGA
Plasma emission monitoring
Process control
OR0504

**Crystalline structured ultra thin film synthesis by nano clusters deposition using 3D magnetic confined magnetron source**

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This work reports an integrated approach, combined with an advanced magnetron and plasma diagnostic systems, utilized for the enhancement of the crystallinity, the carrier concentration, and the mobility of the ultrathin ITO thin films. For the requirement of flexible and transparent electrode applications, ultrathin films with superior crystallinity are necessary. However, demand and involvement of high deposition temperature and high temperature annealing often provide a limitation for the fabrication of the material as well as the deposition process. It is realized that ITO films with nanoclusters could be a useful tool for synthesis of high quality ultrathin ITO films. To increase the efficiency of nanoclusters generation, we create a very high density plasma environment by the design of magnetically confined rectangular magnetron source which is a novel highly confined 3-D magnetron source. The high ion density trapped by this source results in a very high sputtering rate of ITO species, which are localized inside the source and combined together to form cluster due to sufficient residence time. Further, due to weak diffusivity of neutral clusters, they do not reach the chamber walls during their motion in the flow. The flows of argon atoms in addition to the ITO clusters pass through this source regime and are deposited on a substrate. Overall, we have investigated the formation, growth and transport of nanosized ITO clusters in an advanced magnetron discharge and the deposition of these clusters on a substrate. Also the effect of different contributions such as electrons, positive ions, negative oxygen ions and deposition energy on the film growth and their properties are investigated by combining in-situ plasma diagnostics and ex-situ analysis.

**Keywords**
3D-confined magnetron sputtering
cluster deposition
ITO films
ultra thin film
transparent and conductive thin film
Cluster tool for in situ processing and characterization of thin films at high temperatures

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In situ processing and comprehensive characterization is essential for design and development of thin films and coatings used in high-temperature applications and processes. Here, a new cluster tool for processing and depth-resolved compositional, structural and optical characterization of layered materials with thicknesses ranging from sub-nm to 1 µm and for temperatures of -100 to 800 °C is described. The implemented techniques comprise magnetron sputtering, ion irradiation, Rutherford backscattering spectrometry, Raman spectroscopy and spectroscopic ellipsometry. The combination of techniques enables sample processing by scalable, clean, waste-free, and industry-relevant technologies, quantitative depth-profiling for elements with Z ≥ 6, structural and chemical characterization, sensitivity and nm-precise thickness and optical information for single layers, multilayers and mixtures. The performance of the cluster tool is demonstrated for metal-induced crystallization of a model layer stack MgO/ a-Si (~60 nm)/ Ag (~30 nm), and for high-temperature characterization of two solar-selective coating types developed for concentrated solar power applications, namely AlₓTi₁₋ₓ(OₓN₁₋ₓ)-based single and multilayers as well as an n-type doped transparent conductive oxide. Financial support by the EU, grant No. 645725, project FRIENDS², and the HGF via the W3 program (S.G.) is gratefully acknowledged.

Keywords
Thin films
in situ
processing
characterization
high temperatures
The testing of new drugs since long time relies on animal models. However, the obtained test results could often not be directly transferred to humans due to differences in the physiology. The discovery of human induced pluripotent stem (iPS) cells contributes to overcome this difficulty in preclinical tests – before entering the clinical phase 0 – by allowing to test the substances in human organ models. The combination of the iPS technology with microfluidic devices is a promising technology in this field of application. Both the microphysiological environment and 3D tissue structure with its functions can be reproduced on a small dimensional scale suitable for optical investigations without further necessity of histological preparation. Same time, in a high number of identical systems can be produced which is important for parallelization and high-content-screening approaches. Examples are “heart-on-a-chip”, “retina-on-a-chip”, and “fat-on-a-chip”. These systems remain functional over multiple weeks.

The function of organ-on-a-chip systems (OoCs) is governed by multiple interfaces between different technical (polymer) materials, biological tissues, and liquid media which for instance may contain drugs, growth factors, or specific proteins. In particular in case of liquid media, care must be taken not to lose drug molecules by absorption into the building material as otherwise, the concentration profile does not remain constant and the action of drugs is falsified. The desired interface properties are therefore diverse, ranging from adhesive to non-fouling, from absorbing to barrier functions. We have developed a multilayered flexible barrier coating by plasma enhanced chemical vapor deposition (PECVD) on PDMS substrates. The coatings are effective against the permeation of small molecules as shown by permeation measurements with fluorescent dyes. Furthermore, the coatings allow for diffusion of oxygen which is substantial for cell growth in the OoCs. Furthermore, the coatings are transparent in a broad range and are free of intrinsic fluorescence which is important for all optical screening technologies.

**Keywords**
lab-on-a-chip
organ-on-a-chip
diffusion barrier
Tailored degradability of plasma polymers with semi-classical structure

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Polymers prepared by classical “wet” chemistry methods typically possess well-defined molecular structure. However, significant degree of crosslinking without residues of the crosslinking agent is not easily achievable for many types of polymers. In contrast, plasma polymers usually exhibit very high degree of crosslinking, yet with poorly defined molecular structure. Plasma assisted vapour thermal deposition is a combination of these two approaches. Powder of bulk polymer (“precursor“) is heated under vacuum to the temperature at which the cleavage of macromolecular chains starts to occur. Oligomeric fragments are released into the gas phase through a glow discharge, forming a thin film. The retention of the macromolecular structure and the crosslink density are tuned by the conditions in the plasma.

In this work, thin films based on poly-lactic acid, polyethylene oxide and polyurethane were prepared at temperatures of 150-350°C under low pressure (1-5 Pa) with/without the RF plasma (0-20W) involved. The molar mass distribution and the chemical composition of the resultant films were characterized in comparison with the “precursor” polymers. Swelling and hydrolysis of the films were monitored as a measure of their degradability using liquid chromatography and in situ spectroscopic ellipsometry. Permeability of model molecules (e.g. nisin) through the films was studied. In general, the films replicated well the structure and the chemical composition of the original counterparts. The degradation and permeation properties were found to be tunable to a significant degree by the deposition conditions.

Acknowledgements: This project is supported by the grant GA17-10813S of the Czech Science Foundation.

Keywords
plasma polymer degradability control
OR0602

**Plasma polymerization of precursors containing stable radicals**

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In this paper, we present the results of the plasma polymerization of precursors containing stable radicals. The retention of the radical sites in the plasma polymer was probed by electron-paramagnetic resonance (EPR): besides the assignment of different radicals, a time-dependent study was carried out as well. The overall chemical composition was examined in detail by x-ray photoelectron spectroscopy and ToF-SIMS. It is further shown how the plasma process parameters affect the radical composition, the radical density and the stability of the polymer films. Potential applications range from controlled polymer grafting to the control of biological signaling on coated surfaces. For example, these thin film coatings were capable of interfering with the quorum sensing of the opportunistic pathogen Staphylococcus epidermidis for a time period of 21 hours while exhibiting low toxicity towards human Kg1a cells.

**Keywords**
- Stable radicals
- EPR
- antimicrobial
- biomaterial
The role of confined water within plasma polymerized vertical gradient films in protein adsorption

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The protein-surface interaction at the solid-liquid interface is of paramount interest in surface sciences such as bio-compatibility, non-fouling and bio-sensing. The suppression of non-specific protein adsorption is sought for the prevention of the initiation of undesired biological reactions. In view of changing surface chemistry to diminish protein adsorption, the water molecules in the vicinity would play an unanticipated role. Plasma polymerization offers a possibility to design subsurface gradient architectures comprising a hydrophilic to hydrophobic gradient for adsorption studies. The addition of a precise amount of oxygen to hexadimethylsiloxane in the plasma leads to the deposition of a hydrophilic SiOₓ base layer, while the oxygen is removed from the nm-thick hydrophobic termination yet still allowing water penetration. Moreover, the sub-surface water uptake properties are modified to enhance the gradient by changing film composition (e.g. increasing oxygen/carbon ratio of the base layer). The response of the gradient matrix to aqueous environments was investigated by neutron reflectometry. Regardless of the hydrophobicity of the terminating layer, penetration of water molecules through gradient is energetically favorable which results in enrichment of water molecules underneath the surface. The impact of this water mediated gradient on protein adsorption was observed via a unique instrument, Transmission Interferometric Adsorption Sensor. It was notably perceived that the protein adsorption is substantially reduced on the hydrated gradient compared to reference surfaces. It is even much more suppressed in the presence of an enhanced hydrated gradient. This remarkable result is attributed to the directional orientation of penetrating water molecules in the designed gradient that yields to the separation of molecules in a distance of 5-6 Å. Hence, the dipole moment of ferro-electric water molecules creates long range interaction forces in the crosslinked sub-region. To go beyond this hypothesis, the force-distance characteristics of both non-hydrated and hydrated state of films have recently been characterized by Kelvin probe force microscopy. Furthermore, the hydration time effect on protein adsorption kinetics will be examined.

Keywords
vertical chemical gradient film
BSA adsorption
Generation of functional coatings by atmospheric pressure plasma spraying for medical and technical applications

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Atmospheric pressure plasma spraying is a well-established method for film deposition providing unique process and coating properties including high deposition rate, high surface roughness, porous structure and the ability to coat a large range of materials including ceramics and metal-based materials. The versatility founds the diversity of applications ranging from the coating of turbines for corrosion protection and heat insulation up to the modification of medical implants aiming at the enhancement of the biocompatibility or to generate antimicrobial surface properties. Especially in healthcare facilities, infections pose a main challenge for implants due to the severe impairment of the quality of patient’s life and the high costs involved. An approach to solve this problem is to promote the adhesion of human bone cells for a faster ingrowth of the implant and simultaneously, suppress the proliferation of microorganisms by the release of biocidal agents.

Within this presentation, we show results on the generation of innovative plasma sprayed coatings comprising hydroxylapatite - a cell adhesive bone-like mineral - and defined admixtures of antimicrobial agents (e. g. copper), which are released from the surface.

Furthermore, we will present results regarding the coating of high voltage electrodes with a ceramic material to reduce their abrasion significantly and drastically increase their lifetime by a factor of at least 50.

We are focusing on surface analysis by AFM, SEM, XRD and XPS along with microbiological tests and cell proliferation assays as well as on new approaches for material combinations used in plasma spraying processes, while also considering the effect of different particle sizes.

Keywords
plasma spraying
atmospheric pressure
coating
medical
technical
**QTF-Based Mass Sensitive Immunosensor for Phenylketonuria Diagnosis**

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The diagnosis of phenylketonuria in early stage prevents potentially serious consequences in many newborn. To avoid these consequences, it is compulsory to analyze each newborn blood by law in East European and Caucasian countries even in Turkey. However, today’s protocol do not meet the requirements such as low response time, cost, and false positive or/and negative rate. With this research, we aimed to produce QTF-based immunosensor, which is far from false negative results, and have response time in minutes to decrease the expenses. For this purpose, QTF prongs should be functionalized to immobilize antibody and kept its properties in liquid medium. Therefore, n-Hexane was chosen as a pre-coating precursor for plasma polymerization process. All experiments were achieved at low pressure RF plasma system. After pre-coating step, QTF were functionalized again by plasma polymerization technique by using ethylenediamine as a amine source with different exposure times (1, 5, 10 min) and power (25, 50, 75, 100 W). Aging test also applied to ethylenediamine coating to understand the preservation period of forks. Surface activation was achieved by using 25 % (v/v) glutaraldehyde solution. Finally, Anti-L-phenylalanine immobilization was performed and the response to L-phenylalanine was studied. The surface physical and chemical characterization of modified quartz tuning forks was performed with Attenuated Atomic Force Microscopy (AFM), Contact Angle Analyzer, X-ray Photoelectron Spectroscopy (XPS). The results showed that plasma polymerization technique is useful tool for QTF’s prongs functionalization. The coatings provide good stability in liquid mediums which is crucial for biomedical applications. QTF based immunosensor for phenylketonuria diagnosis was successfully achieved by the utilization of plasma polymerization systems.

**Keywords**

Plasma polymerization
thin film
biosensor
amine-rich thin films
piezoelectric
Magnetron sputtered hard and fracture resistant metal-boron-carbon based coatings

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Nowadays used hard protective coatings are often based on ceramics. They generally exhibit high hardness and high stiffness, however, these positive features are often accompanied by negative brittle deformation behavior. If a crack is formed, it can easily and rapidly spread which can lead to a sudden premature failure of the coating as well as the whole coated tool. The current trend in surface engineering is to sacrifice some of the hardness in favor of enhanced ductility and fracture toughness. According to the ab-initio models, boron and carbon-based nanolaminates such as Mo₂BC should exhibit an unusual combination of high stiffness and moderate ductility [1]. Nanolaminates with tantalum, tungsten and molybdenum were predicted to exhibit the best mechanical properties making them the best candidates for experimental synthesis. These materials (Mo-B-C, W-B-C and Ta-B-C) were sputter deposited at moderate temperatures employing DCMS or HiPIMS. The coatings are prepared in a fully amorphous form, as nanocomposite system and also in a fully crystalline form. The hardness of these coatings was higher than 20 GPa and the fracture resistance of the coatings is shown to be significantly enhanced compared to the state-of-the-art protective coatings such as TiN or TiAlN. The highest hardness achieved was 31.6 ± 0.8 GPa and was coupled with extremely high fracture toughness – it was even impossible to form a crack in these coatings at extremely high indentation load with cube corner indenter where both the coatings and the underlying hard-metal substrate were severely plastically deformed. Only a shear/slip plane defects typical for ductile materials were detected. Tribotests revealed the formation of the solid state lubricants Magnéli phases at high temperatures reducing the coefficient of friction. [1] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J.M. Schneider, J. Phys.: Condens. Matter. 25 (2013) 045501

Keywords
protective coatings
fracture toughness
Sputter deposition of Mo-based multicomponent thin films from rotary targets: experiment and simulation

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Sputter deposited Mo thin films play a key role in the manufacturing of modern flat panel displays and microelectronic components. They are widely used as source/drain electrodes, as gate material or as metallization layer for signal and data bus lines. Annealing steps during production of devices can lead to oxidation and discoloration of the Mo layer and an increase in electrical contact resistance to adjacent (semiconducting) thin films. The alloying of Mo with Al and Ti prevents surface oxidation of sputtered thin films without significantly changing electrical resistivity and etching rate. Within this work, the sputter performance of a MoAlTi target was investigated to correlate the processing conditions to material properties. An industrial-scale in-line magnetron sputtering system with a rotatable MoAlTi target was used to deposit a series of thin films on silicon wafers at different argon pressures. The center of the substrate carrier was kept at a constant offset from the target axis. The thin film thickness and chemical composition was evaluated for substrates located at different positions. The morphology of surfaces and focused ion beam prepared cross sections of the films were examined via scanning electron microscopy, revealing two different types of surface topography: directly opposite the target, a dense structure is predominant, while a change to a fine granular structure was observed at extended distances. Energy dispersive X-ray spectroscopy revealed a depletion of Al in favor of Mo enrichment opposite the target and a reverse trend at extended distances. The plasma used for sputtering was modeled after realistic target geometries using S³M and served as input for subsequent SRIM scatter simulations. These simulations allow to distinguish between a high flux regime with high-energetic film forming species and a low flux regime with mainly thermalized species, leading to different film structures and chemical compositions.

Keywords
sputter deposition
ICP-Assisted Reactive Sputter Deposition and Plasma-Enhanced Annealing Processes for Low-Temperature Formation of High-Mobility In-Ga-Zn-O Thin-Film Transistors

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Plasma-assisted reactive sputter deposition system has been developed via co-installation of magnetron sputtering source with inductively-coupled plasma (ICP) sustained by low-inductance antenna (LIA) for fabrication of next-generation devices including flexible electronics, which require large-area and low-damage processes with reactivity-control capabilities for lowering the device-formation temperature [1,2]. Major advantage of the ICP-assisted sputter deposition system is that the reactivity during film-deposition process can be controlled via independent control of film deposition process (magnetron discharge) and reactivity (radicals and ions generated with ICP). Furthermore, plasma-enhanced annealing processes have been developed using the ICP for lowering process temperature via reactivity enhancement with radicals and ions.

The ICP-assisted reactive sputter deposition has been applied to film formation of transparent amorphous oxide semiconductor a-InGaZnOₓ (a-IGZO) [3], which has attracted great attentions as key material for next-generation flexible electronics. Conventionally, thermal annealing at elevated temperature as high as 400 deg.C was required for stabilization of the as-deposited IGZO thin-film transistor (TFT). Thus the conventional fabrication process has been constrained to the device formation on glass substrates. Using the ICP-assisted reactivity-controlled sputter deposition and plasma-enhanced annealing processes, IGZO TFTs with mobility higher than 40 cm²/Vs was successfully formed at substrate temperature less than 250 deg C. In this presentation, process controllability and low-temperature formation of IGZO TFTs are to be discussed with evaluation of TFT characteristics and TFT stability by stress test.


Keywords
ICP-assisted reactive sputter deposition
In-Ga-Zn-O
Low-temperature process
Impact of alloying on properties and oxidation resistance of magnetron sputtered Zr–Hf–Cu based metallic glasses

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Thin-film metallic glasses are a class of metallic alloys with an amorphous disordered structure and a viscous flow in the super-cooled liquid region. Their extraordinary properties make them promising for widespread applications, e.g. microelectromechanical systems, diffusion barriers, surface modification of crystalline materials. One of the prerequisite to use them at elevated temperatures in air is their sufficient oxidation resistance.

Recently, we have showed that a gradual substitution of Hf for Zr in ternary Zr–Hf–Cu thin-film metallic glasses prepared by magnetron co-sputtering allowed us to tune their mechanical properties and glass transition temperature. In the present study, we focus on alloying of the Zr–Hf–Cu thin-film glasses with additional elements (X=Al, Ho, Si) up to ~15 at.% and investigation of a possibility to further tune or enhance their mechanical and thermal properties, and oxidation resistance. The films were deposited using four unbalanced magnetrons equipped with Zr, Hf, X and Cu targets in pure Ar. The magnetrons with the Zr, Hf and X targets were operated in a dc regime while the magnetron with the Cu target in a high-power impulse regime. The Zr, Hf, X and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The films were deposited without substrate bias voltage and external heating onto rotating substrates.

All Zr–Hf–X–Cu films investigated (up to ~15 at.% X) exhibit an X-ray amorphous structure. The glass transition detected by differential scanning calorimetry can be, however, recognized only to about 10 at.% X. An alloying with Al or Si enhances the mechanical properties of the films and the thermal stability of their amorphous state while an alloying with Ho is detrimental in this respect. In addition, Al or Si extend the width of the super-cooled liquid region of the alloys and maintain their high oxidation resistance even in the super-cooled liquid region.

Keywords

Zr–Hf–Cu
Amorphous alloys
Metallic glasses
Oxidation resistance
Magnetron sputtering
Predicting Behavior for Non-saturated Reactive Sputtering Processes

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In a series of papers we have presented results from simulations of reactive sputtering processes. Most of those simulations were based on the so called "Berg model". It should be pointed out that this model in its present form only may treat reactive gases like oxygen and nitrogen. We prefer to call such processes saturated as the film composition saturates to chemical compounds like oxides and nitrides. In contrast to oxygen and nitrogen, gases like hydrocarbons, sulfides, silane and diborane may decompose into solids of carbon, sulfur, silicon and boron respectively. These solids will be deposited onto the substrate area even if they do not form a compound. As a consequence of this, such processes may result in film compositions from zero to 100% of the decomposed reactive gas (e.g. carbon, sulfur, silicon and boron). There exists no natural limitation of the composition of the deposited film. We therefore choose to call such processes non-saturated reactive sputtering processes.

In this presentation we will outline a quite simple first order model that may serve to reasonable well describe processing behaviour for such non-saturated reactive sputtering processes. The simulations will visualize that the non-saturated behaviour introduces a severe processing problem to obtain desired compositions of the deposited films.

Keywords
sputtering
modelling
reactive
thin film
Niobium coating of large-area copper substrates for CERN accelerating structures

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Particle accelerators are complex machines integrating components from several technological domains. Radio-Frequency (RF) accelerating cavities is one of the core technologies commonly used to accelerate charged particles. Most of these accelerating structures make use of superconducting materials and work at cryogenic temperatures in order to reduce the RF-losses and achieve high accelerating gradients.

Two technologies are currently in use: bulk niobium cavities and copper cavities coated with a niobium layer on the inner surface. The latter option present the advantage of lower material cost and better thermal stability. Different cavity designs (depending on the particle velocity, working frequency, accelerating/deflecting modes, etc.), lead to a wide variety of substrates, having different shapes and with sizes ranging from tens of centimetres up to two meters.

In this work, we present the different geometries of niobium-coated cavities in use and under development at CERN. We review the different approaches to coat these complex substrates by adapting the coating techniques (DC-bias diode sputtering, DCMS, HiPIMS) and the cathode design to the given geometries. Finally, we discuss the resulting layer uniformity and properties. This approach is supported by plasma, transport and film growth simulations studies.

Keywords
PVD
large-area
niobium
superconducting
simulation
On the nature of suboxide formation during reactive DC magnetron sputtering

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The authors recently demonstrated the presence of suboxides on the target surface during reactive DC magnetron sputtering in the poisoned mode using an in-vacuum XPS study. This feature is however not observed for every metal-oxygen combination. For some metals, only stoichiometric oxides were noticed after target poisoning. The possible occurrence of suboxides is consistent with former ion beam experiments in literature. These studies suggested that ion-induced preferential sputtering of oxygen atoms is the main mechanism to reduce oxides on the substrate surface. There is however an essential difference between ion beam sputtering with noble ions on an oxide substrate and reactive DC magnetron sputtering. In the latter, one starts from a pure metallic target and the oxide formation occurs due to the presence of oxygen in the sputtering chamber. During reactive DC magnetron sputtering, oxygen ions are implanted and they will react with the metal atoms inside the target. This oxide formation mechanism is the key feature of the so-called RSD model [1], which predicts the existence of a critical oxygen fraction. At this fraction, sufficient oxygen is implanted to form the stoichiometric oxide on the target surface. Below this fraction, the amount of implanted oxygen is too low which may result in suboxide formation on the target in the poisoned mode. The existence of this critical oxygen fraction is now experimentally demonstrated using in-vacuum XPS on the target surface. This study suggests that during reactive DC magnetron sputtering, not preferential removal of oxygen but the lack of oxygen during oxide formation predominantly leads to suboxide creation.


Keywords
Magnetron sputtering
XPS
oxide
The Time Domain Effect of Micropulse on Nb Coatings Generated by DOMS

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High ionized pulsed vapor fluxes, generated from Deep Oscillation Magnetron Sputtering (DOMS), are employed to study the effect of time domain characteristic on Nb coatings by using microsecond scale multistep micropulse through controlling both pulse-on time and pulse-off time. Increase pulse-on time from 6 μs to 12 μs with pulse-off time keeping constant at 30 μs, the peak power increases from 120.6 kW to 156.9 kW. While increase pulse-off time from 10 μs to 40 μs with pulse-on time keeping constant at 8 μs, the peak power in each macropluse goes up to 131.0 kW from 115.0 kW which energy is inferior to the pulse-on time controlling mode. The deposited coating by changing pulse-on time mainly show (110) and (211) preferred orientation, yet the deposited Nb coatings by changing pulse-off time mainly show (110) and (211) preferred orientation which intensity gradually decrease as the increase of pulse-off time. The achieved hardness and modulus for the coatings deposited by changing pulse-off time show significant increase from 6.9 GPa to 20.1 GPa and 178.9 GPa to 238.3 GPa of which hardness is a factor of 3 compared to Nb coatings deposited by DCMS and is near one tenth of the modulus indicating the approach of ideal hardness. All coatings show dense columnar structure with compressive residual stress. The anomalous high hardness attained is mainly caused by Hall-Petch effect and dense microstructure which are controlled by the time domain effect of micropulse on Nb adatom lifetime. The long pulse-off time provides essential time for adatom surface diffusion and island coalescence.

Keywords
Deep Oscillation Magnetron Sputtering (DOMS)
Time domain effect
Nb coatings
Micropulse
Adatom
Optical and Electrical Properties of reactive/nonreactive Magnetron Deposited SnZnOx Coatings Annealed at Various Temperatures

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ZnSnOx coatings were deposited from two 2in magnetron targets made of ZnO and SnO₂ connected to DC pulsed and RF power supplies, respectively. The pure Ar and reactive gas mixture Ar/O₂ were used. DC pulsed power applied on ZnO target was kept constant 50W 50kHz, 20% d.c. and the RF power applied on SnO₂ target was set to values from 0W (pure ZnO deposited) up to 150W (up to 8 at.% of Sn in films). The deposited films were investigated by multiple techniques as deposited at RT as well as after annealing at temperatures 200°C and 450°C. The lower annealing temperature is still compatible with many common polymeric substrates. The amount of Sn in the films is proportional to applied RF power on SnO₂ target. But there is also significant influence of the post deposition annealing on the film compositions. The ratio Zn/Sn is reduced by the annealing process. Therefore the annealing is promoting the migration of Sn toward the surface and Zn to inside. Moreover the films deposited in oxygen rich reactive gas mixture does not reduces the resistivity with added Sn in contrary to films deposited in Ar where the resistivity was reduced by 5 orders of magnitudes. The plasma parameters were investigated and mean energies of dominant species were in DC pulsed only about 3eV and DC + RF powered plasma up to 15eV. The expected higher energetic particles in the RF influenced plasma deliver an additional energy to the growing film. Therefore, we observed systematic differences between refractive indexes in the films deposited with low RF powered SnO₂ magnetron at RT and post-annealed at 200 ° and practically no difference between RT and post-annealed film at higher RF power above 50 W. The XRD results proved the transitions from an amorphous to more crystalline structure by post-annealing of the films.

Keywords
reactive sputtering
plasma diagnostics
optical films
TCO
Magnetron Sputtering as a Tool for Producing Metallic and Bimetallic Multifunctional Nanoparticles: The Case of Zn-Fe

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Magnetron sputtering (MS) has been for many years acknowledged as an outstanding technique for the production of coatings to modify the performance of a material by using a wide spectrum of compositions and structures. However, with the exceptional performance of nanoparticles (NP) for a large types of applications, magnetron sputtering has been extended to manufacture nanocomposite materials, where NPs are embedded in a matrix, thus capable of producing multifunctional properties, including good mechanical and tribological performance, antibacterial character, biocompatibility, chromatic sensitivity and oxygen absorption.

In this work, two techniques based on magnetron sputtering are used to produce Zn and Zn-Fe nanostructures onto carbon substrates, including classic magnetron sputtering and a hybrid process with both gas agglomeration and magnetron sputtering, with the intention of studying their capacity to absorb oxygen. The oxidation process was evaluated by high angular annular dark field (HAADF) scanning transmission electron microscopy (STEM) images and energy dispersive X-ray spectroscopy mapping (EDX-mapping), on an corrected FEI Titan ChemiSTEM operated at 200 keV. The samples were analyzed before and after exposure to an oxidation environment. Pure Zn nanostructures formed Zn/ZnO core-shell configurations, where the two phases were crystallographically aligned, as confirmed by electron diffraction. For the Zn-Fe nanostructures, on the other hand, the oxidation is randomly distributed and the core-shell structure is not produced. However, when Zn and Fe are coupled in an agglomerate–like morphology, a galvanic oxidation accelerates the oxidation.

**Keywords**
Nanoparticles
Magnetron Sputtering
Oxidation
STEM
Bi-metallic, metastable and Janus Nanoparticles formed by combined Plasma-in-liquid and laser treatments

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The formation of complex nanoparticles (NPs) such as bi-metallic, alloyed or core/shell, Janus etc... is still challenging, and conventional chemical processes remains unsufficient. An attractive technique consists in combining plasmas and laser treatments in liquids. A basic solution consisting of a suspension of pure metallic particles (typically µm size) in ethanol is been used and Electric discharges are then ignited between tungsten electrodes immersed in the aforementioned solution. Eventually, the solution is further treated with second harmonics of Nd:YAG ns laser. The present communication deals with the Cu-Ag system in which no defined compound exists and the solubility of one element in the other is only a few percents. High-resolution Transmission Electron Microscopy shows that laser treatment leads to better defined spherical NPs with a noticeable increase in NP size, which can be attributed to co-melting. Moreover elemental analyses have given a Cu:Ag ratio in the range [63 at % Cu – 37 at % Ag]. Even though no defined thermodynamically stable compound corresponds to that composition, selected area diffraction patterns show that larger particles (typ. above 40 nm) are composed of a single phase – presumably metastable – and can be either mono or polycrystalline. On the other hand, smaller NPs are composed of both a copper-rich and a silver-rich phase. After annealing the NPs, Cu and Ag split and form a Janus structure with a Cu-rich phase on one side of the NP and Ag-rich phase on the other side. After single plasma treatment and combined plasma and laser treatment, scattering spectra of single NPs shows a plasmon resonance around 560 nm. After annealing, plasmon peak splits in two peaks at 470 and 670 nm.

Keywords
Nanoparticles
Plasma in liquids
Plasmon
Nanoparticles synthesis from solid precursor using RF-ICP plasma. A tailored process for tailored nanoparticles.

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An original plasma-based process has been developed for the synthesis of metal nanoparticles on a carbon powder substrate (xerogel, graphene, CNT or carbon black). The process consists in the mixing of the carbon substrate and a solid organometallic precursor and its exposition to a RF-ICP plasma treatment. This process, which does not require the use of solvents, offers a high flexibility in terms of fine control of the nanoparticles morphology and their chemical state.\(^1\)\(^-\)\(^3\) I will present the different nanoparticles structures and chemistries that have been realized during recent works: namely, we explored precursors containing different elements such as Pt, Ni and Co, treated in different plasma chemistries (Ar, O\(_2\), NH\(_3\), N\(_2\)). Optical emission spectroscopy measurements performed during the treatment combined with ex-situ XRD measurements reveal that the precursor degradation by the plasma and the subsequent nanoparticles formation can be monitored in real time. Analytical characterizations (XRD, TEM-EDS, XPS) show that a wide variety of nanoparticles structures (amorphous, crystallized, core-shell), morphologies and chemical compositions (metallic, oxides, nitrides) can be obtained by varying the treatment conditions. In addition, the size of the nanoparticles can be controlled by the treatment duration and power. These aspects result in an appealing method to tailor the design of "green" catalysts.

References:

Keywords
nanoparticles
ICP-RF plasma
Deposition of metal core@plasma polymer shell nanoparticles using gas aggregation cluster source

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The recent studies have shown that the applications of gas aggregation cluster source (GAS) are not limited just for deposition of single phase (pure metal or polymer) nanoparticles (NPs) but can be extended also for fabrication of nano-objects with more complex heterogeneous structures, e.g. core@shell NPs. In this work the GAS based on the DC magnetron (3 inch in diameter) sputtering of Ag target in the Ar/HMDSO working gas mixture was applied. The sputtering procedure was performed under the pressure 150 Pa and magnetron current 600 mA. The main discharge parameters and the properties of formed NPs were found to be strongly dependent on the amount of organic precursor in the working gas mixture. The increase of the HMDSO percentage from 0 to 4 % induced the growth of magnetron voltage from around 300V to 440V. The XPS analysis was performed to study deposited NPs. An apparent correlation between the concentration of monomer in a gas mixture and atomic concentration of carbon, oxygen and silicon was found. At the same time the signal detected from Ag 3d peak deteriorated with increasing of monomer concentration. The observed changes in the chemical composition of NPs deposit originated from increase of organic layer thickness on the metallic NPs cores. This assumption was further proved by HRTEM: whereas the sputtering of Ag target in the Ar atmosphere resulted in deposition of spherically shaped NPs with the mean diameter 30 nm, introduction of the monomer HMDSO lead to the formation of smaller (~10 nm) Ag NPs enveloped in a thin plasma polymer (ppHMDSO) shell. Moreover, under 4% of HMDSO the NPs were composed of many small Ag cores enveloped in a plasma polymer shell (so-called Ag multicore@ppHMDSO shell NPs). Obtained nanocomposite films were characterized by optical and electrical properties.

Acknowledgments: This work was supported by the grant GACR 17-22016S from the Czech Science Foundation

Keywords
nanoparticle
core@shell
Phase-resolved nanoparticle collection with biased substrates during particle growth cycles in an acetylene plasma reactor

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Controlled growth and size-selective collection of nanoparticles are desired for applications in catalysis, pharmacy and for the fabrication of nanofilms and nanodevices. Controllable particle growth in low-temperature plasmas seems to be very promising for the generation of well-defined nano-sized particles. In this work, we propose a simple scheme for the collection of nanoparticles (NPs) generated in a capacitively coupled RF plasma in Ar/C₂H₂ mixtures by the use of differently biased substrates at different positions in the particle cloud. The ever moving dust cloud, in turn, induces spatial variations of the plasma potential. By this method, the nanoparticles can be guided to a certain position of the reactor where they are directionally collected. Also, the time at which the collection starts is well defined. As important parameters, we monitored the self-bias voltage at the powered electrode, gas pressure and the shape of the dust cloud with by laser light scattering and a CCD camera.

Collection experiments were carried out at different distances from the RF electrode as well as different times during the growth cycles. A correlation of the collection time with the self-bias voltage and SEM results of the collected particles on Si substrates are discussed.

The SEM photographs show that different threshold potentials are needed to overcome the NPs confinement due to the spatial and temporal variation of the plasma potential inside the particle cloud. Moreover, the dispersion of the nanoparticles on the substrate is determined by the bias applied to it.

These results based on the phase-resolved collection method allow to control depositions of carbon nanoparticles of a well-defined size distribution with the highest density available their growth.

Keywords
dusty plasma
plasma-grown nanoparticles
particles collection
particles dynamics
capacitively-coupled RF plasma
In this first attempt to sputter metal onto liquid substrate, we first used a DC magnetron device to sputter Ti and Ag atoms onto a solution of pentaerythritol ethoxylate (PEEL).

In this case, our data reveal that Ti atoms sputtered in low-pressure argon plasma first form a film over the liquid surface. However, the latter dissolves after venting the sample. Anatase TiO₂, asymmetric, and facetted nanoparticles (NP) are found as if they were originating from a dismantled polycrystalline thin film. In the case of Ag atoms sputtered on PEEL, a film also forms but solvation does not occur, even after exposing the sample to air. The silver film precipitates and stays in the bottom of the vial. Quantum chemistry based calculations confirm that the chemical interaction of an oxidized surface (TiO₂, AgO) with the PEEL molecules is more favorable as compared to metallic Ag or Ti. These results suggest that oxidation of the material is a prerequisite for its incorporation inside the PEEL solution. Silver is not incorporated because its enthalpy of oxidation is not large enough, therefore spontaneous oxidation of the Ag film is not likely while it is the case for Ti.

In a second step, Ag was also sputtered on 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIMTFSI) ionic liquid (IL) which shows a completely different chemical structure as compared to PEEL. Therefore, a different metal-liquid interaction is expected. Indeed, in this case, film formation is not observed and spherical, crystallized Ag-NP are obtained. This result suggests a favorable interaction between Ag atoms and the ionic liquid allowing for instance the direct incorporation of the sputtered Ag atoms inside the liquid medium.

**Keywords**

Sputtering
liquid substrate
titanium dioxide
Silver
nanoparticles
A strategy for producing advanced nanoparticles, nanowires and nanotrusses: dual-target High Power Pulsed Hollow Cathode Sputtering

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By the use of two sources in combination with variation of smart pulsing sequences we have been able to controllably generate Ni/Fe nanoparticles (NPs) in the form of the pure metals, alloys of the two metals and core-shell NPs, respectively. The process is based on a rapid synthesis method, high-power pulsed hollow cathode sputtering [1]. With this method, NPs are synthesized in the plasma and, as in the present case with magnetic materials, self-assembles into wires and trusses. To grow a NP into a size >20 nm, several pulses from the hollow cathode are required. This can be exploited when growing NPs from several different materials. By pulsing different targets individually, we show that it is possible to change both the composition and constitution of the NPs, such as generating core/shell structures. Magnetic NPs do not agglomerate inside the plasma because of electric repulsion, but self-assemble into one-dimensional strings, nanowires, at the substrate. The particles in such wires have a narrow size distribution of about 30-50 nm. If a permanent magnet is placed behind the substrate, the size distribution of the NPs on the substrate broadens to about 10-60 nm, resulting in cross-linking of the nanowires, generating nanotrusses. This yields a more rigid and stable structure, giving rise to a variety of different 3D structures with a length of several hundred µm. The structures are suitable for catalysis because of their huge surface area, combined with their electrical properties. We demonstrate this through electrocatalytic water splitting, where Fe nanotrusses are used as electrodes in the process.


Keywords
Nanowires & Nanotrusses
Alloys
Self-assembly
Fast and Cost-Efficient Synthesis of Zinc Oxide Nanowires with an Atmospheric Pressure Plasma Jet

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Due to its piezoelectric properties, zinc oxide is a promising candidate as sensor material for condition monitoring and in haptic sensors, especially in the form of nanowires (linear structures with diameters < 100 nm and with a few to one hundred micrometers length).

Although there are many ways to synthesize ZnO-NWs, such as hydrothermal growth, the plasma flight-thru process offers several advantages, namely short process times, high throughput and cost-efficiency. However, there are only a few examples in literature, and that work exclusively with microwave APPJ reactors.

It is the aim of our present work to develop a method for the fast and cost-efficient synthesis of ZnO-NWs with a commercially available APPJ setup based on a direct current arc discharge.

Therefore, we studied the formation of ZnO-NWs in the APPJ. Different currents and plasma gases were tested, and zinc powders of different mean diameters were introduced into the plasma jet.

In order to collect the nanoparticulate matter, we built a semi-closed reactor, which consisted of two steel tubes. Temperature measurements on the outside of the inner tube assured reproducible reaction conditions. The experiments were repeated with different reactor geometries.

SEM images taken from the samples show a great variety of structures, including half-molten particles, nanowires and filigree nanoscale networks. Most promising are needles grown on stainless steel mesh, with diameters of 20-50 nm and lengths of 1-4 µm. The molecular ratio of zinc to oxygen found in EDX spectra is almost 1:1, which indicates that ZnO was formed successfully.

After further optimization, we should be able to synthesize and harvest ZnO-NWs in a semi-continuous, cost-efficient way, so that we will meet the requirements needed in condition monitoring and haptic sensors, soon.

Keywords
Zinc Oxide
Nanowire Synthesis
Atmospheric Pressure Plasma Jet
Modeling and Experimental Study of a Wurster type Fluidized Bed Reactor coupled with a Pulsed Arc Air Blown Atmospheric Pressure Plasma Jet for the treatment of Polypropylene Powders

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Polypropylene (PP) powders are used for various purposes. However, its good mechanical properties are accompanied by a poor wettability. The PP powder was therefore modified by a pulsed arc air blown atmospheric pressure plasma jet (APPJ) in a home-made Wurster fluidized bed batch reactor (Wurster-FBR). The physical and chemical modifications of the treated PP powders as compared to the nontreated ones were determined by water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS), and SEM for morphology observations. PP powders are basically hydrophobic but after plasma treatment in the plasma enhanced fluidized bed they became strongly hydrophilic, because of the oxygen uptake of the surface of the particles determined by XPS. An internal Wurster tube was added to fluidized bed to control the residence time of the particles in the plasma jet, and therefore the homogeneity of the treatments.

A 2D axisymmetric non-isothermal k-ω turbulent Euler-Euler model was applied to determine the fluid and powders dynamics inside the reactor and compare with fast imaging, thermocouple and anemometry experimental results. These investigations are very important to control the homogeneity of powder treatments, i.e. the distribution function of the effective treatment time and moreover since PP is a thermally sensitive material, to avoid its thermal degradation. The results show that the 200 g of PP powders treated per batch during 5 minutes are characterized by an average effective treatment time of 2 milliseconds, which correspond to 20 cycles per particle, the PP temperature rises from r.t. to about 60°C while the surface energy of the latter increases from 29 to 40 mN/m. Finally, this process is suitable for large scale treatments of polymer particles and the scaling-up will be discussed.

Keywords
Atmospheric Pressure Plasma Jet
Wurster-Fluidized Bed Reactor
Polypropylene Plasma Treatment
CFD Modeling
Heat transfer Modeling
MoS\textsubscript{2} based nanocomposite films: structural designing and tribological properties

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Magnetron sputtered transition metal dichalcogenides film possess excellent lubrication performance due to of their unique layered structure. In this work, Mo-S-C and Mo-S-C-N composite films were synthesized by sputtering, and the influence of C and N dopant on the nanostructure, morphology, mechanical and tribological properties of composite films in different sliding conditions were discussed [1-3]. Increasing the sputtering power applied on graphite target contributed to a significant increase of film hardness, and improved lubricant performance was obtained, which produced MoS\textsubscript{2}/Mo-S-C (N) nanoperiod multilayer film by a novel self-assembled mechanism, further introducing nitrogen into deposition promotes the formation of self-assembled nanoperiod multilayer structure. The HRTEM observation shows phase segregation of MoS\textsubscript{2}-riched domain layers and Mo-S-C (Mo-S-C-N) composite capping layers initiating from substrate-film interlayer and diffusing mutually in a quasiperiodic pattern throughout the entire thickness of film. Based on the tribological results, clear evidence on the selective transferring behavior according to sliding atmospheres was found, particularly in vacuum and dry inert artificial atmospheres, in which amorphous carbon in graphitic form was selectively released outwards from tribofilm as non-lubricant phase, turning into debris or partly dumping into the ploughed valleys on wear track, while the MoS\textsubscript{2} molecular layers finely reordered in (002) orientation were formed on the topmost surfaces of tribofilms and wear tracks playing a lubricant role. The more exhaustive release of non-lubricant phase, the lower friction of rubbed counterparts can be obtained. Meanwhile, the initial preference of (002) orientation in MoS\textsubscript{2}-riched domain layers facilitate the reordered evolving process of shearless tribofilms in sliding contact, which provides a feasible way of structural tailoring in MoS\textsubscript{2}-based lubricant films for improved properties.


Keywords
MoS\textsubscript{2} based composite films, nanostructure, lubricant mechanism
Effect of surface self-adaptation on the tribology of the Mo-S-C coatings

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Transition metal dichalcogenides (TMD) coatings such as sulphides or selenides of tungsten, molybdenum and niobium are frequently used as solid lubricants in dry air or vacuum environment. The main disadvantages of pure TMD that limit its practical applications are low hardness, low load-carrying capacity, and common effects of tribo-reaction with ambient atmosphere which may determine chemical alterations hence deteriorate the tribological properties. There are several ways how to improve the tribological properties of TMD films, such as doping with specific elements or compounds. In recent years, several TMD’s alloyed with carbon (TMD-C) were tribologically tested. These films exhibit excellent tribological properties both in dry and humid air and perform well even under extremely high contact pressures. The TMD-C coating microstructure usually consists of randomly oriented TMD platelets embedded in an amorphous carbon matrix. Based on these studies, it has been showed that the low friction sliding is attributed to the formation of highly oriented tribolayer at the sliding interface caused by sub-surface re-orientation of the TMD platelets and release of the carbon graphitic phase from the contact area. In this study, Mo–S–C coatings were deposited and tested for their structural, mechanical and tribological properties. The tribology was studied on a pin-on-disc apparatus at room temperature, elevated temperature, as well as in the vacuum environment. The presence and properties of surface tribolayer were determined by Raman spectroscopy and HR-TEM imaging. The results confirmed that the existence of the oriented surface tribolayer is highly sensitive to the testing conditions and plays an important role in the TMD-C tribology.

Keywords
Mo-S-C
dichalcogenides
TMD
tribology
Raman spectroscopy
Advanced coating design as an effective tool for protective coatings operating under severe conditions

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Increasing requirements on tool surface protection during cost effective machining of difficult-to-cut materials creates new challenges for design of hard protective coatings. Severe conditions on tools during high-performance or high-speed dry cutting of very abrasive or hard materials are beyond thermal and/or mechanical stability of standard hard coatings. In order to design coating with such complex properties, an approach to combine various materials with specific elemental and phase composition in a dedicated coating architecture is very promising as it can simultaneously address necessary properties such as good adhesion, optimized stress depth-profile, high hot hardness and wear resistance, enhanced thermal stability, suppressed bulk diffusion and diffusion across interfaces at elevated temperatures as well as improved oxidation resistance. This approach will be demonstrated on multilayer systems combining nanostructured AlCr(Si)N and AlTi(Si)N materials in a variety of architectures. The coatings were synthesized in an industrial PVD deposition system (alpha400P, eifeler-Vacotec) equipped with multiple arc evaporation sources. The effect of the elemental composition (in particular Al/Me ratio and Si content), deposition conditions and architecture on the development of the coating structure and phase composition was studied by advanced position-resolved X-ray diffraction (XRD). The stress state was studied by XRD and curvature methods, hardness and elastic properties by nanoindentation, wear resistance by pin-on-disc method and the thermal stability and oxidation resistance were studied by thermogravimetry and differential scanning calorimetry. A combination of extreme mechanical, tribochemical and thermal loads on substrate-coating system with complex geometry during machining of difficult-to-cut materials was simulated by dry milling of hardened steel providing valuable data on cutting edge wear, cutting forces, formation of chips and temperatures under various cutting speeds. The results were used to establish correlation between coating composition, architecture and properties and provide feedback for design of coatings operating under extreme conditions.

Keywords
arc evaporation, coating architecture
New nanostructured tribological coating for energy efficient engine components

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Nanostructured PVD coating systems in highly stressed engine components are already successfully used in mass production for high energy efficiency. One application is the tribological contact bucket tappet/cam(shaft) in the valve train that offers potential for friction reduction but also places high requirement for coatings due to its complex kinematics and different contact pressures. One new approach is a nanostructured tribo-catalytic PVD coating system that continuously form protective tribofilms on the tribologically stressed surface driven by the interaction with the base oil and its additives. The influence of that new nanostructured tribo-catalytic coating on the friction and wear behavior was investigated for the first time within the contact bucket tappet/cam. This tribological contact was analyzed by means of single cam/bucket tappet component test-rigs with series-production valve train components ensuring high transferability of the results into real application. The tribological mechanisms were also analyzed in a pin-on-disc tribometer using same tappets and steel balls (100Cr6, AISI 52100). A nanostructured hard nitride coating and a superhard DLC coating coating were deposited on the bucket tappets (16MnCr5, AISI 5115). PAO (polyalphaolefine) as synthetic base oil was used for the tests. The influence of the coatings on the friction and wear behavior for engine oil temperatures between 50 °C and 90 °C was tested according to WLTC. Wear was analyzed by means of confocal laser scanning microscopy (CLSM). The tribofilms on the coatings were investigated by Raman spectroscopy and secondary neutral mass spectrometry (SNMS). The results were correlated with the friction and wear behavior observed in the pin-on-disc tribometer. The results from the test runs and analyzes clearly point out the formation of a tribo-film consisting of Ferrum-Oxide compounds or/and carbon on the nanostructured hard nitride coating. This led to the same wear behavior as the superhard DLC coating achieved in the tribometer and in the single cam/bucket tappet component test-rig.

Keywords
Energy efficiency
Nanostructured tribo-catalytic coating system
Addition of Ta or/and Y in Al-Ti-N base hard PVD coating: what are the individual and conjugated effects of these additional elements on their oxidation and wear property at high temperature

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Hard metal nitride coatings have become increasingly used in the industry in the past few decades. One of those coatings, Ti-Al-N, is now widely used in the machining industry, owing to its outstanding oxidation resistance properties. The structure change of this ternary coating at 1223 K has followed to conduct research and to put out on the market quaternary coatings, with for example, an alloying element as Ta [1,2] or a doping element as Y [3] to shift at higher temperatures, the spinodal decomposition and/or to improve the oxidation resistance. Here, it is proposed a complete comparison study of 4 coatings, all deposited on the same industrial coater machines by arc process: Ti-Al-N, Ti-Al-Y-N, Ti-Al-Ta-N and Ti-Al-Ta-Y-N. It will be summarized the structural and mechanical properties of these as deposited coatings and also their behaviors at high temperature during oxidation tests and wear measurements. On the as-deposited coatings, the influence of Ta or/and Y will be discussed based on the results obtained from internal stress coating evaluations and nanohardness measurements. The oxidation kinetic of these coatings will be also reported and completed by cross-section oxide observations with SIMS analyses and by the study of the oxide friction behavior of the thin oxide layers. All these results will then be associated to a discussion regarding the individual effects of Ta or of Y and of a conjugated effect when they are both associated to the composition of a hard nitride coatings. [1] Khetan, V., Valle, N., Duday, D., Michotte, C., Delplancke-Ogletree, M.-P., Choquet, P. (2014) ACS Applied Materials and Interfaces, 6 (6), pp. 4115-4125. [2] Khetan, V., Valle, N., Duday, D., Michotte, C., Mitterer, C., Delplancke-Ogletree, M.-P., Choquet, P. (2014) ACS Applied Materials and Interfaces, 6 (17), pp. 15403-15411. [3] R. Aninat, N. Valle, D. Duday, P. Choquet, Corrosion Science, 111 (2016) 454-466.

Keywords
TiAlN
oxidation
wear
Friction and wear between moving parts is a main reason for unwanted energy loss and considerable efforts are made to reduce such losses. Therefore, it is desirable to understand the physical principles of friction and wear processes and to apply the knowledge for the development of materials with improved surface properties.

Hundreds of tribological test methods exist but there are only a few which allow an investigation of sliding contacts with a lateral resolution of one micrometer or less and a simultaneous measurement of a surface layer removal in the nanometer range. Such high-resolution tests give a better access to processes which cause surface modifications and failures. The nanomechanical tester ZHN from Zwick equipped with a lateral force unit is used to study the friction and wear behavior of hard surfaces and coatings with ultra-high lateral and depth resolution. Normal and lateral movement are completely decoupled and do not influence each other. Force and displacement are measured with four sensors and a high frequency feedback loop exist for both directions. The instrument allows a simultaneous mapping of contact stiffness or modulus, friction coefficient and contact resistance between a conductive tip and the surface with a lateral resolution of better than one micrometer and a depth resolution of one nanometer. This will be demonstrated by several examples. First, the frictional behavior of diamond sliding on diamond was investigated for a polished polycrystalline diamond coating and a diamond-SiC composite material. The contact pressure was between 1 GPa and 22 GPa. A clear pressure dependency of the friction coefficient and a violation of Amonton’s law were found. Under certain conditions, the friction coefficient was below 0.01 under wet sliding conditions in pure water. The determination of the diamond crystal orientation by EBSD in the area of the friction mapping has revealed that the friction coefficient is depending on the crystallographic orientation. Other examples will be given for DLC coatings and metallic coatings which are used for electrical plugs. In these cases, friction and wear have been investigated for different contact conditions.

Keywords
Friction
Wear
Novel entropy-stabilized ultra high temperature ceramics thin films prepared by magnetron sputtering

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The entropy stabilization concept recently has been successfully applied to oxides and borides of transition metals, and induce the great interest especially in the case of ultra-high temperature application. These materials typically are a single-phase mixture of 4 or 5 elements in equiequiatomic proportions. Here we show the new thin film ceramic system (Hf\textsubscript{1/4}Zr\textsubscript{1/4}Y\textsubscript{1/4}Ce\textsubscript{1/4})O\textsubscript{2-δ} which exhibit superior thermal stability up to 2000°C. Films were prepared by the reactive magnetron sputtering using two metallic HfZr and YCe targets in Ar+O\textsubscript{2} atmosphere. Sputter deposition we performed at room temperature and 500°C. We show relationships between sputtering parameters such as magnetron power density, total pressure, gas mixture and properties of produced film such as mechanical properties, density, phase evolution and thermal stability. We determine the sputtering parameters “window” were sputtered films are characterized by the single-phase cubic structure. We use thermogravimetry measurements and test in an oxygen-acetylene torch in order to characterize thermal properties of studied films. Also we have studied the role of the fifth element addition with different crystal structure (MgO) on the entropic stabilization of the coatings.

Keywords
UHTC
high entropy ceramics
magnetron sputtering
Steel products for the automotive market are most often coated with a Zn or ZnMg layer to protect against corrosion. These coating layers are in general deposited by a hot dip galvanising (HDG) or electro-coating (EZ) process. However, for automotive parts, Advanced High Strength Steels and Ultra High Strength Steels (A/UHSS) are becoming more and more interesting, which are sometimes challenging to coat. Therefore Tata Steel is developing a novel physical vapour deposition (PVD) technology for depositing Zn and ZnMg based coating layers on these types of steel. The key drivers for developing such a coating technology are the possibility to coat a broad range of A/UHSS with a lower coating weight, which at the same time perform equal or even better than commercial coatings. This technology also enables us to be flexible to tune the coating performance to the end user requirements.

In this perspective, the composition and microstructure of the Zn and ZnMg based PVD coatings will have a large influence on their performance. Their microstructure can be tuned by changing the cleaning and vacuum deposition conditions. However it is difficult to indicate, a priori, the relation between the coating deposition conditions and the final coating properties. Therefore we investigated the relation between the coating microstructure and coating performance. The most important results with respect to coating adhesion, corrosion, and forming properties are presented. We will show that these are comparable or even can exceed those of commercial state-of-the-art coatings such as GI140 and GA90, and even AlMgZn HDG coatings.

**Keywords**
- ZnMg
- PVD
- Automotive
- A/UHSS
Corrosion Protection of Mild Steel Substrates for Complex Tribological and Corrosive Stresses by Innovative PVD Coatings

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Establishing PVD technology as a serious competitor to hard chromium platings requires coatings, which fulfil or even improve the wear and corrosion protection properties of chromium platings.

One serious approach are TiMgREN (RE = Rare Earth) based coatings. In previous works of the authors, monolithic TiMgGdN coatings were synthesized in an industrial magnetron PVD unit by using multi-component targets consisting of segments of the coating material metals Ti and Mg-Gd. With an only 5 µm thick TiMgGdN coating onto mild steel substrate, a corrosion resistance of at least 800 h could be achieved in the salt spray test without any macroscopic corrosion attack.

In the present work, the influence of the chemical coating composition, the deposition parameters, the substrate roughness and the sputter mode on the coatings microstructural, physical and mechanical properties, the corrosion properties and the wear behaviour were examined.

Besides the application Gd as alloying element, the influence and the effect of other rare earth metals (La, Ce) on the corrosion performance was examined.

The coatings were characterized concerning their microstructural, mechanical and chemical properties. Salt spray tests as well as electrochemical measurements were carried out to examine the corrosion properties of the coated specimens.

Furthermore, ball on disk wear tests were conducted by reciprocal dry sling tests by using a SRV 3 tribometer.

It will be shown that the coatings chemical composition influences the corrosion and wear performance in opposite direction. A compromise in chemical composition between good corrosion and wear resistance was identified. By variation of the deposition parameters, the coating properties could be improved concerning both, corrosion and wear behavior. Furthermore, the effect of the used rare earth metal type and the rare earth metal content on the coating properties will be discussed.

Keywords
PVD
TiMgGdN
corrosion
salt spray test
electrochemistry
Self-lubricant and multilayered coatings as a solution for machining operations

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High performance dry machining is one of the major trends in modern manufacturing. This is a very hot topic inside the tribology community; PVD tool-coaters and cutting tools costumers are seeking innovative coating solutions which could improve the performance and lifetime of tools, as well as, increase the material volume removal rates through increasing cutting speeds. Dry machining cutting conditions generate severe shear stresses and high temperature harsh conditions on the cutting zone which, consequently, lead to a premature degradation of the tool. Thus, a promising coating should exhibit simultaneously high toughness, low friction coefficient, low wear rate and thermal stability at high temperature conditions. This work presents new insights on the development of: i) self-lubricant coatings with control release of the lubricious phase (TiSiN films alloyed with V deposited by HiPIMS) to reach long term lubrication and ii) developing of coating systems in multilayer structure (altering layers of Cr(Al)N/Ti(Al)N) which could allow cracking deflection. The results showed that HiPIMS allowed tailor the nanocomposite structure of the TiSiVN films (change of grain size and Si-N thickness) at low deposition temperature independently of the Si concentration on the film in such way that V diffusion can be controlled. Drilling performance of multilayered Cr(Al)N/Ti(Al)N films conducted at low cutting speed (50 m/min) is 2 times worse than monolayered Ti0.47Al0.46N reference film due their low hardness. However for high cutting speeds (100 and 200 m/min) Cr containing coating displayed better cutting performance due to the: i) formation of a protective Cr-O rich tribolayer, ii) high oxidation resistance and iii) cracking deflection.

Keywords
Self-lubricant nanocomposite TiSiVN films
HiPIMS
Multilayer TiAlCrN films
High temperature tribology
Cutting performance
The motivation for plasma boriding is its excellent surface hardness and wear protection of low alloyed steel.

The wear resistance of parts in mechanical engineering and automotive industries made of low alloyed steel can be improved by optimizing their surface using heat treatments such as plasma nitriding or -carburizing. Nevertheless, in the case of combined stress from high abrasive wear, adhesive stress and very high shearing forces, most kinds of economical surface modification will be overloaded. In particular, the plasma boriding process renders the possibility of producing layers with excellent properties under these stress conditions [1]. However, in industrial scale plasma diffusion treatment only plasma nitriding and carburizing are widely applied. Plasma boriding has not achieved the necessary market maturity until now, even though plasma boriding of steel leads to the same excellent wear protection as harmful powder or paste boriding.

A brief introduction to the plasma diffusion treatment outlines the way to the current state of the technology. Then the contribution exemplifies recent efforts in plasma boriding. The formation of pores during the plasma boriding is the problem that has to be solved. To overcome the difficulties in plasma boriding it is necessary to optimize the treatment gas distribution in the process chamber and the temperature profile during the whole process. The hardness is in the range of 1600 HV up to 30 µm depth or more. The wear was measured by the calo test and shows the best results for Fe₂B phase. The formation of pores was determined by SEM and optical microscope. The amount of pores was reduced to less than 1 % by optimizing the gas distribution due to simulation of the gas flow.

**Keywords**

Boriding
plasma
low alloyed
wear
hardness
Effect of Plasma Nitriding Pretreatment on the Mechanical Properties of AlCrSiN Coated Tool Steels

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AlTiN and AlCrN hard coatings have been widely used in cutting tools, dies, molds and mechanical components due to their good oxidation resistance. However, the specific applications of these hard coatings deposited on steel substrates in some harsh conditions are limited due to tool failures caused by hardness inconformity and poor adhesion between the coating and the substrate. In this study, a duplex treatment combining plasma nitriding followed by cathodic arc deposition is used to strengthen the adhesion strength and tailor the hardness gradient of AlCrSiN hard coatings on H13 Tool steels. The different nitriding layers were tailored by PN with various N2/H2 flow ratios on polished H13 steel. The AlCrSiN coatings were deposited on plasma nitrided and merely polished non-nitrided H13 steels by cathodic arc deposition. During the coating process of AlCrSiN, CrN was deposited as an interlayer to enhance adhesion strength between the coatings and nitrided substrates. By controlling the temperature and mixture of N2/H2 atmosphere of PN, the duplex treated AlCrSiN coated tool steels possessed different microstructures and mechanical properties. The microstructure of the deposited coatings were investigated by field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray analysis spectrometer (EDS). XRD was used to characterize the microstructure and phase identification of the duplex-treated coatings. The hardness of the coatings was measured using nanoindentation. Rockwell indentation was conducted to evaluate the coatings adhesion. To evaluate the impact fracture resistance of the coatings, an impact fatigue test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. It is expected that the adhesion strength and wear resistance for duplex-treated coatings increase significantly due to a gradient hardness support. The combination of proper PN and hard coatings is to increase the life of metal molding and forging dies.

Keywords

duplex treatment
plasma nitriding
hard coating
cathodic arc deposition
Advanced surface treatments are used more and more in daily manufacturing of parts for the automotive industry to serve functional and decorative purposes. Higher specific loads (thermal, mechanical etc.), weight and friction reduction (CO2 emission reduction), longer components lifetime, and improved corrosion resistance are demanding for modern automotive systems. Within the last decades, high performance surface solutions and new or improved surface treatments, especially in the group of plasma assisted processes, both for diffusion and deposition processes (IONITOX, PVD, PACVD, Thermal Spraying) were developed to provide economic applications for automotive parts. It will be shown that these new treatments are becoming more common in engine applications and powertrain. The potential of optimized functional surface generation by proper coating selection is demonstrated. Due to the fact, that an enormous wide property field of surfaces is adjustable within these competing surface treatments more and more components are treated. It becomes common to substitute the more limited traditional treatment-substrate-systems (e.g. galvanizing etc.) with the described advanced treatments. Besides the wear and friction reduction of various components also decorative applications even for multifunctional purposes are successful implemented in daily production. In addition new surface solutions are required for green car development.

**Keywords**
Automotive
Thermal spraying
PVD
DLC
thermochemical
OR1004

Functional characterization of hybrid surfaces: dimple-shaped anodized Al alloy surfaces coated with WS-CF sputtered coatings

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Aiming to avoid or reduce the use of lubricants, surface engineering can control the surface wettability, by mimicking features and structures existing in the living beings, which in synergy with the modification of the surface chemical composition is a potential solution for solving lubrication problems. As well-known surface modification technologies, anodization and magnetron sputtering emerge as two effective techniques to both alter the chemistry and roughness of a materials surface. This work aims to create a wear resistant aluminum alloy surface (Al6016T4) with a specific non-common wettability behaviour (hydrophilic-oleophobic), which can be simultaneously self-cleaning and anti-greasing. To reach this goal, nanostructuring, promoted by anodization, complemented with the deposition of a low friction coating based on tungsten disulphide (WS₂), were proposed to tailor the wettability and tribological behaviour of Al-alloys. In regard to Al alloy anodization, dimple-shaped morphologies with different pore diameter (~ 31 nm and ~223 nm) were produced using two different electrolytes at different potentials. Afterwards, hybrid structures were obtained by coating the anodized surfaces with the WS-based coatings alloyed with F and C, with 100-200 nm thickness. The morphology, chemical composition / bonding, structure and wettability characterization were respectively performed by SEM-WDS, XRD techniques and water/oil contact angle measurements. Mechanical properties such as hardness, elastic modulus and adhesion were also performed by nanoindentation and scratch testing. Tribological performance of the structured surfaces was also evaluated against 100Cr6 steel balls using a pin-on-disc configuration at 20 N load. The results revealed that the coatings enhanced the repellence to oil induced by the bottom anodized Al surfaces. However, the friction coefficients were not reduced in comparison with polished surfaces coated with similar film.

Keywords
low friction
wettability
anodization
sputtering
lubrication
Development of Hybrids Nanocomposites materials based on graphene and siloxane polymer by DBD Discharges to Improve the Corrosion Behaviour of Steel

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The present study proposes an alternative eco-friendly multiphase hybrid coating based on graphene embedded siloxane plasma polymers to enhance the resistance against corrosion over the steel. The nanocomposite coatings were performed by Dielectric Barrier Discharges (DBDs) at atmospheric pressure operated in a Townsend regime using nebulized graphene nanosheets colloidal suspension in hexamethyldisiloxane (HMDSO) as the growth precursors. In the first place, the dispersion of (1-2wt\%) of Gr nanosheets in HMDSO and ethanol (EtOH) were carried out using an ultrasonic homogenizer in order to obtain a colloidal solution with optimized Gr nanosheet sizes to ensure good protection but also to avoid its aggregation which will cause delamination in the hybrid films formed respectively. Siloxane coatings with embedded Gr nanosheet nanocomposites were characterized by X-Ray photoelectron spectroscopy (XPS), ellipsometry and Raman spectroscopy. Similar Raman spectra of Gr nanosheets and for Gr nanosheets embedded in HMDSO coatings were obtained which show that plasma exposure does not alter the crystalline structure of the Gr nanosheets injected into the discharge. Additionally, scanning electron microscopy (SEM), confirm the synthesis of micro/nanocomposites with a fairly homogeneous dispersion of the nanoparticles in the polymer matrix. The corrosion resistance of the steel coated substrates was evaluated by potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS). The multiphase hybrid coatings (HMDSO-Gr nanosheets) showed better corrosion inhibition properties when compared to the polymer matrix alone which confirm that the inclusion of Gr nanosheets into the SiOx film enhance the protection performance of SiOx film by reducing the micro-porosity and increasing the diffusion path length of the electrolyte.

Keywords
DBDs
Graphene nanosheets
Hybrid Coating
Corrosion
Preparation and characterization of multi-layer barrier films on PET substrate via PECVD

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The flexible and transparent barrier films, its wide applications, such as the solar cell encapsulating materials, flexible organic light emitting diodes, electronic paper, etc., have attracted an increasing amount of research interests. In order to prepare high water barrier film, high compactness, pinhole-free SiO$_x$ inorganic layer and flexible SiO$_x$C$_y$H$_z$ organic polymer layer were prepared on PET substrate using hexamethyldisiloxane as the precursor and oxygen as the oxidizing gas. By changing the ratio of HMDSO and O$_2$, continuous alternating structure of organic and inorganic films can be obtained. This work studied the effect on the water barrier properties of layer interface morphology, and number of alternating layers. The chemical structure, surface morphology and barrier properties of the films were analyzed by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope, ultraviolet-visible spectrophotometer and water vaper transmission rate tester. The organic/inorganic permeability rate was 0.21g/m$^2$•day in one cycle, and the three cycle organic/inorganic permeability rate was 0.0023g/m$^2$•day. The results reveal that the defects and compactness of the inorganic layer directly affect the water barrier performance. The inorganic layer is mainly responsible for the water vapor barrier effect, while the organic layer take effecton flexiblility. The interfacial properties of alterating layers has an important effect on the water barrier properties. In addition, the effect of thermal cycling damage on the SiO$_x$C$_y$H$_z$-organic coating and SiO$_x$-inorganic coating were investigated respectively. The results show that the barrier performance and adhesion of SiO$_x$C$_y$H$_z$ coated film remained unchanged even after repeated thermal cycles, while that of SiO$_x$ coated film decreased.

Keywords
Barrier film
Multilayer film
PECVD
WVTR
Surface selective plasma-enhanced CVD of hard carbon films

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Hydrogenated amorphous carbon (a-C: H) films have received a considerable attention due to their high chemical stability, optical transparency and hardness and have applied in various areas, especially in protective coatings and tribological applications [1]. Here we report two kinds of surface selective plasma CVD of a-C:H; structure selective one and surface material selective one. Structure selective plasma CVD is realized by tuning kinetic energy and flux of ions impinging onto surface. So far, we have succeeded in controlling deposition profiles of carbon films on trench substrates, and realized sub-conformal, conformal and anisotropic deposition profiles. Surface material selective plasma CVD brings about selective deposition using local surface temperature and local electric potential of the local surface depending on surface materials. Experiments were performed using an H-assisted plasma CVD reactor, in which a capacitively-coupled main discharge and an inductively-coupled discharge of H atom source were sustained independently [2-5]. Toluene was supplied at flow rate of 5 sccm, and the total flow rate of \( \text{H}_2 \) and \( \text{Ar} \) was 90 sccm. Gas flow rate ratio was set from 11% to 55%. The bias voltage was -60V. The substrate temperature was 100 °C. AFM images of a-C:H films show presence of concave-convex structures scattered throughout the scanned area. RMS roughness decreases from 9.9 nm to 3.9 nm with increasing the gas flow rate ratio from 11% to 55%. These results indicate that a-C:H films have RMS roughness below 10 nm can be obtained by tuning the gas flow rate ratio. Details will be presented at the conference.


Keywords
plasma CVD
a-C:H film
surface morphology
surface selective deposition
The ability to controllably micro-nanostructure a surface, and at the same time control the surface chemistry allows extreme flexibility for functional surface fabrication. For example, control of wetting properties at the extremes of wetting states (superhydrophilic and superhydrophobic) can impart functionality such as self-cleaning, anti-fogging, anti-icing, and antibacterial to name a few.

Here, we will first describe our plasma micro-nanotexturing technology of polymers which creates topography on any organic or inorganic polymer at will, as well as hydrophilic or hydrophobic surface chemistry. The technology is based on extremely fast anisotropic etching of a polymer in a high density plasma source, with a simultaneous flux of etching inhibitors arriving on the etched surface. We will focus on the control of topography and chemistry towards a) superomphiphobic surfaces sustaining ultrahigh pressures of tens of atmospheres, b) Cancer cell enrichment surfaces.

We will then discuss the incorporation of such surfaces in microsystems, and their applications. We address a) Metering microfluidics, incorporating hydrophilic capillary pumps and superhydrophobic valves, b) bacteria capture microfluidics for food pathogen analysis.

Finally, we conclude with prospectives and challenges for manufacturability of this technology.

Keywords
plasma texturing
superhydrophobicity
microfluidics
rare cell capture
bacteria capture
On the uplift phenomena induced by plasma assisted nitriding of the lightweight intermetallic FeAl40 grade 3 alloy

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It is known that the introduction of nitrogen, carbone, boron or hydrogen into metal alloys induces deformations which result in swelling of the surface [1]. This phenomenon of volume expansion, which occurs during diffusion treatment such as nitriding, has important consequences from a technological point of view. Especially, this uplift phenomenon can be advantageously used to pattern metallic surfaces and thus find innovative applications in lubricated friction, wettability and thermal management. Nevertheless, the underlying mechanism that makes possible this uplift phenomenon up to 100s of nm is quite complex. Indeed, it combines multiple effects such as phase transformation (mainly AlN nitride precipitation) that was previously investigated [2], the generation of internal stresses that must be evaluated and anisotropic deformations of the treated parts that is experimentally accessible. Explorations of this mechanism is the main objective of the present communication. For this purpose, nitriding treatments were conducted using a MDECR plasma (600 W, - 50V, N₂/H₂ 95 % / 5 %, 2,26 Pa, 8 h, 475 °C). Different patterns were elaborated using masks with various dimensions. Parallel stripes consisting in a periodic alternation of open grooves and plugged grooves were created by laser cutting in the range of 10-1000 µm in width. Observations of the cross-sectional views of the nitrided samples evidence both a lateral diffusion beneath the edge of the mask and an uplift spatial gradient of the nitried part. Results also show that the microstructure, the depth and the swelling of the nitried parts are greatly influenced by both the width of the open grooves of the masks and by the periodicity of the parallel stripes. Finally, mechanical simulations using a finite element software (Abaqus) give access to the stresses distribution through the nitrided parts and help us to better understand the role played by the stresses on the uplift phenomenon.

Keywords
Micro-patterning
Plasma assisted nitriding
Intermetallic iron aluminide
stress simulation
Nanowire Bundles to Repel High-Speed Waterdrops on Polymer Surface by Plasma Nanotexturing

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Waterdrops impacting windshields of high-speed trains and aircraft as well as blades in steam turbine power generators obliquely and at high speeds are difficult to repel because they penetrate the void regions of nanotextured and microtextured superhydrophobic coatings, this pinning resulting in the loss of drop mobility. In order to repel high-speed waterdrops, a capacitatively coupled radiofrequency plasma (CCRP) is utilized to fabricate superhydrophobic surfaces textured with modulated nanowire bundles. The nanotextured polymer surfaces with nanowire bundles are separated from their neighbors by microscale void regions, the nanowires in a bundle being separated from their neighbors by nanoscale void regions. The nanowire aspect ratio, the bundle width, and the inter-bundle spacing distance were adjusted simply by varying the plasma-treatment duration. A spontaneous dewetting transition during waterdrop impacts was found to occur on the nanotextured polymer surfaces with modulated nanowire bundles. Waterdrops with speeds exceeding a critical speed rebound partially, but residual droplets that begin to be pinned undergo a spontaneous dewetting process and slide off. The natural oscillations of residual droplets drive this dewetting process in the inter-bundle void regions, resulting in a transition from the sticky Wenzel state to the slippery Cassie state without external stimuli. The dewetting process occurs even when the waterdrops impact the surface obliquely rather than normally. The restoration of high drop mobility after partial rebounding of waterdrops impacting at high speeds is a highly desirable feature for superhydrophobic surfaces for deployment on high-speed train and aircraft windshields as well as in steam turbine power generators.

Keywords
Plasma nanotexturing
Nanowire bundles
Superhydrophobicity
Waterdrop impacting
Dewetting
Polypropylene (PP) is a versatile thermoplastic polymer used in a wide range of industrial sectors due to its ease of processing, low cost and its excellent mechanical properties. On the other hand, inkjet printing exhibits many advantages with respect to other printing processes, especially in those applications where a digital process is required. Water-based inks have received special attention during the last years due to environmental and health concerns, with the objective of minimizing the use of hazardous solvents. Especially interesting for many applications, mainly in the consumer good industry, is the possibility of inkjet printing on PP substrates using water-based inks. However, the adhesion and wettability of polypropylene by hydrophilic or polar ink systems is very low. This causes problems such as low printability and delamination. In this work, we aim at determining a suitable surface pretreatment for PP plates in order to increase their printability when using water-based inks in an industrial inkjet printer. For this purpose, we carry out surface activation of the PP plates using Low Pressure Plasma, Corona Discharge and Atmospheric Pressure Plasma Jet systems. A comprehensive characterization of the PP plates before and after the different treatments is carried out including contact angle measurements, ATR– FTIR, AFM and XPS. Printing tests using a CMYK set of water-based inks allow us to determine differences in the printability depending on the treatment and ink composition. Finally, adhesion of the inks to different substrates is evaluated by cross-cut tests and water resistance of printed layers by double rub tests. Calculation of the surface energy shows that all the different treatments lead to the desired increase in the surface energy. AFM images reveal a significant change in the microstructure of PP before and after the plasma treatment. However, adhesion and printing tests show very different results depending on the pretreatment technique.

Keywords
Inkjet printing
Polypropylene
Pretreatment
Adhesion
Combinatorial modification of metal surfaces by dielectric barrier discharges using 2D gradients

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The present contribution reports on plasmachemical surface modification of ZnMgAl-alloy coated steel sheets and pure Al samples based on dielectric barrier discharges (DBD). The reactor used in these experiments enables a two-dimensional gradient of process parameters: a concentration gradient of a reactive gas $i$, $\frac{dc}{dy}$, transverse to the gas flow direction, and a gradient in $x$ direction (flow direction) of the temperature of the surface and the gas phase, $100 \, ^\circ\text{C} \leq T_s \approx T_{\text{Gas}} \leq 300 \, ^\circ\text{C}$.

The aim of the project work reported herein is to modify surface composition and properties of metal foils or sheets by using DBDs in different reactive gases and to study the influences of the concentration of active species and the temperature. Properties of interest are, for example, the thickness of the oxide layer on the surface, its chemical composition, zeta potential, and wettability, and to correlate these characteristics with application-relevant qualities such as the corrosion resistance or adhesion of paints and coatings. Gases used for the modification are oxygen, hydrogen, water vapor, and xenon in concentrations ranging from a few ppm to 10 $\%$, the carrier gas is Ar 6.0. The effects of the treatments are analyzed using FTIR spectroscopy, XPS, SEM/EDX, zeta potential measurements, wetting tests and 90$^\circ$ peel tests.

Using combinatorial methods to reduce the experimental effort is of special interest for studying such processes owing to their multi-parameter dependence. Plasma-based oxidation, for example, is generally expected to depend on type and concentration of oxidizing species, temperature, and UV irradiation of the oxide. Treatment time dependence is near logarithmic, requiring potentially long treatments to achieve the limiting oxide thicknesses.\textsuperscript{[1]}


Keywords
Combinatorial surface technology
high throughput experimentation
plasma-assisted surface modification
OR1105

Effect of plasma functionalization on the performance of superconducting microwave resonators for quantum computing applications

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Superconducting TiN resonators are important to quantum information and astronomy detector applications. In this work, we show the effect of plasma functionalization in Ar/C₄F₈, Ar/SF₆ and O₂ gas environments on superconducting resonators performance. We found that the most hydrophobic (Ar/C₄F₈) and the most hydrophilic (O₂) treated resonators had low quality factors. However, the Ar/SF₆ plasma treatment yielded good results most likely linked to moderate concentrations of fluorine and oxygen atoms on the resonator surface. Thus, for Ar/SF₆ plasma, we further investigated the effects of plasma processing parameters, namely plasma treatment time and RF power, on the resonators function. We found that at optimal conditions (moderate bias of -214 V and short treatment times of 20 seconds) the resonator quality factors were greatly improved due to combined effects of modified surface chemistry, morphology and resonator structure.

Keywords
plasma functionalization
chemistry
morphology
resonators
Sequential run of the PEO process with various current waveforms

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Plasma Electrolytic Oxidation (PEO) process is an electrochemical process to produce multifunctional ceramic coatings on light-weight metals. Growth of the oxide layer is assisted by the generation of micro-discharges (MDs) over the processed surface. By using a pulsed bipolar current we previously evidenced that ignition of MDs is delayed with respect to the rising edge of the anodic current. This delay (Δt) has been found to be sensitive to the processing time and the applied anodic to cathodic charge quantity ratio (RCQ). A mechanism of charge accumulation taking place through an electrical double layer (EDL) at the oxide/electrolyte interface was proposed. The present work investigates the PEO process consisting of two different successive RCQ values. Results are compared with those collected from reference treatments within a single RCQ value. The detection of light emission reveals that switching from high to low RCQs leads to an instantaneous and significant increase in the MDs ignition delay Δt. The opposite behaviour is strictly observed when the reverse order of sequences is used. In both cases, after a certain processing time following the switching, Δt tends to converge to the values obtained for reference treatments. These observations are discussed by considering that the dynamic response of the EDL is influenced not only by the applied electrical signal but also by the morphology of the growing coating, especially its thickness and porosity. SEM observations reveal that switching from high RCQ = 6.0 to low RCQ = 0.9 results in the combination of the highest coating thickness (65µm) with the lowest coating porosity (2.3 %). In this particular case, during the switching, the fast video measurements and the electrical measurements detected the disappearance of visible MDs and a sudden drop in the voltage amplitude. So, this particular sequencing promotes an earlier transition into “soft”-regime compared to the reference treatment run only with RCQ = 0.9. These observations are discussed by considering a synergetic effect of this sequence: a rapid growth of a porous oxide layer during the first sequence, followed by a mechanism of “self-healing” when pores are progressively filled during the second sequence, within the “soft”-regime.

Keywords
Plasma Electrolytic Oxidation (PEO)
Role of Plasma ion flux in GaSb nanodots pattern formation for sensing and plasmonic solar cell applications

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Abstract: In this study, a bottom-up approach of ion irradiation from hot cathode DC discharge plasma was used to investigate the role of energetic ion flux on the self-assembly of GaSb nanodots (ND) at normal incidence inside plasma sheath [1]. It is observed that increasing the flux in the range of 1014 to 1015 ions cm\(^{-2}\) s\(^{-1}\), the lateral dimension and the RMS roughness of ND reduces in the ion energy range from 400-800 eV [2]. The evolution of the surface morphology for different flux regimes is simulated using nonlinear isotropic damped Kuramoto-Sivashinsky (DKS) equation. By introducing a redeposition term, DKS equation is found to be in good qualitative agreement with the experimental results. We have demonstrated the linear dependency of the redeposition coefficient on the ion flux and also reported the nonlinear dependency on the thermal diffusion coefficient, transition time, and the characteristics length with the flux. Plasma produced ND later used as template to grow highly ordered silver nanoparticles using magnetron sputtering and have shown immense capability as an active surface enhance Raman scattering (SERS) substrate for molecular sensing and light absorber for the plasmonics solar cell application [3-5]. Closely arranged nanoparticles produce hot-junctions, which enhance the light filed significantly to produce large SERS signal and also help to trap the light in nanogaps for increasing the light absorption [3,4].

Reference


Keywords
plasma sheath, dot pattern, SERS, Plasmonics
Micro Electro Mechanical Systems (MEMS) at Bosch look back on more than 25 years of development and production. MEMS elements are small mechanical systems, acting either as sensors or as actuators. From the historical point of view MEMS manufacturing technology started based on the established silicon semiconductor process technology. In contrast to semiconductor components, MEMS sensors and actuators are 3-dimensional movable elements. This required the development of additional, new and application specific manufacturing technologies besides typical semiconductor processes. Nowadays, some of these specific processes are MEMS key manufacturing technologies. Silicon Deep Reactive Ion Etching (DRIE), also known as the „Bosch Process“, is one of the worldwide established MEMS key manufacturing processes on the market. The starting point of this plasma trench etch process for silicon dates back to the development in the early 90’s at Bosch corporate research on a prototype equipment. With the „Bosch Process“ 3-D structures in silicon can be etched with high etch rates and aspect ratios at high mask selectivity and without restrictions in crystal orientation. It was an enabler for a large variety of interesting bulk and surface micro machined MEMS applications helpful in our daily life. Throughout the years, a wide base of equipment suppliers for MEMS key manufacturing processes and tools established on the market. MEMS provides low-cost mass products like microphones, micro mirrors, pressure and inertial sensors for automotive and consumer applications. New applications like e.g. autonomous driving or virtual reality require inertial sensors with higher sensitivity and resolution. A close co-operation between equipment suppliers and MEMS manufacturers helps to enhance equipment hardware and processes and MEMS products in parallel, in order to fulfil enhanced MEMS product requirements for the future.

**Keywords**
MEMS
Plasma Etching
Trench
Bosch Process
Challenges in thin film deposition of magnetoresistive Sensors

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Magnetoresistive (MR) sensors play an important role in our everyday life as they are ideal for a vast variety of applications like the electronic compass, current detection, speed-, length- and angular-sensing. In general, the MR-effect describes a change of the electrical resistance of a material in an external magnetic field. The origin of the magnetoresistance effect could be for example the anisotropic (AMR), giant (GMR) or tunneling (TMR) magnetoresistance. Today, Sensitec produces different kinds of sensors based on AMR and GMR effect, while sensors based on TMR are still under development. In this talk we will explain the basic effects and their differentiation, and we will show a few examples of sensors and their application.

To control the magnetic and electric properties of such sensors, the control of the fabrication of the magnetic, metallic and insulating thin film layers and thin film deposition processes is crucial. The layer stacks for GMR and TMR sensors may contain more than 20 subsequent layers with thicknesses in the low to sub-nanometer range. Some layers with special functionalities have to be controlled to below 10ths of a nanometer. Some of the challenges in the fabrication of MR sensors with respect to the thin film deposition process will be detailed in this talk.

Keywords
magnetoresistive sensors
AMR
GMR
TMR
thin film deposition
Heatable Scanning Probes, from Data Storage to Nanolithography

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IBM’s probe storage technology, internally known as ‘Millipede’ project, featured massively parallel operation of > 1000 MEMS cantilevers fabricated by silicon micromachining techniques to perform simultaneous storage operations with high data rate. The information was stored in the form of indents in a polymer layer by heated tips at record densities of up to 4 Tbit/in2. The technology has now evolved to a nanolithography platform combining the high data rates and resolution from the storage device with a precise actuation of the levers to form nanometer accurate depth profiles in a thermally sensitive polymer resist. This nanolithography method called thermal scanning probe lithography (t-SPL) is competitive to traditional methods such as electron beam lithography in terms of throughput at sub 20 nm resolution. Moreover, the excellent imaging capabilities of the scanning probe and the direct write character enable a novel and intuitive approach to nanolithography. For example in so called closed loop lithography, the tool uses the imaged information to control the writing parameters on the fly and it achieves nanometer accuracy in patterning depth control. These capabilities are currently used to fabricate unique electrical, optical and nanofluidic devices.

Keywords
MEMS
polymer
thermal scanning probe lithography
Piezoelectric MEMS: Materials, Devices and Applications

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In a compact introduction, I will motivate the benefits of piezoelectric thin films for MEMS and will give a short overview to state of art application scenarios on device level. Next, I will highlight latest results on the electrical, mechanical and piezoelectrical characterization of sputter-deposited aluminium nitride (AlN) including the impact of sputter parameters, film thickness and substrate pre-conditioning [1,2]. I will present the impact of doping of AlN with scandium, which leads to an increase of the moderate piezoelectric coefficient of AlN up to a factor of four. In a next step, these films are implemented into fabrication processes of cantilever-type MEMS devices. In combination with a tailored electrode design, resonators are realized featuring Q factors up to about 300 in liquids covering the frequency range of 1-2 MHz. This enables the precise determination of the viscosity and density of fluids up to dynamic viscosity values of almost 300 mPas [3]. Besides this application, such high Q factors are useful when targeting mass-sensitive sensors, thus paving the way to e.g. particle detection even in highly viscous media. Given the low increase in permittivity of ScAlN compared to AlN, another field of application for this material are vibrational energy harvesters, where the benefit of ScAlN compared to pure AlN is demonstrated [4]. Finally, I will present some selected results of ScAlN thin films within SAW devices ranging from high temperature applications to droplet manipulation in microfluidics [5].

References:

Keywords
piezoelectric MEMS
aluminium nitride, scandium aluminium nitride
viscosity/density sensor
SAW devices, MEMS vibrational energy harvester
Thin film solutions for MEMS and Sensors

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The coming “Internet of Things” (IoT) with its countless opportunities relies on the availability of thin film materials with precisely designed electrical, mechanical and chemical properties. Digging underneath the surface of the shiny IoT reveals a fascinating new reality of various technology combinations. Numerous types of substrates require process steps and coating of materials way beyond classic metallization of Si wafers. The ubiquitous combination of advanced functional materials and their layer stacks is the enabling technology for various sensors and actuators we find in every node connected to the IoT.

This presentation illustrates these needs using examples from different areas, where thin film systems enable the requested functions for MEMS and IoT. These encompass piezoelectric materials like AlN, AlScN or PZT for microphones and speakers, multilayer stacks that form soft magnetic cores for on-chip inductors and transformers, and last but not least, the integration of highly precise optical interference coatings using metals and dielectrics on 8” wafer level. These three examples with their respective challenges necessitate corresponding equipment concepts for volume manufacturing. Advanced stress control, prevention of cross-contamination, parallel processing or dynamic sputtering in batches will be explained. Specific features and options complete this overview, but not without pointing out to still existing challenges, which both device manufacturers and equipment providers have to overcome. We try to shed light on what is commonly known as “More-than-Moore” paradigm from the perspective of an equipment supplier, and for potential device manufacturers we will highlight criteria and requirements before entering and investing in these fascinating technologies.

Keywords
Magnetron Sputter Tool Concepts
Advanced Functional Materials
Piezoelectrics
Soft Magnetics
Optical Interference Coatings
MEMS (micro electro-mechanic systems) have found their way into many kinds of applications. Especially microsensors are used by each of us every day in products like cars and smartphones. These mass products are produced by the big companies in that area, whereas the focus of Hahn-Schickard is the development and the production of highly specialized MEMS products. This enables especially small and medium companies the access to the MEMS technology. The portfolio includes specific inertial sensors like gyroscopes or acceleration sensors for crash test dummies, microfluidic devices for biological and medical applications, actuators like micro valves used in space applications and unconventional high precision products like micromachined watch springs consisting of crystalline silicon. All these devices are manufactured in the cleanroom of the institute in volumes from single devices up to hundreds of thousands chips. In the final talk MEMS productions processes will be explained using recent projects. This includes plasma deposition processes like PE-CVD (plasma enhanced chemical vapor deposition) and sputtering as well as physical and chemical etching techniques. Whereas plasma deposition processes are used for metallic and dielectric thin films, plasma etching methods are used for both, thin films with isotropic etching processes like RIE (reactive ion etching) and for deep trenches highly anisotropic techniques like DRIE (deep reactive ion etching) with high aspect ratio up to 40. The high aspect ratio is achieved by periodically switching of etching and passivation of the sidewalls with a polymer. Finally, the multitude of application scenarios of these procedures will be demonstrated by a high variety of MEMS components realized by these plasma based production processes.

**Keywords**
MEMS
Plasma
Advanced Ion Beam Trimming Technologies for Recent and Newly Developing MEMS-Applications

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An increasing variety of MEMS devices have to fulfil tighter specifications year by year. Bandwidths for RF filters shrink continuously to meet the higher demands for wireless data communication. The internet of things will require operation of simultaneous adjacent wireless communication channels without interference. In addition, a rapid increase in numbers of new sensors and actuators will require high performance under challenging environmental conditions. Many of these MEMS devices will need a highly precise control of structural dimensions or film thickness. For a few of the manufacturing steps of such MEMS devices ion beam milling is applied, especially where nanometer precision, or sometimes sub-nanometer precision, is required. The physical nature of ion beam milling allows for a wide variety of materials to be processed. A specialized version of ion beam milling, where material can be locally and selectively removed from different parts of a wafer, is known as Ion Beam Trimming (IBT). Ion beam trimming of RF-MEMS devices is a well-established manufacturing technique in the industry. Certain further activities for yield improvements will be shown, such as new chucking techniques and reactive processing. The authors will describe the working principles of these technologies and present application examples. Beyond established usage, ion beam trimming has found new applications in manufacturing of advanced RF-MEMS like temperature compensated SAW devices and Murata’s incredible high performance SAW devices based on bonded wafers. The application market has extended from device manufacturers to wafer material providers. From that, new end products can be targeted, but new cost challenges rise as well. The higher achievable accuracy of Silicon on Insulator (SOI) film thickness homogeneity will enable better yields and precision in sensor manufacturing. Actuator production may gain advantage from that advanced film quality as well. Examples will be given for both.

Keywords
ion beam trimming
RF-MEMS
bonded
SOI
In situ monitoring of growth morphology and stress evolution in ultra-thin metal films: interfacial and alloying effects

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The growth of high-mobility metals on weakly interacting substrates (e.g. glass or SiO$_2$) proceeds in a 3D mode, accompanied by a complex stress evolution which underpins the distinct stages of nucleation of isolated islands, coalescence and formation of a continuous film. The control of islands size and shape at the beginning of growth regime is vital for many applications ranging from architectural glazing, plasmonics to catalysis, as the characteristic length scales and physical attributes of ultrathin films are mostly set-in during the coalescence stage.

We have recently shown that combining in situ and real-time optical and electrical diagnostics can provide some insights on the growth characteristics and stress evolution of Ag and Cu films, enabling a direct determination of percolation threshold and film continuity. Although a control of the film microstructural attributes can be achieved by changing the deposition process conditions (working pressure, temperature, deposition rate), strategies based on interfacial or alloying design have recently gained popularity.

Here, we report on the optical and intrinsic stress responses of Ag and Cu films to interaction with Ge, introduced either as sublayer or as solute atoms during co-sputtering. The stress and reflectance evolutions are monitored in real-time during growth by coupling simultaneously multiple-beam optical stress sensor and surface differential reflectance spectroscopy. Overall, the incorporation of Ge during co-deposition results in grain size refinement and larger compressive stress. A stronger chemical affinity is found in the Cu-Ge system compared to Ag-Ge, resulting in the formation of germanide compound. As a buffer layer, Ge acts as a wetting layer, reducing drastically the film roughness. These findings are complemented by ex situ TEM, AFM and XRD characterizations.

Keywords
In situ diagnostics
Intrinsic stress
Growth
Alloying
Hybrid HIPIMS + RF reactive sputtering system for the deposition of non-stoichiometric oxide thin films with defined electrical and optical properties.

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The non-stoichiometric oxide thin films have recently gained an attention due to their practical applications. These semiconducting materials can have interesting optical, electrical and hotoelectrochemical properties with possible applications in various types of optoelectronic devices or different types of solar electrochemical cells working here as the cocatalysts. The defect engineering (DE) has become an attractive research direction for improving the optical and electronic properties of these materials towards highly efficient PEC processes. The main limitation related to the current DE approaches is that they are realized via a high-pressure high-temperature gas reduction. In the presented work the non-stoichiometric oxide thin films such as WO$_{3-x}$, TiO$_{2-x}$, CuO$_{1-x}$ were deposited by a reactive high power impulse magnetron sputtering (HiPIMS) and by HiPIMS in combination with additional RF plasma induced by ICP working with the resonance of electron cyclotron wave (ECWR). By adjusting the deposition conditions, we can regulate the extent of induced defects under reduced temperature. Defined Ar+O$_2$ working gas mixture at different pressures in the range from 0.1- 10 Pa were used for the deposition process with eventual substrate annealing in the RF-ECWR reactive plasma after the deposition process. This annealing could further control the stoichiometry of deposited films and change the crystal structure with other properties. The plasma was monitored during the deposition process by an optical emission spectroscopy, Langmuir probes, RF impedance probe, calorimetric probe and retarding field analyzer. Films were analyzed by XRD, Raman scattering, conductivity and optical absorption measurements. Photoelectrochemical properties of these films were investigated by photoelectrochemical measurement.

Keywords
magnetron
sputtering
films
plasma
oxide
AN EXPERIMENTAL / THEORETICAL STUDY ON THE CRYSTAL STRUCTURE AND THE ELASTIC PROPERTIES OF TA1-XOX COATINGS

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The production of Ta₁₋ₓOₓ coatings has attracted a lot of attention due to their variety of industrial applications, namely biomedical applications. Nonetheless, to properly control the functional properties of these coatings, a good understanding of their structural properties must be achieved. Indeed, all Ta₁₋ₓOₓ phases have structural similarities since they are formed by the distortion of the Ta base structure, and therefore a clear and unequivocal identification of the crystalline phases is not trivial. In this work, the coatings were deposited by DC magnetron sputtering onto SS316L substrates in an Ar+O₂ atmosphere. Film structure and morphology were assessed by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and scanning electron transmission microscopy (STEM). Corrosion behavior was assessed. Bioactivity tests demonstrated that highest O-content coating, showed an increased affinity for apatite adhesion. Elastic properties of the coatings were measured by surface acoustic waves (SAW) and simulated through ab-initio DFT calculations to complete the structural information of the system. The structural results demonstrate the formation of an unusual bcc α-Ta phase in the non-reactive Ta coating, transitioning to a mixture of phases composed by α-Ta and β-Ta and/or Ta₄O nanocrystalline phases for low oxygen contents and to amorphous phases for high oxygen incorporation. The combination of the structural and mechanical experimental results with ab-initio DFT calculations shows that the increasing addition of oxygen to the Ta phase leads to leads to the distortion of Ta crystal structure, causing a decrease in its density and an increase in the elastic constants.

Keywords
sputtering
bioactivity
potentiodynamic tests
structure
Structure, mechanical properties and thermal stability of reactively sputtered AlTaTiVZr high-entropy nitride coatings

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In the field of materials research, a novel alloying concept, so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiaatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary nitrides, carbides, oxides, or borides. Within this work, we investigate the structure and, mechanical properties of thin films based on the high-entropy materials concept, with emphasis on the thermal stability. According to the Gibbs free energy, the thermal stability should be improved in the high temperature regime.

Therefore, AlTaTiVZr nitride coatings were reactively sputtered in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target. The coatings in as-deposited state show a columnar growth and crystallise in a single-phase face-centred cubic structure. The hardness of our coatings is with 32.8±1.1 GPa in the range of TiN and TiAlN prepared with comparable growth parameters. The structural evolution of free-standing powdered coating material upon annealing was investigated by DSC and X-ray diffraction, showing only marginal structural changes between 900 and 1200 °C which indicates a stabilisation due to the high-entropy effect. Upon annealing up to 1500 °C there is a slight indication of a second phase emerging from the dominant fcc-structured matrix. Up to an annealing temperature of 1100 °C the hardness values of around 30 GPa are maintained. Annealing above 1100 °C, leads to thermally-induced grain growth and partial decomposition causing a decrease of the hardness.

Keywords
high entropy alloys
thermal stability
reactive sputter deposition
The contribution reports controlled deposition of optically transparent and electrically conductive films prepared by an advanced magnetron sputtering systems without any post deposition thermal treatment/annealing. Low temperature deposition is appreciated since it allows coating of thermally sensitive optical fibers used as bio-sensors working on lossy-mode resonance (LMR) principle. LMR sensors appeared a few years ago and represent a hot topic in the field of fast, small and smart sensors; the optical sensitivity is based on spectral shift of transmission power of the light passing through the fibre. Furthermore, the active electrically conductive surface serves as an active electrode in electrochemical processes, too.

Our main aim represents ITO film tailoring to achieve relevant optical and electrochemical properties with adequate LMR and electrochemical response. It is shown that (i) reactive admixture of N$_2$ and O$_2$ gases to the process and (ii) pressure in the deposition chamber enable to optimize optical properties of ITO films. Doping admixture shows minor influence on the optical constants, while it leads to a substantial decrease in electrical resistivity. It was shown that ITO film resistivity can be tuned in range of an order of magnitude by nitrogen admixture. The variation of these ITO properties are attributed to change of crystalline structure measured by XRD methods. The films were also homogeneously deposited onto optical fiber to test efficiency of LMR for selected biomolecules.

**Keywords**
magnetron sputtering
ITO
optical fiber
LMR sensor
optical and electrical properties
In situ micro-cracking study of PVD Ti-Ag thin metallic films deposited on PET substrates for biomedical applications

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Recent investigations in biomaterials showed advantages of using polymeric substrates coated with thin films to functionalize surfaces, and gives them conductive, biocompatible and/or antibacterial activity. Ti-Ag thin films display excellent biocompatibility and reveal great potential to be used as conductive materials for prosthesis pressure sensors. In such a case, the film deformation on flexible substrates needs to be better understood to optimize the mechanical durability of the devices, and to ensure transfer of the electrical information during deformation.

In this study, microscale characterization of Ti-Ag thin films was followed in situ using a tailored micro-tensile test machine implanted into a SEM chamber. 4 binary films were synthesized by magnetron sputtering using a Ti target with Ag pellets placed on the racetrack. The amount of Ag in the final film was monitored by the respective Ti/Ag exposed area and ranged from 0 to 55at.%. Investigations rest upon a qualitative approach of cracking events as a function of deformation, together with on their quantitative explanation regarding micro-mechanical properties. Results are then discussed in light of the composition of films (XRD, EDX) and of their microstructural features (TEM, SEM).

For Ti-rich films, cracks dynamics involves a first initiation at growth defects, propagate perpendicularly to the tensile direction, then film buckling occurs due to a further lateral compressive contribution (Poisson effect). For the silver richest film, cracking mechanism is drastically changed: cracks indeed appear at significantly higher deformation rates (3% instead of 1% for low Ag films), and their morphology is totally different with propagation of short discontinuous cracks. Such an unexpected cracking mechanism implies high levels of deformation, and allows transferring the biosensor electric signal despite of local ruptures of the conductive layer.

Keywords
PVD Bio-sensor
µ-tensile tests
in situ SEM-scale test
Microstructure-cracking behaviour
A TiB₂ cathode assembly for DC arc evaporation

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Titanium diboride exhibit a hardness of up to ~50 GPa, and is promising for the next generation of hard and wear resistant coatings. However, deposition of TiB₂ coatings by physical vapor deposition (PVD) has to date been demonstrated primarily by sputtering techniques, as there has been no reproducible synthesis of TiB₂ from arc evaporation. From reported attempts to use TiB₂ cathodes for arc thin film synthesis, extensive instability, cracking, and cathode failure can be concluded. A reason thereof is limited movement of the arc spot on the cathode surface, which can be reduced with removal of any external magnetic field. However, absence of such field allow the spot to reach the edges of the cathode. In the present work we show an approach for stable and reproducible thin film synthesis of TiB₂ from cathodic arc. The method is based on I) a Mo ring around the cathode, to limit the arc spot movement, II) introduction of a few % of C in the cathode, to change the cathode resistivity and limit crack propagation, and III) introduction of a separate anode, to increase the plasma density and enhance the spot dissipation. Using this method, we have studied the plasma characteristics and have deposited film, which are characterized with SEM, XRD, and XPS. The relative boron content in the plasma and the films are found to be correlated, and dependent on the discharge gap geometry, and with a B/Ti ratio in the range 1.8-2.2. The results are of importance for realization of synthesis of metal borides from cathodic arc.

Keywords
vacuum arc
titanium diboride
plasma deposition
layer deposition
SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) OF TARGET MATERIALS FOR DEPOSITION OF PROTECTIVE COATINGS

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Mechanisms of combustion in Mo–Si–B, Cr–Al–Si–B, Zr-Si-B-(C), Ta-Si-C systems were studied. Developed SHS technology allows producing the targets with unique compositions. Ceramics ZrB₂–SiC with H= 25 GPa, E= 418 GPa, λ= 56.2 W/(m×K) has oxidation resistance till 1200 °C due to protective film ZrSiO₄. Ceramic TaSi₂–SiC exhibit superior properties H=19 GPa and K₁c =6.7 MPa·m¹/₂ due to hierarchical structure.

Zr-Si-B-(N) coatings deposited by magnetron sputtering at low nitrogen partial pressure consist of 1-3 nm of hexagonal ZrB₂ crystallites and amorphous phase. N-rich coatings exhibit fully amorphous structure. Combination of high hardness, wear and oxidation resistance, optical transparency makes Zr-Si-B-(N) coatings promising candidates for protective purposes. Oxidation resistance at 1500°C was achieved due to formation of dense SiO₂ top-layer reinforced with ZrO₂ nanoparticles.

Mo-Si-B-N coatings contained phases of nc-MoSi₂ and nc-MoB surrounded by amorphous a-SiNx phase. Coatings demonstrated adhesion strength more 30 N, H=35 GPa, E=350 GPa, and wear rate less than 10⁻⁵ mm³N⁻¹m⁻¹. Decreasing the friction coefficient (K₁) from 0.8 at RT down to 0.3 at 500°C was explained by formation of MoO₃ phase as a solid lubricant. Oxidation resistance achieved 1700°C when Si content was raised to 60 at. %.

The XRD amorphous Cr-Al-Si-B coatings demonstrated H=30 GPa, oxidation resistance up to 1300°C. Reactively deposited Cr-Al-Si-B-N coatings had lower H=20 GPa, oxidation resistance up to 1100°C, K₁~0.4 and wear rate ~ 2·10⁻⁶ mm³N⁻¹m⁻¹.

The Ta-Si-C-(N) coatings were obtained by pulsed DC magnetron sputtering of TaSi₂-30% SiC target in Ar, Ar+N₂. In the context of structure, increase on N₂ partial pressure resulted in crystallite size decrease and partially amorphisation. Crystalline coatings revealed H=17-21 GPa, amorphous - H= 10 GPa, K₁ = 0.4 at 600 °C due to dense silicon oxide layer.

Keywords
target
sputtering
coating
structure
properties
A study of AlTiN coatings produced by a pulsed arc discharge

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A study of AlTiN coatings produced by a pulsed arc discharge Vacuum-arc evaporation is a well-established process for the deposition of abrasion-resistant coatings (e.g. AlTiN, AlCrN). The advantages of the process are a high ionization, deposition rate and optimal stoichiometry. However, the main disadvantage is the occurrence of droplets in the deposited layers. This may cause a decrease of corrosion resistance or can initiate cracks. One possible solution in decreasing the droplets is to produce a coating by pulsed arc discharge. For our experiments, we used the technology developed by the company Platit. The frequency of the pulsed arc was 20 kHz and maximum current 500 A.

We chose the ternary nitride system AlTiN as our studied coating that is commonly used for cutting applications because of its sufficient thermal stability, high hardness, oxidation resistance and adhesion resistance. We compared the topography of surfaces (standard vs. pulsed arc). We investigated the mechanical properties (micro-hardness, modulus of elasticity, roughness) and the structure (SEM, XRD) with regards to dependence on the composition (Al:Ti = 66:34, 60:40, 50:50 at. %), pressure of gas and bias of substrates.

AlTiN produced by a pulsed arc showed higher internal stress and a different crystalline structure compared to the standard non-pulsed arc. The pulsed arc also was more stable at lower pressures and we even observed an increase of micro-hardness.

At the end we prepared a cutting test (milling) and evaluated the wear.

Keywords
Pulsed Arc
AlTiN
Mechanical properties
Diffraction analysis
New progress on double-glow plasma surface metallurgy technology

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Since the “Double Glow Plasma Surface metallurgy Technology” (Xu-Tec) was invented in 1980, A large number of experimental studies have proved that the Xu-Tec process not only can be applied to any solid and non metal chemical elements in the periodic table to form surface alloys with high hardness, abrasion resistance and corrosion, but also to form the gradient ceramic layers. In this paper, based on the Xu-Tec process, the gradient-ceramic layers doped rare-earth (RE) element (e.g. Er-ZrO₂ layer) and the large-scale graphene and semiconductor films are introduced. Due to the surface gradual distribution of chemical element along the depth of the alloyed layer, the luminescence characteristics of RE-ions in ZrO₂ are concentration-dependent. The correlation of the emission intensity with the doping concentration can be used to determine the optimum Er ions concentration in the samples. The study have a role important application in the early-warning of material failure by real-time on-line monitoring without interrupting their service. In addition, the Xu-Tec process provides a promising alternative for the preparation of the large-scale graphene, ZnO and graphene/ZnO nanorod composite films on non-metal or soft metal surfaces, which can be used in photoelectrochemical detection, photocathodic protection and the ultraviolet (UV) photo-induced surface modification. Our study suggests for the first time that double-glow plasma-sputtered graphene is not only successfully prepared on quartz plates and soft metals, but also is introduced into the surface of ZnO nanorod (ZnONR) composite films. The as-prepared graphene film exhibited the obvious surface hydration behaviors and the tribological properties under the UV irradiation. Simultaneously, the preparation of graphene/ZnO nanorod composite films enhanced the charge transfer on the surface and reduced the impedance in the solid state interface layer. In a word, we will study more functional films prepared by Xu-Tec process in the future.

Keywords
Xu-Tec
gradient-ceramic layers
graphene
ZnO films
Kn1300

Plasma Polymerization of Hydrocarbons – A Comparison of Low- and Atmospheric-Pressure Processes Based on Energy Uptake per Molecule

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Recent developments in the field of plasma polymerization have re-emphasized the importance of gas-phase processes during deposition, in particular those associated with raising pressure up to one atmosphere. While surface processes are largely governed by energetic particle bombardment and surface losses, the generation of film-forming precursor species strongly depends on the energy input per “monomer” molecule, Eₘ, in the plasma. In our two laboratories we have developed methods for measuring Eₘ (or somewhat equivalent, Eₐ, the “activation energy”) in low- (LP) and atmospheric-pressure (AP) discharge plasmas. By varying the externally-applied energy input into the plasma, apparent values of Eₐ could be deduced; these were found to be independent of pressure for the case of different starting compounds (monomers) such as acrylic acid or hexamethyldisiloxane.

In this present work we compare different hydrocarbon monomers such as methane, ethylene and acetylene, which are initially plasma-activated by hydrogen abstraction. LP and AP processes were found to proceed in comparable manners, despite different activation processes (predominantly electron impact for LP, versus Ar metastables for AP) and very different EEDFs (electron energy distribution functions). The importance of Eₘ is further underlined when one introduces the so-called energy conversion efficiency, ECE, which relates Eₘ to the external input energy. Thereby, valuable additional information is gained with respect to fragmentation and recombination processes, as well as to reactivity of the formed species.

Keywords
plasma polymer
energy input
pressure
hydrocarbons
conversion
Predicting the main hydrocarbon chemistry pathways and deposition mechanisms in magnetron plasma enhanced chemical vapor deposition of amorphous hydrogenated carbon with a hybrid simulation approach

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Diamond-like carbon (DLC) coatings are well known for their exceptional properties. However, complex substrate geometries and variable experimental arrangements are challenging in terms of film homogeneity, reproducibility and overall process stability. Furthermore, some particular experimental set-up process could be difficult to transpose to others, and measurements only gives access to limited insights on those processes. This is why theoretical and experimental studies have to be conducted together to understand better the underlying processes. Nevertheless, computational costs often limit PECVD simulations to small sized reactors with simple geometries and to reduced number of reactives and reactions considered.

The aim of this study is to understand through simulations and experiments those underlying processes for magnetron PECVD deposition of amorphous hydrogenated carbon (a-C:H) thin films. We will base our model on an actual semi-industrial scale magnetron reactor with acetylene as the precursor gas. Our approach is to simulate the creation of radicals, their transport, the gas phase reactions and the surface interactions in an accurate 3D meshed model of our experimental reactor. For that, we use a hybrid simulation scheme consisting of a fluid model of the plasma bulk, giving us the ability to distinguish the leading constituents and reaction pathways, coupled with a highly parallelized DSMC code. In a second time, the findings of the fluid model will be completed and compared with PICMC plasma simulations. We use a well-known 2-terms Boltzmann equation solver and a 0D fluid model to predict the evolution of the concentration of the different species. Particular attention is given to limit the number of considered reactions to the most contributing ones. Surface chemical reactions and sticking coefficients are included into the DSMC simulations as well as the sputtering emission from the cathodes.

\textbf{Keywords}
DLC
PECVD
Hybrid Simulation
Antibacterial composite coatings with controllable drug release for biomedical applications

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Antibacterial films deposited by means of atmospheric pressure plasmas is a topic of high industrial demands especially for a medical sector and healthcare. However, the engineering of high quality films with control of the incorporated drug release and low toxicity is still a challenging problem. In this contribution two approaches of an atmospheric pressure plasma deposition of antibacterial coatings loaded with Ag, Cu and ZnO are presented and analysed. Atmospheric pressure RF and DC plasma sources operating either in N₂ or Ar are used for engineering of antibacterial nano-composites. In first approach nanoparticles of Ag, Cu and ZnO are incorporated in between two layers of organosilicon film in "sandwich-like structure" whereas in second approach SiO₂ porous nanoparticles loaded with Ag or Cu ions are incorporated in the coating structure. Obtained coatings are analysed in terms of surface chemistry by XPS, AFM, and SEM as well as in terms of biomedical behaviour by study of the antibacterial properties and toxicity of the coatings. It is shown that both antibacterial and toxicity characteristics of the coatings strongly depend on nanoparticles load and have a minimum threshold value of 0.5 mg/ml of NPs in suspension required to achieve considerable bacterial reduction. This effect is explained by kinetics of the ions release measured by ICP-MS method. It is shown that release kinetics is a key parameter for low toxicity of the coatings. The former can be precisely controlled by the use of our new approach based on SiO₂ particles loaded with Ag or Cu ions. The results of this study indicate that plasma deposition at atmospheric pressure can be a versatile tool in the engineering on novel biomaterials with high antibacterial efficiency and low toxicity.

This work is supported by the M.Era-Net project IWT 140812 “PlasmaTex”.

Keywords
coatigs
plasma deposition
nanocomposites
drug release
A comparison of barrier properties of plasma polymerized HMDSN- and HMDSO-based films

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In the last decades, Plasma Enhanced Chemical Vapor Deposition (PECVD) processes aimed at the production of thin films, which are later to act as oxygen barrier layers, have been widely employing siloxanes, chiefly among them hexamethyldisiloxane (HMDSO), as precursors, in order to take full advantage of their Si-O-Si backbone for the purpose of achieving SiOₓ-based plasma polymers. For such goals silazanes – among them hexamethyldisilazane (HMDSN) – are by comparison far less employed and investigated, being usually considered to be virtually equivalent to their siloxane counterparts: moreover, lacking the main Si-O-Si backbone, they actually require an additional oxidation step.

In the current work, hexamethyldisiloxane- and hexamethyldisilazane-based oxygen barrier films have been deposited by means of a microwave-sustained Electron Cyclotron Resonance (ECR) low-pressure plasma in a wide range of different process parameters. The chemical compositions of the deposited films have been then investigated and compared by means of infrared and photoelectron spectroscopy, their barrier properties against oxygen have been tested and surface pinholes investigated by means of a new, non-destructive method that allows numerical defect densities to be calculated. Results show how, for the same operating parameters, hexamethyldisilazane-based films show improved barrier performances and favorable mechanical properties over an extended range of operating conditions: such discrepancy can be ascribed to different growth mechanisms and chemical reaction in the plasma phase, in particular to the additional oxidation step for the HMDSN Si-NH-Si backbones, thus proving the latter to be the preferable precursor for oxygen barrier films.

Keywords
- Barrier layers
- HMDSO/HMDSN
- Microwave plasma
- ECR
- PECVD
Area-selective surface modifications by atmospheric pressure micro-plasmas allow cost-effective surface modifications and chemical functionalization. Plasma patterning technologies are utilized for example in optical components production, semiconductor back-end, MEMS, flexible electronics manufacturing, in combination with inkjet printing or fluid dispensing and may also be implemented in biosensor and tissue engineering applications. InnoPhysics has developed and commercializes the μPlasmaPrint technology, which enables area-selective functionalization by means of a dot-wise patterning of the plasma treatment/deposition with resolutions from millimeters down to 150 µm. μPlasmaPrint utilizes a multi pin-to-plate dielectric barrier micro-discharge at atmospheric pressure which can be independently activated according to a digitally programmed pattern. In order to improve the μPlasmaPrint resolution and to improve the processing and substrates flexibility, InnoPhysics has developed new hardware and process options. Recent developments will be shown related to process feedback through surface wettability mapping, in-situ monitoring of the plasma energy for improved process feedback. On the process side, developments will be presented to enable non-fouling hydrophilic coatings in plastic biomedical devices by combining μPlasmaPrint with liquid coating dispensing. Furthermore recent developments which enable selective chemistry to obtain patterns of chemically functionalized substrates as an alternative to direct μPlasmaPrint deposition will be shown. Examples will involve a plasma ALD-like approach to obtain TiO\textsubscript{2} for photocatalytic and electron transport layer applications, and the formation of selectively grown diamond patterns on Si wafer. These process options broaden the scope of potential applications of digital μPlasmaPrint surface modifications at present for low volume science applications and for future high volume industrial applications.

Keywords
atmospheric plasma
plasma assisted ALD
printing
surface modification
Industrial Microwave PECVD Coatings for Emerging Automotive Applications

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In the recent years, the automotive industry has been quickly moving towards E-mobility and in parallel further optimizing conventional combustion systems. In both cases, coatings on various components are used to achieve optimal performance. Next to the typical tribological requirements, new demands need to be met as well. These include coatings for sensors, electrical insulation, chemical resistivity, barrier layers and corrosion protection. The energy efficiency requires decreasing of the weight of the components. This results in more and more plastic components, which often also have to be coated. However, coating plastics has its limitation due to process temperature restrictions and lack of electrical conductivity. Ideally, one coating technology should be capable of delivering the above properties on both metallic and plastic substrates. Although magnetron sputtering has been widely used for that, it has limited success in corrosion protection due to intrinsic coating defects and is with very low efficiency when insulating coatings are needed. Alternatively, microwave PACVD can provide both tribological from one side and corrosion protective, electrically insulating, chemically inert and barrier coatings from other side. Typical example for the first group is DLC and for the second – SiO₂.

In this study, an industrial PACVD method based on microwave generated plasma in a commercial PVD machine is presented. The method improves the deposition rate by a factor of tree to six in comparison to magnetron sputtering and conventional PACVD and does not require sophisticated control mechanisms. Results for DLC and SiOx films deposited on both steel and plastic substrates are shown. The influence of the control parameters on the coating properties and process stability is discussed. The tribological, electrical and anticorrosion properties are reported and their relation to the coating characteristics is explained.

Keywords
PECVD
microwave
corrosion
DLC
insulation
Extremely high rate PE-CVD deposition up to 3.2m by a novel Hollow Cathode Design

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A new type of Hollow Cathode device has been developed by AGC Plasma, the industrial vacuum equipment manufacturing segment of AGC. The scale-up of this device has been successfully performed for Plasma-Enhanced Chemical Vapor Deposition [PECVD] coatings on lab samples (a few cm$^2$) up to jumbo-sized plates (3.2x6.0m$^2$).

Plasma generation is accomplished between multiple linear hollow cathodes cavities, alternately driven by commercially available mid-frequency AC or pulsed power. This allows for a dense, uniform plasma that is scalable to relevant sizes for any typical vacuum processes. Based on plasma and vacuum simulations, the electrode cavity design has been dramatically improved and can run using a variety of input gases, such as O$_2$, N$_2$, Ar, He, and H$_2$. Plasma operation is also possible in an extremely wide range of pressures from 1 mTorr to 1 Torr. The wide Hollow Cathode pressure operation range allows for the deposition of multi-layer coating stacks by PVD and PECVD in existing vacuum coating lines. Electrode faces have also been enhanced using surface coatings to avoid erosion during high power operation, also reducing subsequent debris and extending source lifetime even under extremely high input power densities of 40-80 kW per meter of plasma length. Depending upon process conditions, dynamic deposition rates for inline PECVD coatings of 200-500 nm*m/min have been demonstrated for SiO$_2$ on flat glass products.

This unique process opens a new range of possibilities to be investigated for a variety of substrates. These plasma sources are now commercially available in either lab or industrial sizes to explore new applications.

Keywords
PECVD
Hollow Cathode
Simulation
Elucidation of the relationship of the physical properties and the chemical composition of silicon organic PE-CVD coatings with respect to the degree of cross-linking

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The presentation describes the main results of an investigation which follows the goal to get a deeper understanding of the relationship between the physical properties of a carbon rich silicon organic PE-CVD coating system and its chemical composition and structure. The deposition of all coatings was performed by power variation keeping the gas mixture and the total amount of gas stable. These coatings were produced in a capacitive coupled plasma at 13.56 MHz. The process was designed such that the self-bias is in the range of zero volts.

Initial, the complete elemental composition, obtained via XPS and micro elementary analyses, was analyzed with a low error of the average. Furthermore, the chemical structure was investigated by XPS-peak fitting and additional FTIR analysis. Additionally, a broad range of physical properties such as Young’s modulus, mass density, refraction index, absorption, thermal expansion coefficient, thermal stability and free surface energy was analyzed and optimized.

The evaluation of all the results can be explained not only by the well-known Si-O-crosslinking but additionally by an independent second crosslinking mechanism. This extra bridge forming mechanism is necessary to explain a power dependent increase of the Young’s modulus and the film density. In detail, the formation of ethylene-based bridges is discussed. The amount of this second crosslinking mechanism depends on the applied plasma power.

By taking all information on the chemical composition into account, a chemical structure is suggested using a least-squares algorithm and a specific amount of different chemical structure elements. Based on this calculation a new index is introduced characterizing the degree of crosslinking. Taking this index into account different organic PE-CVD coatings can easily be distinguished.

Keywords
PECVD-coating
Elemental composition
Mass density
degree of crosslinking
Association of PECVD process and chemical synthesis for the development of TiO2/SiO2 nanocomposite material: a new approach

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During the past few decades, the Microelectromechanical systems (MEMS) have emerged in our daily life, giving us access to a wider variety of applications. Hence, the synthesis of new nanocomposite materials, that allows us to improve those systems, is of great importance. In view of enhancing the properties of these materials, the present work is devoted to the synthesis of titania/silica nanocomposite thin films through an original approach. The most significant challenge in the development of such nanocomposites is to control their morphology, their growth mechanisms, the incorporation of the nanoparticles in the composite and the distribution of them. In the past, numerous elaborations have been established, aiming at tuning and improving the synthesis of such materials, such as sol-gel, (plasma enhanced) chemical vapor deposition (PE-CVD), or physical vapor deposition (PVD). In this work, the coupling of the chemical synthesis and the plasma process for the development of TiO2/SiO2 nanocomposite films is reported. Initially, a colloidal solution consisting of TiO2 nanoparticles is spin coated on thermally oxidized SiO2 silicon wafers. Subsequently, the spin-coated samples are exposed to atmospheric or low-pressure plasmas in the presence of hexamethyldisiloxane (HMDSO) for the deposition of a silica matrix. Scanning electron microscopy (SEM) of these treated samples shows a good control over the distribution of the TiO2 nanoparticles dispersed in the SiO2 matrix. The morphology of the thin films is investigated through atomic force microscopy (AFM) and the chemical analysis of their surface by X-ray photoelectron spectroscopy (XPS). Preliminary results obtained by ellipsometry are used to describe the distribution of the nanoparticles in the matrix. Finally, the nanocomposite films obtained using a low pressure and an atmospheric pressure PECVD reactor have been compared.

Keywords
PECVD
colloidal solution
TiO2/SiO2 nanocomposite thin films
Insights into the high temperature oxidation resistance of cathodic arc evaporated nitride coatings with different layer architectures

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The present work has been addressed to look for new functionalities of well-known nitride coatings usually applied in the hard coatings field. The outstanding properties of these coatings in relation with their mechanical performance, thermal stability and corrosion resistance in air have suggested the possibility of extending their use as protecting coatings operating in vapour media. In order to improve the performance of the vapour turbines employed in power plants, an increment in the temperature of the steam impelling the blades is desired. It is for this reason that the energy industry is in continuous search of competitive materials which withstand such aggressive working conditions. A previous work showed the suitability of monolithic CrAlN based nitride coatings to protect a ferritic steel at the working conditions of supercritical turbines [1]. In this work nitride-based coatings with alternating layers of CrN and TiN have been investigated and compared with monolayers of the nitrides counterparts. The study has been carried out by means of thermogravimetric analysis, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), glow discharge optical emission spectroscopy (GDOES) and nanoindentation analyses. The behaviour of the coatings, tested up to 2000h at 650°C in 100% steam atmosphere, has shown some insights into the consequences of the multilayer design in the oxidation resistance and the mechanical properties.


Keywords
oxidation coatings steam nitride multilayers
Polycrystalline CVD diamond thin films are mainly deposited by means of either microwave or hot filament assisted CVD coating techniques. The latter one being discussed here is a suitable coating method for cutting tools with complex geometries and is well established on an industrial scale. Besides addressing the basics of the coating equipment and deposition technology, this presentation discusses the results of case studies dealing with cutting applications on machining of various classes of highly abrasive materials with pure CVD Diamond thin films. These case studies include applications with Carbon fiber reinforced plastics (CFRP) systems for aerospace industry, zirconium oxides systems for dental applications up to direct milling of cemented carbide. In addition a novel class of coating materials which combines thin film HIPIMS and CVD Diamond is introduced. This merging of ultra-hard CVD diamond coatings and extremely dense and extraordinary smooth HIPIMS coatings creates the possibility of completely new cutting tool performance. The extreme hardness and excellent thermal properties of diamond is a clear benefit for the overall tool performance. The HIPIMS contribution provides excellent heat flow properties into the chips, serves as a well-suited protection mechanism at high cutting temperatures and improves the reduction of friction. Coating technology, film properties and application results for HIPIMS-Diamond coatings will be discussed in the scope of this work.

Keywords
Hot filament
CVD
Diamond
cutting tool applications
HIPIMS
Thermal stability and tribomechanical properties of hard Cr-doped DLC coatings deposited by HiPIMS

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Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp³-sp² structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated the thermal stability of DLC coatings doped with Cr deposited by HiPIMS technique. Extraordinary highly ionized plasma discharges were obtained during chromium and carbon codeposition with HiPIMS. EELS, RBS, XPS and Raman spectroscopy were used for structural characterization of the films. The high ion energy bombardment allowed doping with Cr the DLC structure while reaching high sp³ contents. Accordingly, enhanced mechanical properties (hardness up to 35 GPa) were observed with nanoindentation. High temperature nanoindentation tests were also performed from room temperature to 450°C in order to evaluate the evolution of hardness and Young Modulus with temperature. The results confirm that the mechanical properties at high temperature mainly depend on the sp³ content. Tribological tests were carried out in air from room temperature to 250°C. Cr-doped DLC coatings showed lower friction and wear compared to pure DLC. The formation of Cr protective carbides together with a high sp³ bonding structure obtained with HiPIMS deposition improves the stability of DLC coatings for high temperature applications.

Keywords
DLC
HiPIMS
Tribology
Tetrahedral amorphous carbon coatings (ta-C) have outstanding tribological properties under both lubricated and unlubricated conditions. Besides their ability to provide low friction and low wear with conventional oil lubrication their capability for superlow friction is of high interest. In such a special tribological state, also called superlubricity, the coefficient of friction is below 0.01. While several lubricant substances have been identified that enable superlubricity for ta-C coatings and functional models have been proposed, a broader understanding of the lubricant chemistry is still missing.

In this work we investigate various model lubricants based on simple molecules in a self-mated ta-C tribosystem, using a reciprocating ball-on-disk experiment and accompanying tight-binding simulation. Results of experiment and simulation are in good agreement and show that carboxyl groups can passivate the ta-C surface and contribute to a low wear and steady friction state if compared to a simple hydrocarbon chain. Furthermore, the combination of both a carboxyl group and an unsaturated carbon chain enables superlubricity. Tight-binding simulation indicates that unsaturated fatty acids bridge the tribo gap by covalent bonds between the ta-C surfaces and the carboxyl group or the double bond, respectively. This results in a rapid decomposition of the molecule and a subsequent ta-C passivation. A tribo-induced phase transformation layer can be detected by Raman spectroscopy and nanoindentation in those cases where the friction coefficient is above the state of superlubricity.

Keywords
DLC
ta-C
superlubricity
tight-binding
rehybridization
ta-C coatings for automotive applications

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Diamond Like Carbon (DLC) coatings and in particular the hydrogenated a-C:H coatings are widely used where friction and wear reduction is required. However, a-C:H coatings have a limited thermal stability and start to graphitize at temperatures higher than about 300°C. Depending on the contact pressure, graphitization might even occur at much lower temperatures. In addition, the tribological performance of a-C:H coatings can be negatively influenced by different lubricants and additives. To overcome the drawbacks of a-C:H coatings, hydrogen-free DLC coatings like ta-C and a-C are currently investigated as a possible solution. ta-C shows a significant higher coating hardness than a-C:H coatings and due to the lack of hydrogen a different surface chemistry which results in a different behaviour under lubricants. ta-C is usually deposited by high-energy deposition processes like arc evaporation; the arc evaporation is possible with or without filtering. Inherent to these processes is the generation of coating defects like droplets. A suitable post-treatment is mandatory to reduce the roughness to an acceptable level. High roughness in combination with a high coating hardness would lead to significant counter body wear.

In this work, we investigated the thermal stability of ta-C coatings and their compatibility with different lubricants and additives. The results of ta-C were compared to the results of a-C:H. We analyzed in detail the influence of different deposition methods and post-treatments on the surface roughness and the tribological performance. The ta-C coatings under evaluation performed well and gave some advantages as compared to a-C:H. Surprisingly the maximum operation temperature in dry running systems was not as high as expected. The surface topography which leads to counter-body wear cannot be described with simple parameters like $R_a$ or $R_z$.

Keywords

DLC
ta-C
automotive
post-treatment
OR1405

Effect of angular deposition and intermittent deposition conditions on properties of ta-C and Tungsten/ Boron doped ta-C films.

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Hydrogenated Diamond Like Carbon has been spread widely in the industry and applied as a coating to increase wear resistance and reduce friction losses. Non-hydrogenated DLC is now in focus of many industries due to its better temperature stability and higher hardness. Hydrogen-free DLC coatings are prepared from graphite targets by means of arc evaporation deposition, pulsed laser deposition, magnetron sputtering, HiPIMS, etc. The hardness of the applied films is directly related to the ratio between sp³ and sp² bonding. Higher sp³ fraction will result in a higher hardness. As described in the reviewed papers, independently from the deposition method, the structure of tetrahedral bonded amorphous carbon (ta-C) is mainly determined by the energy of the impinging with the substrate carbon ions, the angle of incidence, the deposition rate and the substrate temperature. To influence the properties of the deposited tetrahedral amorphous films can be manipulating them by doping with various elements. Two models were investigated: ta-C and Tungsten/ Boron doped ta-C, where the dopants percentage varied. By manipulating the angle of incidence of impinging carbon ions and periodically applied deposition parameters we have checked how the film properties are affected. The results from the two models investigation tests are described in details.

Keywords
ta-C
Boron doped
Hardness
DLC
Stress
Large-area, low-temperature deposition of dense and transparent silicon nitride layers using bias-controlled, high-rate PECVD

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Recently, there is an increasing demand for hard and scratch-resistant coatings of displays, windows, lenses etc. with superior optical properties as well as for pinhole-free, electrically insulating and sometimes transparent barriers for (opto-)electronic devices operating under either dry or humid conditions. The combination of these superior properties must be achieved on substrates held at the required low temperatures, if the degradation of temperature-sensitive substrate materials shall be avoided.

Here, we report on the plasma-enhanced chemical vapor deposition (PECVD) processing of near-stoichiometric amorphous silicon nitride (a-SiNx:H) films well-grafting on various substrates held at temperatures below 100 °C. While some of the results have been reported by others previously, we focussed on the technological implementation on the industrial scale. In this context, high throughput and cost efficiency has been achieved through the use of linear microwave (2.45 GHz) antenna arrays and radio-frequency (13.6 MHz) substrate biasing, as well as large substrates (substrate area up to 1000 mm × 1000 mm) employed in large inline systems. Transparent and dense, near-stoichiometric films (refractive index n of up to 1.86, extinction coefficient ε below 0.002 at 400 nm) have been processed with a rate of about 2 nm/s from silane and ammonia precursors. Although the layers can be up to two microns thick, the film stress can be maintained at a low level between +100 MPa and -250 MPa. Peel strengths above 1 N/cm² on plastics, epoxide resins, glass, sapphire and metals (e.g. copper and tin alloys) are a sign of a good grafting of the coating on various surfaces.

The inline processing of multilayers combining either silicon dioxide, aluminium oxide or silicon carbide and silicon nitride layers provides scratch-resistant, anti-reflective coatings for which a reduction of the reflectivity to below 3 % for uncoated glass and uncoated sapphire substrates is observed.

Keywords
PECVD
RF bias
silicon nitride
Formation of Tribochemical Reaction Layers on Amorphous Carbon Coatings

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Lowering frictional losses and wear in lubricated contacts through the application of diamond-like carbon (DLC) coatings in gearboxes of the automobile powertrains offer the potential to meet the current and prospective requirements on sustainable mobility. Due to the increasing use of DLC coated components in lubricated tribological contacts e.g. on engine components, analyses of the chemical interactions between lubricants, additives and DLC coatings are becoming increasingly important. The aim of this paper is to analyze the formation of tribochemical reaction layers on metal modified DLC coated tribological contacts by using formulated lubricants. Therefore, four different industrially relevant gear oils - mineral oil (MIN), polyalphaolefin (PAO), polyaklyleneglycol (PAG) and ployethylene (PE) as well as the additives molybdenum dialkyl dithiophosphate (MoDTP), zinc dialkyl dithiophosphate (ZnDTP) and anglamol 99, containing sulphur and phosphorus (S-P), were used. The study was conducted using the hydrogen and zirconium modified DLC coating a-C:H:Zr (ZrC₉) deposited by means of direct current magnetron sputtering (dcMS). The tribological tests of the pairings steel/steel, steel/DLC and DLC/DLC were carried out in a pin-on-disk (PoD) tribometer under boundary and mixed friction conditions at T = 90 °C and a contact pressure p = 1,300 MPa regarding the application of DLC coatings on gears. Chemical analyses on the wear tracks of the DLC coated specimens by means of Raman spectroscopy (RS) and energy-dispersive X-ray spectroscopy (EDX) prove the formation of tribochemical reaction layers. The results of the tribological tests with the contact DLC/DLC show that additive-free lubricants lead to a further friction reduction in comparison to tribological contacts using formulated lubricants.

Keywords
DLC
Lubricants
Tribochemical interaction
Raman spectroscopy
Boundary and mixed friction
**Functionality of Ag-doped low friction nanocomposite coatings in wide temperature range**

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In order to increase reliability and durability of the friction assemblers and enhance energy efficiency of tribomechanical systems, different types of solid lubricants are widely used worldwide. Nanocomposite coatings can combine advantages of hard and self lubricating phases and therefore are good candidates for various tribological applications. In the present study, metallic Ag and Ag-consisted phases were considered as solid lubricants. The study highlights various multicomponent nanocomposite coatings: MoCN-Ag and VCN-Ag, as well as TiNbCN-Ag and Ta-Si-C-N-Ag coatings. In case of VCN-Ag and MoCN-Ag coatings it was supposed silver play a role of active component which reacts with hard matrix components at elevated temperatures and forms lubricious phases. Contrariwise in case of TiNbCN-Ag and Ta-Si-C-N-Ag coatings silver phase does not interact with hard matrix and provide lubrication and self-healing ability in metallic state. It was shown that a significant reduction of CoF values can be achieved either by the formation of lubricious $V_2O_5$, $MoO_3$, $Ag_xMo_yO$, $Ag_xV_yO$ phases during high-temperature tests. Melting of silver molybdates and vanadates was triboactivated at high temperatures that promoted CoF 0.18 at 700 °C. In case of TiNbCN-Ag coatings it was shown that a relatively high amount of Ag (15 at.%) is required to provide enhanced tribological behavior in the temperature range of 25-700 °C. Also TiNbCN-Ag coatings provided an active oxidation protection and self-healing functionality due to the segregation of Ag at the sites of coating’s cracking or oxidation. The Ta-Si-C-N-Ag demonstrated extremely high oxidation and wear resistance at high temperatures due to formation of protective nanolayer on the surface.

The authors acknowledge the financial support from the Russian Scientific Foundation (Agreement 14-19-00273-П).

**Keywords**
tribology
nanocomposite coatings
solid lubricants
Development of plasma a-Si(NO)C:H/metal thermo-optical selective multilayers for thermodynamic concentrated solar power plants

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Concentrated solar energy thermal conversion technologies, combined with a thermodynamic cycle [CSP], have an important place in the global energy mix. Different scenarios (SolarPACES, ESTELA, Greenpeace) estimate their contribution will range between 8 and 12\% in 2050 (830 GW deployed). Development of new CSP projects (China, Chile, South-Africa...) is accompanied by a drop in produced electricity rate offers. CSP enables large-scale storage of energy in thermal form to face solar intermittence. Efficiency of a CSP plants depending on solar concentration level, it is sought to increase temperature of heated transfer fluids in solar receivers whose surfaces reflect, concentrate, modify and convert local spectral solar flux into heat. Solar field being the first loss station in CSP plants, receivers efficiency must be optimized. Absorbers coated surfaces must have a high absorptivity in the solar spectrum (0.25-2.5\textmu m) and a low IR emissivity (selective thermo-optical surface). To reach high temperatures (>400\textdegree C), selective coatings with high thermal resistance in air must be developed. Our work focuses on coupling between plasma elaborations, characterizations of layers, optimization by design simulations, of dielectric/metal multinanolayers. For the case of SiC:H/W couples, developed by microwave PACVD of Tetramethylsilane and Tungsten PVD, study of plasma parameters on chemical and thermo-optical characteristics gave various optical (n(\lambda), k(\lambda)) monolayers families [1.7<n<2.7(SiC:H), 3.2<n<3.7(W)], stacked into multilayers. Optimized W/SiC:H/W/SiC:H designs present absorbance up to 80\% and IR emissivities (550\textdegree C) down to 15\% (high solar thermal efficiency). Multilayers deposited onto solar metals (steels, Inconel) do not exhibit degradation of their thermo-optical properties and adhesion after long annealings in air at 500\textdegree C.

Keywords
CSP
PACVD/PVD
thermo-optical selectivity
multinanolayers
ICE vehicles are under pressure by governments and public opinion. Hybrids, battery and fuel cell vehicles are gaining interest in the market place to replace ICE technology. The fuel cell option offers a low weight alternative and can be used as a range extender with a small battery. Current efforts focus on affordable fuel cells having a long and stable lifetime. Within the fuel cell stack the bipolar plates are facing corrosive conditions and need to facilitate currents of over 2 A/cm². This paper discusses a coating technology for bipolar plates meeting performance metrics at an affordable price for the automotive industry.

Stainless steel (SS) is the best candidate for metal bipolar plates in polymer electrolyte membrane fuel cells (PEMFC). SS has good general corrosion resistance, high conductivity, suitable mechanical properties and good formability.

The major barrier for SS bipolar plates is its high surface electrical contact resistance and ion leaching under PEMFC conditions. The corrosion resistance relies on its native surface chromium oxide layer. This surface layer is fairly electrical resistive and its thickness grows over time. Unprotected SS shows a slow leaching of iron, nickel and chromium ions during PEMFC operations. The leached ions will poison the electrocatalyst and the membrane leading to performance degradation.

A low cost coating technology for SS bipolar plates, based on a hybrid coating technology with a post-treatment, is presented. It is based on providing a corrosion barrier with parallel highly conductive dots of a noble metal. Due to the potential, ions are preferably interacting with the noble metal dots. In that way a fairly thin coating can provide an effective corrosion barrier, also at higher Voltages. The technology has demonstrated long term operational stability in PEMFC applications, even at higher voltage levels compared to typical operating voltages. The coating is very cost effective compared to the gold coating solutions and more stable than graphite based coatings.

Keywords
fuel cell
bipolar plate
dots
Advances in the field of hydrogen-based technologies bring new challenges for material researchers working in the field of gas sensors. Metal oxide semiconductors (MOSs) are well established as active materials in gas sensor assemblies. Especially nanostructured MOSs attract the attention because of the unique electronic properties of nanomaterials and a high reactive area. Here, we present the study of nanostructured MOS films prepared by use of a gas aggregation cluster source. The combination of materials enhanced the sensorial response and allowed us to form gas sensitive nanostructured materials without the need of use of any wet technique.

Various combinations of thin films and nanoclusters of tungsten trioxide (WO$_3$) and cupric oxide (CuO) were prepared. The thin films were deposited by conventional reactive dc magnetron sputtering, the nanoclusters were prepared using the gas aggregation cluster source.

Sputtering conditions were tuned to vary the chemical composition and structure of the prepared films. The films were examined for their sensorial response when assembled into a hydrogen gas sensor. Noble-metal catalysts (Pd or Pt) deposited by dc magnetron sputtering were used to amplify the response and to lower the working temperature. The specimens were tested for the response to a time-varied hydrogen concentration in synthetic air at various temperatures. The sensitivity and the response time were evaluated. It is shown that optimization of the structure and composition results in enhanced sensorial properties.

Both the magnetron sputtering and deposition of clusters are techniques compatible with industrial microelectronic procedures which is of key importance for further expansion of hydrogen-based technologies.

**Keywords**
gas sensor
hydrogen
nanocluster
WO$_3$
CuO
Synthesis and applications of 1D and 3D supported nanostructures developed by plasma assisted vacuum deposition methods

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One-dimensional (1D) materials are pillars in nanoscience with applications in microelectronics, optoelectronics and photonics, energy storage and scavenge, catalysis, biomedicine and fluid manipulation. This topic has experienced a huge growth during the last two decades and recently reached the stage to move forward from the academia to the technological development. Nevertheless, there is still urgent need for the study from the fundamental point of view of these nanostructures and, overall, for the research on low cost procedures for their production in high rates with a strict control on composition, structure and microstructure. The synthesis of heterostructured 1D materials such as core@shell and core@multi-shell nanowires and nanotubes provides a straightforward route for the fabrication of multi-functional nanostructures that opens the lead towards the realization of single-wire devices and optimization of high-density arrays devices. We have recently developed a full vacuum / plasma-assisted methodology for the fabrication of supported heterostructured nanowires, nanorods and nanotubes with controlled shells composition, microstructure and porosity that has been extended also to the formation of 3D nanostructures.[1-8] Several examples will be shown for the fabrication of semiconducting organic and inorganic nanotubes and core@shell/multishell nanowires with advanced performances as superhydrophobic and ice-phobic surfaces, waveguides, photoelectrodes, piezoelectric nanogenerators and nanosensors.


Keywords
nanowires
core@shell
template
solar cells
nanogenerators
The wrinkling concept applied to plasma polymer films: a novel route for controlling their nano-architecture

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Plasma polymerization has become a well-established technique for the synthesis of organic thin film, the so-called plasma polymers films (PPF). Nowadays, despite a highly complex growth mechanism, it is possible to finely control the chemical composition of the PPF by a clever choice of the process parameters. On the other hand, tailoring their morphology at the micro/nano scale is much more challenging limiting further development in the field. In this context, in this work, an innovative strategy allowing the control of both the chemical composition and the architecture of PPF is established. The proposed method is based on the controlled generation of surface instabilities in bilayer systems formed by a mechanically responsive PPF and a stiffer thin film.

As a case study, propanethiol is used as a precursor and the mechanical properties of the PPF are controlled varying the substrate temperature (T_s). Scratching experiments using the tip of an AFM reveal that for T_s < 10 °C, a deformation of the PPF takes place when applying a force on the polymer surface followed by a recovery of the material over a time scale of about 3 min. As an important result, these data disclose the possibility to produce soft and visco-elastic plasma polymer layer. Furthermore, the stiffness of the PPF is found to increase with T_s. These data are correlated with an increase in the cross-linking degree with T_s. In a second step, in view of inducing the morphological reorganization of the material, an aluminium coating is deposited by the magnetron sputtering technique on the top of a mechanically responsive PPF giving rise to the formation of a wrinkled surface. By tuning the thickness of the Al and the PPF layers as well as the cross-linking degree of the PPF, the height (i.e. from 0.4 to 5.2 µm) and the width (i.e. from 0.6 µm to 6.5 µm) of the nano/micro objects can be easily tailored in a wide range offering a great flexibility in term of surface engineering. Finally, the formed pattern is homogenously covered by an additional PPF with the desired functionality.

Keywords
plasma polymer
nanostructuration
wrinkling
Roll-to-roll plasma equipment for surface modification of fibers

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The fibers must be surface-treated or coated to match their surface properties (physical, chemical, topographic) to their application. Low temperature plasma may be used as a gentle but powerful tool for surface treatment (chemical and/or physical altering of the fiber surface) or coating (plasma polymerization) of fibers, retaining their bulk properties if appropriate plasma conditions are used. Plasma polymerization can be used to deposit protective, barrier, biocompatible, or multifunctional films of tailored physical, chemical, and surface properties on fiber surface with controlled adhesion. The roll-to-roll plasma equipment for surface modification of fibers was designed, constructed, put into operation, and successfully tested. The process of plasma surface modification was optimized for glass fibers used as reinforcement for polymer composites to demonstrate the usability of the equipment. The bundle of glass fibers (1600 filaments) was pretreated with oxygen plasma and coated with plasma polymer of tetravinylsilane operated at monomer deficient conditions to functionalize the surface of glass fibers. Plasma equipment was characterized along with the physical, chemical, and surface properties of functional films. Surface-modified fibers were tested as reinforcement in polyester composites. Using a mixture of tetravinylsilane and oxygen gas, it was found that incorporation of oxygen atoms into the plasma polymer network and formation of polar groups (hydroxyl, carbonyl) improves composite performance. The polyester composite reinforced by plasma-coated fibers exhibited higher shear strength than the composite reinforced by industrially sized fibers.

Keywords
plasma polymerization
surface modification
roll-to-roll equipment
glass fiber
polymer composite
Aerosol-Assisted Pulsed Dielectric Barrier Discharges: A new route to synthesize tunable catechol-bearing thin films

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Since the discovery of the versatile chemistry of catechol from the study of the remarkable adhesion of mussel, numerous catechol-based polymers have been synthesized, mainly from wet chemical techniques, and successfully exploited for the production of advanced materials for biomedical or energy applications. In previous work, we reported the plasma deposition of catechol-quinone functional layers using a Liquid-Assisted PECVD (LA-PECVD) approach. [¹, ²] It was also shown that LA-PECVD has limited action possibilities for controlling the morphology and chemistry of the deposited layers. [³] As a result, the potentialities of an Aerosol-Assisted Pulsed Dielectric Barrier Discharge (AA-pulsed DBD) process were investigated for the simultaneous synthesis and deposition of tuneable catechol-bearing thin films.

In this presentation, we will show how the tuning of the electrical parameter led to the deposition of coatings with different chemistry, morphology and deposition rates. In this aim, the electrical discharge was operating in a pulsed mode with ON-time (t_ON) ranging from 1 to 15ms and a fixed 15ms OFF-time (t_OFF). The layer chemistry was investigated by combining bulk analytical analyses, such as FT-IR and UV analyses, and surface analyses, such as XPS. In addition, to accurately estimate the catechol content in the deposited film, a novel analytical technique, based on potentiometric measurements, has been developed and will be presented. Secondly, in an attempt to determine the optimal t_ON/t_OFF ratios to maximize the catechol functional group retention in the deposited film, the influence of various t_OFF duration on the layer property was investigated. Finally, a comparison between the traditional polydopamine method and the AA-pulsed DBD’s one will be done, highlighting the usefulness of the novel dry plasma route.

Keywords
Plasma-polymerization
atmospheric-pressure plasma
Aerosol-Assisted Pulsed Dielectric Barrier Discharge
Catechol
Catechol Characterization
Influence of the structure of 3D printed scaffolds on film deposition with an atmospheric plasma jet

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An interesting new approach for the regeneration of lost bone fragments is the implantation of 3D-printed biodegradable polymer scaffolds. These polymer scaffolds replace the bone fragments until new bone cells form mineralized tissue that grows and matures into new bone inside the porous structure. To achieve good cell adhesion and growth, the surface chemistry of the scaffold material is important. Previous works show that plasma polymerized layers with nucleophilic and electrophilic groups promote cell growth for pre-osteoblasts. Because of its porous structure, it is not possible to coat the whole surface of the scaffold with conventional dielectric barrier discharge (DBD) deposition techniques. For this reason, we investigated chemical vapor deposition processes using an atmospheric plasma jet. This type of process provides the possibility for higher penetration depth into the scaffold structure as well as the option to integrate the deposition process in the 3D printing process of the scaffold. The plasma jet was powered with high voltage (HV) and radiofrequency (RF) and can be pulsed to achieve a good retention of precursor molecules. To achieve nucleophilic plasma polymer films (3-aminopropyl)trimethoxysilane (APTMS) was used as a precursor. A mixture of vinyltrimethoxysilane (VTMOS) and maleic anhydride (MAA) was used to deposit water stable electrophilic layers. The group density and the depth of the film formation into the scaffold structure were investigated by ATR-FTIR-spectroscopy and dyeing techniques. A variation of certain structure parameters of the scaffolds, e.g. diameter of the filaments, pore size, were investigated to optimize the film deposition with regard to an integration of the coating procedure into the 3D printing process.

Keywords
Plasma jet
scaffold
tissue regeneration
PECVD
Highly conductive ultrathin Co films by high-power impulse magnetron sputtering

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Cobalt is a potential replacement for copper in metallization of extremely scaled devices. Due to its shorter electron mean free path, cobalt conductivity is predicted to exceed that of copper at dimensions below 15 nm. Furthermore, the much higher melting point makes cobalt more stable in terms of electromigration.

In this study, we have synthesized ultrathin cobalt films with thicknesses between 6 and 50 nm by direct-current and high-power impulse magnetron sputtering (HiPIMS) without heating. The films were deposited on SiO₂ substrates and characterized with focus on the electrical properties. It is shown that the ionized deposition in HiPIMS result in smooth films with large grains and low resistivities, namely 14 µΩ cm at a thickness of 40 nm, which is close to the bulk value of Co. Even at a thickness of only 6 nm a resistivity of 35 µΩ cm is obtained. This is about an order of magnitude better than direct-current sputtering. We attribute the better HiPIMS films quality to higher nucleation density and densification caused by cobalt-ion dominated plasma. Moreover, we show reduced incorporation of argon in the HiPIMS process.

Keywords
Cobalt
HiPIMS
Resistivity
Metallization
Exploration of spintronic materials in novel combinatorial thin film deposition system

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Spintronic materials have novel properties that are based on the generation and manipulation of spin-polarized currents¹. Their most important application to date is to detect magnetic bits in magnetic hard disk drives. They are now poised to play a fundamental role in advanced non-volatile magnetic memory devices, namely Magnetic Random Access Memory (MRAM), and Racetrack Memory². To accelerate the development of MRAM and Racetrack Memories and to allow for scaling to densities beyond that of charge-based memories, novel materials are required that are based on spin-engineered thin film structures that are formed from atomically layered heterostructures using thin film deposition techniques compatible with mass manufacturing. A combinatorial deposition system was designed to speed up the exploration of needed spintronic structures. The essential feature of the system is the combination of magnetron and ion-beam sputtering and molecular beam epitaxy in individual chambers that allow for the rapid exchange of source materials without breaking vacuum of the main chamber. The co-deposition from multiple sources is a key feature. Ion beam sputtering from 3 distinct materials is possible by the use of three ion beam sources. The system also includes a twelve magnetron sources turret for sputtering from one material at a time with possibility of off-axis sputtering. Overall, up to 44 different materials are available for deposition in the system at any given time. In this talk we present novel approaches for the design of research deposition systems and preliminary results for the deposition of spintronic materials in the system that we have built.


Keywords
spintronic materials
thin film deposition
magnetron sputtering
ion beam sputtering
Influence of the AlN/Si(111) interface on the surface morphology

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Many of today’s indispensable electronic devices such as High Electron Mobility Transistors (HEMT) and LEDs are built of Gallium nitride (GaN), Aluminium gallium nitride (AlGaN) and/or Aluminium indium nitride (AlInN) multilayers. The device performance strongly depends on the perfection of the crystalline structure of the nitride stack. A suitable template for these highly crystalline and defect-free multilayers is epitaxial and smooth AlN. Typically those AlN templates are deposited on Si(111) by Metalorganic Chemical Vapor deposition (MOCVD), which is a time- and hence a cost-consuming process.

AlN films were deposited on Si(111) using an unbalanced magnetron sputtering process on a Clusterline® 200 deposition system. The film properties were investigated for basic process and film parameters as e.g. film thickness and deposition temperature. A special focus has been set to the interface between Si(111) and AlN, where the native oxide removal and the pre-treatment are studied. Wet etching using 1wt% HF of the Si-surface has been compared to in-situ plasma etching. Different high temperature pre-treatments have also been investigated. X-ray Diffraction (XRD), Transmission Electron Microscope (TEM) and Atomic Force Microscopy (AFM) have been used to investigate the film properties and to gain insight on the crystallinity, the lattice constant and the surface roughness.

The deposited AlN films show an exclusive (002) orientation with columns with a diameter in the range of 45nm. The high quality crystalline structure is confirmed by rocking curve (RC) measurements at the symmetric AlN(002) diffraction peak, which shows for 100 nm of AlN on Si(111) under certain conditions a FWHM of less than 1200 arcsec. Thicker films of AlN result in a decreased FWHM, but have the drawback of increased surface roughness. It is shown that roughness and crystal quality are directly correlated due to the columnar growth of the nitride film.

The surface morphology and crystallinity of the presented sputtered AlN templates are suitable to replace the cost-consuming MOCVD AlN films and can be overgrown by MOCVD HEMT structures.

Keywords

AIN
HEMT
H-etching at the interface
Production of zirconium oxynitride thin films by magnetron sputtering: the quest of breaking the chemical composition restrictions.

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Metallic oxynitrides are interesting materials whose properties can be tuned between the corresponding metallic oxide and nitride. In this contribution, we focus on the Zr oxynitrides, since a careful literature review reveals a surprising chemical confinement in quite small region of the Zr-O-N ternary diagram. The objective of this work is to evaluate the characteristics (phases, crystallinity, growth) and properties (e.g. electrical, optical) of films located in areas of the Zr-O-N ternary diagram not explored before. To do so, we have designed several experimental strategies to deposit films by reactive magnetron sputtering while avoiding such chemical restrictions.

In addition, we will report about the influence of addition of other metals (e.g. Ti and Ta) to the Zr-O-N films, leading to quaternary systems composed by two metals and two non-metals. In particular, the Ta addition has been explored with detail, via systematic deposition of films along the edges and faces within the Zr-Ta-O-N tetrahedron. The properties of the films can be selected depending on their location in that space, which also determines their characteristics (chemical composition, phases, etc).

Keywords
oxynitride
zirconium
chemical
XRD
electrical
Surface technology for additive manufacturing with polymers

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Additive manufacturing (AM) has not only become a wide spread application as 3D printing but it is also considered an important enabling technology. It is about to made the step from the preparation of prototypes to industrial production. AM offers the opportunity to produce components with optimized shape for light weight applications and the individualization of products.

Surface technology has the potential to improve AM technology in various ways. For example, the roughness and the porosity of the surface is a systematic feature of many of today’s AM technologies. Surface treatment can help to overcome these issues. In future the additive manufacturing with a combination of many different materials will be required for products which exploit the specific advantages of the particular material at the particular part of the product. In these products surface technology will be required to tailor the interfaces between the materials.

In the presentation we will report about our studies with polymeric products prepared by different AM technologies. In particular we investigated products prepared by selective laser sintering (SLS), stereolithography (SLA), and by fused deposition modelling (FDM). A surface analytical study applying contact angle goniometry and XPS provided some insight in how the preparation technology influences the surface properties of the products. Low pressure plasma and flame treatments were applied for the surface treatments. In particular, the ability of these techniques to penetrate into pores was investigated. Finally, lacquering was applied to make a smoother surface, to close pores, and to provide additional functionality. The influence of the pre-treatments was investigated.

Keywords
additive manufacturing
3D printing
polymer
plasma
flame
OR1801

**XPS investigation of the mechanisms responsible for activation of the surface of ultrahigh molecular weight polyethylene with a medium pressure dielectric barrier discharge**

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Although non-thermal plasma treatment of hydrophobic polymers with the aim to enhance their surface wettability is a common procedure, the mechanisms behind those changes in surface properties are still under debate. In an effort to elucidate these mechanisms, the aim of this study is to try to make a distinction between plasma-induced reactions occurring during plasma exposure and those taking place post-plasma, when the sample is exposed to ambient air. To achieve said goal, an experimental plasma set-up (medium pressure DBD) was designed that can be directly connected to an X-ray photoelectron spectrometer (XPS), thereby avoiding exposure of the samples to ambient air. Basic characterization of the plasma treated polymer was carried out by water contact angle goniometry (WCA) to pinpoint the saturation region of the plasma treatment (in ambient air). Subsequently, different treatment times were selected and samples were investigated in detail, using XPS, to identify and quantify the differences in functional group incorporation for samples that were exposed to air and those that were not. Results show that the oxygen/nitrogen incorporation was significantly altered by post-plasma exposure. To aid in the characterization of the plasma phase, optical emission spectroscopy (OES) was also employed to identify the active species and their relative concentrations inside the plasma reactor that governed the changes in surface properties. Based on these results, a preliminary model was made explaining the different reaction pathways.

Keywords
DBD plasma
UHMWPE
surface modification
ageing
XPS
POLYMER SURFACES MODIFIED BY ATMOSPHERIC PLASMA: CHEMICAL CHARACTERIZATION OF FUNCTIONALIZATION AND MULTILAYER COATING

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Ethylene ChloroTriFluoroEthylene (ECTFE) and PolyEthylene Terephthalate (PET) films have been treated by Atmospheric Pressure Plasma in a controlled atmosphere of pure N\textsubscript{2} with addition of monomers or dopants. Treatments have been done on a R2R industrial plasma reactor developed for achieving high performance surface functionalization and coating deposition on flexible organic films. Advanced surface characterization through X-ray Photoelectron Spectroscopy (XPS) and Time of flight – Secondary Ion Mass Spectrometry (Tof-SIMS) coupled with a Gas Cluster Ion Beam (GCIB) have been used to explain the performances obtained for these treatments. Two different types of surface treatment are presented:

- **Surface functionalization of a ECTFE film** has been performed using different plasma conditions (gas mixture, plasma dosage). The modified surface has been chemically characterized by XPS. Plasma treatments lead to oxygen and nitrogen grafting. The relative proportion of the grafted species is highly dependent on both gas mixture and plasma dosage. These differences in surface chemistries are discussed in relation with surface energy and adhesive properties. It is shown that the adhesion properties are more related to surface chemical composition than to surface energy.

- **Multilayer perfluorocarbon / siloxane coating** has been deposited on a polyester film. Tof-SIMS using GCIB for depth profiling has been able to identify the molecular structure of the different layers and their depth localization in the coating, showing no inter-diffusion. This information is used to explain the surface properties of the multilayer coating.

**Keywords**
- atmospheric plasma
- functionalization
- roll to roll
- XPS
- Tof-SIMS
Large area roll-to-roll processing of flexible polymers by atmospheric pressure hydrogen plasma

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Flexible polymeric substrates were treated by atmospheric pressure plasma generated in pure hydrogen and the mixtures of hydrogen and nitrogen. A novel curved plasma system based on diffuse coplanar surface barrier discharge (DCSBD) in the roll-to-roll arrangement was used to mimic continual in-line processing. Flexible transparent conductive substrates with conductive connection sites were used to etch thin (~ 10-100 nm) film from the surface of the composite polymer substrate with embedded Ag-coated Cu-wires. In contrast to etching in ambient air, pure N₂, and N₂/H₂ mixtures resulting in a strong degradation both the polymer and metal parts of the substrate, the etching in pure hydrogen plasma let to the fast (~ 1s) selective etching of the thin surface polymer film without any destruction of the coated wires. The effect of processing parameters (treatment time, plasma-to-sample distance) on the etching mechanism was studied using SEM/EDX and laser confocal microscopy. Dry etching with hydrogen plasma at longer treatment times (~ 1-10 min) was used for creating a nanoscale roughness on thin (50 um), flexible poly(methyl methacrylate) (PMMA) substrate. Using scanning electron microscopy, X-ray photoelectron spectroscopy, atomic force microscopy, contact angle analysis and the transmittance measurement, it was found that a hydrogen plasma treatment produced nanoscale pillar structures on the PMMA surface resulting in an increase of contact angle of water to ~ 140° after etching from the original contact angle of 75° measured on the untreated surface. The PMMA substrate with initial wetting behaviour thus achieved the superhydrophobic surface properties which can expand the application of thin PMMA foil to many new applications.

Keywords
hydrogen plasma
atmospheric pressure
flexible polymers
etching
roll-to-roll
Ultra-high- molecular-weight polyethylene (UHMWPE) has been widely used because of its excellent mechanical properties but is often unsuitable for use due to its poor wettability. Plasma treatment is a promising technique that enables the surface modification of polymers without affecting the bulk material characteristics. In the present work, the helium transporting discharge and plasma gun were applied to improve the surface properties of UHMWPE films and HDPE tubes. Surface morphology and chemical compositions were performed by means of FTIR, AFM, XPS, and contact angle measurements with the aim of understanding the surface modification effects. The single plasma jet covers only a few square millimeters, which makes it difficult for large-scale treatment of the film surface. To overcome this challenge, we have considered the use of plasma gun arrays consisting of many individual jets placed within close proximity of each other, such structure has a potential to greatly enhance the scale of surface treatment as compared to that of a single plasma jet. FTIR and XPS analyses, indicated that helium plasmas introduced mainly oxygen containing functional groups but also unsaturation has also been observed which has been reported to take place at the same time as surface crosslinking of the UHMWPE. The AFM observations show a surface smoothening with different plasma treatment configurations. Furthermore the stability of the surface properties of the UHMWPE was studied by the measure of the water contact angle. According to our results, transporting discharge and plasma gun have a potential to enhance the surface activation of inner walls of tubes and UHMWPE films. This can be very interesting for biomedical applications such as tissue tolerable polymers, inner walls of vascular grafts and catheters, etc.

**Keywords**
transporting discharge
plasma gun
UHMWPE
surface modification
OR1805

Understanding the growth of ultra-thin plasma polymers on molecularly defined polymer surfaces

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The nucleation and film growth of PECVD deposited SiOₓ films as a function of the substrate surface chemistry (SAMs, acting as a polymeric model system) was investigated. Ultra-thin SiOₓ films were deposited by microwave plasma in a mixture of HMDSO and O₂ and the films were characterized by PM-IRRAS. Cyclic voltammetry was used to probe the defect density of the bare SAMs and the SiOₓ-covered SAMs. Furthermore, the evolution of the SiOₓ surface morphology for increasing film thickness as function of the substrate chemical termination is investigated by AFM. A strong influence of the surface chemistry on the SiOₓ nucleation and film growth was observed. While -CH₄ and -COOH terminated SAMs were degraded during the nucleation leading to defect rich ultrathin films, the -Si(OCH₃)₃ group protected the aliphatic chain of the SAM and lead to ultra-thin SiOₓ-films with a lower defect density [1]. A mechanistic explanation of the results was provided. Following, the results were transferred to the adhesion of a PECVD-SiOₓ coating deposited onto injection-molded PP. The surface chemistry was modified by the by-mixture of PP with small amounts of PDMS to create a Si-enriched top layer. The substrates were characterized by XPS, ATR and ToF-SIMS. The adhesion of the SiOₓ coatings to the PP/PDMS substrates was greatly enhanced with respect to the non-functionalized PP, which shows that adhesion to polymer substrates can be improved without the need to deposit intermediate adhesion layers, and without the need to include a plasma pre-treatment step into the process [2]. The support provided by the German Research Foundation (DFG) within the framework of the Transregional Collaborative Research Center TRR 87/1 (SFB-TR 87) is acknowledged.


Keywords
SiOₓ
PECVD
Polymer surface
Plasma activation of PEEK surfaces: effect of texture and surface energy on practical adhesion.

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Thanks to their low densities and good mechanical properties, polymer composites are good candidates for metal alloys substitutes, especially for transportation industries. However, their surfaces are commonly endowed with poor surface energies, and thus show poor practical adhesion towards coatings. In this regard, we study how both modification of the surface topography and the surface chemistry by Electron Cyclotron Resonance plasma influence and emphasize the practical adhesion of metallic thin films on Poly-Ether-Ether-Ketone thermoplastic.

The goal of this study is to propose a route towards a simple model describing the combined influence of surface texture and chemistry processed by plasma. To simplify the interpretation, we first studied two different processes to separate the chemical and mechanical anchoring effects of surface adhesion enhancement. On one hand, we studied surface activation by atmospheric-pressure plasma – where surface topography modification was kept minimal to obtain the “only-chemical effect” on PEEK adhesion; on the other hand we studied the effect of texturation by infrared femtosecond LASER to obtain the influence of the exclusive surface patterning on PEEK adhesion.

In smooth ECR plasma conditions, PEEK activated surfaces revealed a similar behavior to that one observed with atmospheric pressure plasma, showing direct proportionality between wettability and practical adhesion. In more energetic ECR plasma conditions, PEEK surface texturation occurs under scales of order different to PEEK laser texturation. Our separate understanding of the two adhesion principles – chemical and mechanical – would allow us to grasp the complex behavior when they aggregate under vacuum plasma in order to further increase thin coatings adhesion on polymer surfaces.

Keywords
Vacuum plasma adhesion
atmospheric pressure plasma laser texturation PEEK
OR1807

**Atmospheric Pressure Plasma activation of natural fibres for improved matrix interaction**

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Several investigations have shown that plasma activation is a suitable, environmental friendly method to modify fibre materials. Depending on the plasma chemistry, the surface energy and also the topography of fibres can be significantly changed which can lead to an improved wettability and surface chemistry. This is of particular interest during subsequent processing steps if fibres are implemented into fibre-reinforced polymers (FRPs).

The processing of natural fibres is particularly difficult because their surface chemistry and topography are highly inhomogeneous and depend on the natural growth of the fibres. Additionally, the chemistry of cellulose, hemicellulose, pectin and lignin is not compatible with a lot of matrix systems. One possibility to improve the adhesion between natural fibres and matrix systems is to treat the fibres with cold plasma at atmospheric pressure. Hereby, beside a gentle surface cleaning, functional groups are formed on the fibre surfaces.

Usually, the matrix material is often heated to lower its viscosity before impregnating the fibres. Therefore, it is important to know if the functional groups sustain the heat influence and still allow for a better impregnation.

In this work surfaces of natural fibres were activated by a cold atmospheric pressure plasma source that offers a high treatment width and can be easily integrated into processing chains with regard to industrial applications. After activation the fibres were characterized by SEM, XPS, tensile testing and adapted wetting measurements by a Wilhelmy balance. Additionally, fibres were heated under defined atmospheres to simulate the temperature effects during the injection process.

The results show an increase of oxygen containing groups and surface energy of the fibres after the plasma treatment. However, these activation effects were highly reduced after heating of the fibres. Thereby, the level of remaining activation effects depended on different plasma treatment parameters.

**Keywords**
cold atmospheric pressure plasma activation
thermal stability
natural fibres
Modeling the evolution of rough profiles of polymeric substrates during plasma etching: The interaction between surface charging and roughness

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The interaction of plasma with polymeric substrates induces surface roughness on the substrates. In the semiconductor industry, the surface roughness (line edge roughness, LER) of polymeric masks, induced or enhanced during plasma etching process, was and still is an artifact. In other fields, the surface roughness of polymeric substrates may be beneficial for a variety of applications related to the wetting behavior and the interaction of surfaces with cells. Surface charging of rough polymeric substrates is inevitable during plasma etching as all prerequisites are present: The directionality difference of positive ions and electrons impinging on the etched surface, the dielectric property of the substrates allowing charge accumulation, and finally the surface morphology, facilitating the local imbalance of positive and negative charges. Towards the understanding and, ultimately, the manipulation of plasma-induced surface roughness, the interplay between surface charging and microscale surface roughness of polymeric substrates is investigated by a modeling framework consisting of a surface charging module \cite{memos2016}, a surface etching model, and a profile evolution module \cite{kokkoris2004}. The evolution of initially rough profiles during plasma etching reveals, on the one hand, that the charging contributes to the suppression of roughness and, on the other hand, that the decrease of the roughness induces a decrease of the charging potential. The effect of charging on roughness is intense when the etching yield depends solely on the ion energy and it is mitigated, when the etching yield additionally depends on the angle of ion incidence. The effects of ion reflection and secondary electron emission on the evolution of rough profiles are also investigated. \cite{memos2016, kokkoris2004}

\textbf{Keywords}

surface charging
plasma etching
roughness
simulation
The study is focused on the visualization of ground state atoms, both neutral and ionized, produced in high-power impulse magnetron sputtering (HiPIMS) discharges. The effects of the pulse energy as well as plasma-on and plasma-off time duration on the particle density evolution in the plasma volume have been studied in Ar-Ti case. For particle visualization laser-induced fluorescence (LIF) imaging combined with the data post-processing have been utilized. Additionally, the atom and ion number densities have been obtained using optical absorption spectroscopy. The time-resolved 2-D density distributions of the sputtered atoms and ions obtained by LIF imaging have been post-processed using self-developed MATLAB™ code in order to elucidate the directivity of particle motion in various directions above the magnetron cathode.

The obtained results demonstrate that the plasma-on time duration mainly alters the ionization degree of sputtered Ti and, to a much lesser extent, the time evolution of its number density. At the same time, the plasma-off time mainly affects the number density of the atoms constantly present in the discharge volume. Moreover, time-resolved analysis of Ti ionization degree shows its dramatic decrease after the plasma pulse for more intense pulses (when higher power is applied during a shorter plasma-on time).

This study significantly clarifies sputtering dynamics of the ground state species in HiPIMS discharge, both qualitatively and quantitatively, showing a possibility to determine the atom and ion number density as well as the particle fluxes in the discharge at any moment of time. The obtained results should be of a great interest for the future optimization of HiPIMS processes, especially those related to multi-pulse operation.

**Keywords**
- high-power magnetron sputtering
- ground state atoms
- laser-induced fluorescence
- 2-D imaging
- plasma diagnostics
OR1901

BIPOLAR HIGH-POWER PULSED MAGNETRON SPUTTERING OF METALLIC TITANIUM. ROLE OF ELECTRICAL PARAMETERS.

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Titanium is a light and abundant metal revealing excellent mechanical properties, remarkably high corrosion resistance, low thermal expansion, and low resistivity. Ti thin films are widely used in technological applications, such as surface protection and decoration, adhesion layer for Au and Ag coatings, giant magneto resistance (GMR), etc. This work is devoted to study of the high-power impulse magnetron sputtering (HiPIMS) discharge and the obtained film properties as a result of altering the electrical field polarity applied to HiPIMS cathode. This approach can be called bipolar HiPIMS (b-HiPIMS) discharge, where a negative (plasma) pulse is followed by a positive one, aiming at increasing of ion bombardment of a substrate with growing film. As shown in this study, new parameters such as the delay between the mentioned negative and the positive pulses have a significant impact on the energy of species thus affecting the Ti film growth.

The b-HiPIMS approach has been used in a PVD sputtering process and compared to DC sputtering under different bias voltages applied to the substrate during film deposition. During the process plasma stayed under a somewhat higher potential, allowing positive ion acceleration towards the substrate. As a result, clear effect of film surface modification and its microstructure is shown. Various Ti films deposited using DCMS, PDCMS and b-HiPIMS techniques on Si (100), glass and steel substrates are compared using X-ray diffraction (XRD). It is shown that the b-HiPIMS regime influences the crystallographic orientation and equivalent results compared to the DC mode are obtained on glass and steel.

The study performed in the b-HiPIMS discharge should be further extended including the other metals or composites. In particular, the resistivity and hardness measurements of the films deposited in DCMS and b-HiPIMS regimes are expected further clarify their electrical and mechanical properties.

Keywords
HiPIMS
Titanium
Despite the industrial successes of magnetron sputtering, space propulsion and Penning ion source, aspects of their performance, such as the specific impulse of Hall thruster and the deposition rate of high power impulse magnetron sputtering (HiPIMS), are still far from ideal. In order to optimize the performance of these discharges, among the most common laboratory magnetically confined plasmas, characterized by orthogonal electric and magnetic fields (i.e. $E \times B$ configuration), numerous studies has been devoted over the years.

In this type of plasmas, two important phenomena can be observed along the azimuthal direction ($E \times B$ direction) for a wide range of operations: the rotating spoke and the electron cyclotron drift (ECD) instability. The ECD instability is considered as a short wavelength (mm-scale) and high frequency (bout MHz) kinetic instability, while the rotating spoke is observed many times in the form of large scale (cm-scale) and high density coherent structures. They are considered as the main sources of anomalous transport (across the magnetic field) and electron heating, which greatly influence the performance of laboratory plasma devices. However, the physical nature and the driven mechanisms of ECD instability and spoke formation still remain unresolved today.

In our work, we have proposed and demonstrated the driving mechanisms of rotating spoke and ECD instability by deducing and analyzing the dispersion relation of azimuthal electrostatic waves. The spoke location is also defined by analyzing the azimuthal disturbance potential. By comparing with the several measurements in the literature, the proposed driven mechanisms in this work are able to predict correctly the experimental characteristics of the spoke and the ECD instability, such as their frequency, velocity and wavelength as well as the dynamic process of spoke.

**Keywords**
- magnetized plasma
- rotating spoke
- electron cyclotron drift (ECD) instability
HIPIMS: A plasma surface interaction model

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High Power Impulse Magnetron Sputtering (HIPIMS), also known as High Power Pulsed Magnetron (HPPMS), is a physical vapor deposition (PVD) technique which utilizes magnetron discharges of extremely high power (kW/cm²) in short pulses (100 μs). Compared to conventional magnetron sputtering, HIPIMS is capable of generating films of high density and advantageous microscopic morphology. This capability is generally attributed to the fact that in HIPIMS the critical figure of merit of PVD processes, the average energy per deposited atom, is nearly a factor of ten higher than in other deposition processes [Anders 2009]. This contribution will focus on HIPIMS modeling work conducted within the Collaborative Research Center SFB-TR 87. A plasma surface interaction model is presented which results from coupling two electron models, a heavy species model, and a surface model. The first electron model follows the energetic electrons (which emerge as secondaries from the cathode) by means of a Monte Carlo simulation; the second electron model accounts for the thermalized plasma electrons with the help of kinetic theory. The assumptions underlying the models are via comparison with Particle-in-Cell (PIC) simulations. The heavy species model describes ions and neutrals using a Direct Simulation Monte Carlo method (DSMC). The surface processes are analyzed by means of Classical Molecular Dynamics (CMD). The relevance of this plasma surface interaction model to the simulation of HiPIMS discharges [Gallian et al. 2015] and to the interpretation of recent experimental findings [Hecimovic et al., 2017] is discussed.

Support by Deutsche Forschungsgemeinschaft (DFG) via SFB-TR 87 is gratefully acknowledged.

[A. Anders, Thin Solid Films 518, 4087 (2010)]

Keywords
HIPIMS
HPPMS
modeling
OR1904

Pulse induced modulation of electrical characteristics in ultrathin Molybdenum films

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Ultrathin molybdenum films were deposited on silica substrates by high power impulse magnetron sputtering (HiPIMS). The resistivity values obtained for 10 nm thick films are lower than that of the ones reported for highly conducting ultrathin copper or cobolt films. Even for the film with thickness of about 10 nm, a resistivity of 22.5 µΩ cm is obtained. Energetic impact of molybdenum ions on the depositing surface is a proven technique to obtain smooth and dense films with low roughness and low resistivity. Such characteristics could be attributed to higher nucleation density formed at the early stage of deposition and dense film growth during the deposition facilitated by the energetic impact Mo\(^{+1}\) or Mo\(^{+2}\) ions that dominates the composition of dense HiPIMS plasma. The results obtained here are greatly depend on the duty cycle of HiPIMS pulses, in particular the length of the pulses that are relative to origin and development of gas rarefaction during the HiPIMS discharge that controls the argon incorporation in molybdenum films. The obtained results are correlated to the model developed based on the scattering of charge carriers in grain boundaries.

Keywords
molybdenum film
energetic ion impact
gas rarefaction
Ar incorporation
low resistivity
Controlling the B/Ti ratio of TiBx thin films grown by high-power impulse magnetron sputtering

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TiBx thin films grown from compound TiB₂ targets by magnetron sputter deposition are typically highly over-stoichiometric, with x ranging from 3.5 to 2.4, due to differences in Ti and B preferential-ejection angles and gas-phase scattering during transport from the target to the substrate. Here, we demonstrate that stoichiometric TiB₂ films can be obtained using high-power impulse magnetron sputtering (HiPIMS) in Ar. The B/Ti ratio x is controllably varied from 2.08 to 1.83 by adjusting the length of HiPIMS pulses $t_{on}$ between 100 and 30 µs, while maintaining average power and pulse frequency constant. Energy- and time-dependent mass spectrometry analyses of ion fluxes incident at the substrate position show that the density of metal ions increases with decreasing $t_{on}$ due to a dramatic increase in the peak target current density resulting in strong gas rarefaction. With $t_{on}$ below 60 µs, film growth is increasingly controlled by ions, rather than neutrals, incident at the substrate. Thus, since sputter-ejected Ti atoms have a higher probability of being ionized than B atoms, due to their lower first-ionization potential and larger ionization cross-section, the Ti concentration in as-deposited films increases with decreasing $t_{on}$ as ionized sputtered species are steered to the substrate by the plasma in order to maintain charge neutrality.

Keywords
TiBx
Thin films
high-power impulse magnetron sputtering (HiPIMS)
Pulse length
Gas rarefaction
How to transfer HIPIMS processes using different cathodes and machines

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HIPIMS processes have reached industrial level and there is a number of commercial HIPIMS solutions on the market. Nevertheless, the most efforts in development are still made using lab scale systems and cathodes. Exploiting these results and successfully transferring them to larger scale quite often presents a major challenge. In many cases the current, or better the peak current (peak current density) attached to the cathode is referred as the main parameter for scaling. Transferring processes between different cathodes and therefore different magnetic configuration will influence the electrical parameters applied to the cathode. Even more critical is shifting the coating system. This paper addresses issues concerning the transfer between different cathodes and coating systems. Instead of focusing on the electrical parameters applied at the cathode the situation at the substrate position is observed. Plasma properties like electron and ion density or electron temperature, as well as the ion to neutral ratio of the film forming species are used to characterize the process conditions for the film formation. Tailoring the input parameters at the cathode to reach comparable situation at the substrate is discussed. Finally, results of film growth and morphology are shown as first indication of proper choice for a successful approach for process scaling and transfer.

Keywords
HIPIMS
ion-to-neutral ratio
process transfer
scaling
Different types of DLC coatings by Controlling the ion assistance in highly energetic pulsed magnetron discharges in an industrial coating system

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DLC – coatings in their complexity with most different types are hydrogen-free amorphous carbon (a-C), hydrogenated amorphous carbon (a-C:H), tetrahedral amorphous carbon (ta-C) or Metal-doped DLC (such as Cr-doped DLC). Due to their individual wear-resistant, corrosion-resistant and tribological properties they are widely used on components and wear parts, cutting tools, dies and molds.

For the production of such most different DLC - coatings an industrial coating system xPro4C was developed on the basis of HiPIMS and pulsed magnetron sputtering. Large area rectangular magnetron-sputtering sources with variable magnetic fields were used to deposit multi-layered coatings. The optimum level of ion assistance to the growing films is adapted in the different coating steps by an automatic change of the magnetron magnetic configuration, i.e. the degree of balanced or unbalanced. The plasma can be excited in both HIPIMS and DC-Pulsed mode, that in combination with an optimum adjustment of the magnetic field design, smooth coatings with high hardness and ideal adhesion can be produced efficiently. Detailed process description will be given.

The technology is very much up-scalable.

A wide variety of DLC coatings as described initially can be deposited in the system with hardness values up to HV 4000.

Detailed information on coating properties will be given.

As an additional benefit, the design of the system also allows the deposition of extremely smooth hard nitrides and carbo-nitrides, such as all standard multi-layered, nano-structured TiN, TiC,N, AlTiN, AlCrN and Si-doped coatings.

For industrial production purposes the system runs in a fully automatic mode. For R&D - applications the system can be operated in full manual mode.

Keywords
DLC
HiPIMS
variable magnetics
ionbombardment
industrial coating system
HiPIMS meets Diamond

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This paper will introduce a visionary new class of coating materials with revolutionary properties. It creates added value by merging diamond – the hardest of all materials – with HiPIMS – smooth and dense sputtered films – into one new material.

The starting point of HiPIMS meets Diamond was the search for new coatings for high gloss mirror finish machining with micro-cuttings tools for the 3C industry (Computers, Consumer Electronics & Communications). The extreme requirements set by this industry brought up a new approach of tuning the “knobs” of HiPIMS for novel plasma regimes during etching and the deposition phase. This involves new hardware features as individual parameter sets for all HiPIMS sources while keeping the synchronization to the dedicated HiPIMS bias. Application cases will show that the plasma synchronization is the key to minimize intrinsic stress while having a deposition rate as high as 2µm/h at the same time.

This new way of controlling the pulsed HiPIMS plasma made possible the design of HiPIMS meets Diamond. The exceptionally hard diamond provides the perfect foundation to the HiPIMS film. Furthermore, diamond has an outstanding thermal conductivity and spreads the extreme heat coming from the cutting zone. The smooth, droplet-free surface of HiPIMS coatings reduces friction, protects the diamond against oxidation and optimizes the running in process of the cutting tool. All this makes HiPIMS meets Diamond the perfect candidate for coatings for heatresistant superalloys.

Case studies as the machining of casted CrCo for medical implants and the milling of stacks with extra thick titanium layers show that the radically new materials concept HiPIMS meets Diamond paves the way for new business for cutting tools after the combustion engine.

Keywords
HiPIMS
sputtering
pulsed plasma
diamond
Dielectric coatings for optical application using reactive ion beam sputtering

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The requirements for optical coating have strongly increased with the advancement made in high-power LASER technology and optical applications. Therefore ion beam sputtering of such coatings became the favorable deposition technique, since the high energy particles arriving at the substrate reveal very smooth and dense films. Usually, stacks as anti-reflex coatings and optical mirrors consist of alternating high and low index dielectric layers. As low index material SiO$_2$ is commonly used and for high index several candidates as Ta$_2$O$_5$, ZrO$_2$ or HfO$_2$ are suitable.

In this work, dielectric coatings are deposited using ion beam sputtering. As low index material SiO$_2$ is used, while for high index different oxides were investigated. The films are sputtered reactive by an Ar ion beam from a metallic target. The substrate holder allows to change the incidence angle of the incoming atoms, what can be used to tune the film properties and to deposit on non-planar substrates. The thickness of the layers is controlled by an optical monitor. Hereby, complex stacks up to 200 layers can be deposited by an integrated test glass changer allowing reloading test glasses without venting the chamber. To deposit optical coatings, knowledge of the exact properties of the single layers is essential. Therefore the single layers are characterized regarding stoichiometry, deposition rate, homogeneity, contaminations und optical properties. The relation between the obtained stoichiometry, the refractive index and the used oxygen flow will be discussed. Furthermore, the difference between using oxygen background gas, using oxygen plasma or using an assisting oxygen ion beam are presented. Furthermore, specific multilayer coatings as for instance high-reflective mirrors and transmission filters were deposited. Their performance is characterized by the corresponding transmission and reflection spectra, by measuring the film absorption and by determination of the laser damage threshold.

Keywords
dielectric films
optical coatings
ion beam deposition
metall oxides
OR2001

Plasma-assisted duplex treatment of AISI 316LM steel: surface micro-structuration by ion beam etching following by a nitriding process. Influence of treatment parameters on tribological properties.

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The enhancement of the tribological properties of stainless-steels is a major industrial challenge. This kind of material shows a high mechanical resistance, a low thermal conductivity, a good corrosion resistance if exposed to cold and humid atmosphere, and could be easily recycled. Two techniques are generally used to functionalize stainless steel surfaces without affecting its corrosion resistance: the surface structuration and the plasma-assisted thermochemical treatment. The former technique is commonly used to reduce cinematic friction coefficient whereas the latest is addressed to improve the hardness of the surface. In this study both surface treatments were combined to functionalize an AISI 316 LM austenitic stainless steel.

To implement this duplex treatment, we performed an ion beam etching in Ar/H\textsubscript{2} plasma using special masks of different dimensions followed by a nitriding process performed in an ECR reactor at 400°C. A parametric study of the duplex treatment was performed to characterize the role of mask geometry on the nitrited layer properties. The influence of the duplex treatment and the role of spacing between asperities as well as their roughness were identified by using a "Ball-on-plate" tribometer.


Keywords
nitriding
ion beam etching
structuration
stainless steel
wear
Influence of H2 on the TiN/Si interface microstructure elucidated by X-ray photoelectron spectroscopy (XPS)

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Titanium nitride (TiN) thin films are broadly used in the micro- and nanoelectronics industry. Most of TiN application requires avoiding impurities incorporation, particularly oxygen at the interface, to guarantee good film adhesion to the substrate and physical properties. In fact, minute quantities of impurities, particularly oxygen normally stemming from adventitious residual H₂O, seriously jeopardize the thin film proprieties.[1] In this paper, a comprehensive X-ray photoelectron spectroscopy (XPS) study of the local bonds occurring in the first atomic layers (~3-5 Å) of TiN grown at T< 350 °C by ion beam assisted deposition on crystalline silicon is reported. The XPS analyses is performed in an UHV chamber attached. The main source of oxygen in the preparation chamber comes from H₂O (~10⁻⁷ mbar). The substrates are prepared by ion beam cleaning involving Xe⁺ ion bombardment at different partial pressures of molecular H₂. The studied interfaces deposited on the cleaned c-Si substrates are studied at different hydrogen pressure conditions too. In fact, increasing the H₂ partial pressures during the interface growth promote the formation of Si-Ti bonds in detriment of Si-N and Si-O. The results show that the bombarding cleaning procedure and the interface growth depend on the occupation probability of H₂ and H₂O on the substrate. Clues about the ideal H₂/H₂O ratio preventing as much as possible the incorporation of oxygen are discussed and suggested. The use of these finding to be applied on TiN coating on metals are also presented.


Keywords
Interface TiN/Si
XPS
Oxygen contamination
Ion Beam Assisted Deposition
Customized ion beam technologies for ultra-precision surface machining of optical devices

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Ion beam figuring (IBF) is an established method in ultra-precision surface finishing. For the fabrication of modern optical devices novel processing routes are needed to fulfill the demands for the diversity and increased complexity of surface shapes, the choice of material, and the size range of optical components. A scalable and most flexible technology meeting those requirements is the deterministic ion beam figuring technique, i.e. a small-sized ion beam tool is scanned along the optical surface to attain a customized local surface correction. The contribution gives an overview of the technology covering following aspects:

1. Metal mirrors are most interesting for short wave-length applications. However, because of alloy matrix irregularities the ultra-precision finishing is challenging. Promising potential was found in reactive ion beam machining. For aluminium surfaces the usage of O$_2$ or N$_2$ process gas results in the in situ formation of a defined etch front passivating the matrix irregularities during the ion beam processing. Machining depths up to 1 micron are achievable without surface degradation.

2. For compact and integrated optical systems optics with an aspherical shape or even freeform surfaces are required. Deterministic ion beam machining allows most flexible shape processing and thus provides a sophisticated technology for figure error correction of those individually designed optics. As an example, the machining of a deep paraboloidal mirror is focused. A processing geometry with fast sample rotation is chosen to correct the radial concentric figure error by a set of discrete ring removal steps.

3. Optical devices cover a broad size range depending on the target application, e.g. meter-scale astro mirrors, millimeter-scale laser components, and micrometer-scaled integrated imaging elements. In principle, deterministic ion beam processing is fully scalable. Differently sized ion beam tools for figuring of diversely scaled surfaces are presented.

Keywords
ion beam
figure error correction
optical devices
aspheres
freeform
A new binary Monte Carlo (MC) model of sputtering based on quantum mechanical cross sections is presented. Instead of traditional MC programs based on classical calculation of a scattering angle our model uses quantum-mechanical differential atom-atom elastic cross section. This helped to improve description of small - angular scattering of an incident atom on a recoil one. The developed model works on 3D maps of solid and allows to obtain both 3D images of films at every time step of sputtering process and sliced distribution of trapped atoms and matrix components in any 3D direction.

The model was used to model sputtering of ultra-thin MoS$_2$ films under Ar bombardment. Dependencies of Mo-S, Mo-Ar, S-Ar atomic interaction potentials on distances were obtained with density functional theory (DFT) calculations and compared to empirical Stillinger-Weber Mo-S potential, which was successfully applied for molecular dynamics (MD) modeling of MoS$_2$ monolayer properties, and to semi-empirical Moliere and ZBL potentials that are usually used for describing the interaction between incident Ar ions and atoms in solid medium in MC and MD simulations. Some parameters of the presented MC model, e.g. surface binding energy, were estimated with the DFT method. The obtained results are in reasonable agreement with literature data. The authors expect the developed code will be of help in plasma processing industry.

**Keywords**
MoS2
sputtering
argon
modeling
ultra-thin films
Metal-Microwave Plasma interaction for Hydrogen Storage

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This work is a proof of concept for an efficient, fast and reversible cyclic hydrogen storage principle under ambient conditions for energy storage and next generation transportation systems. It consists of using the interaction between plasma and nanometric metallic materials instead of wide spread techniques. The choice of Ni results from their ability to store hydrogen through hydrogenation process as pure or alloyed particles. The special features of the stable nanomaterial (<100 nm) structure of nickel is (i) the fast ingress and transport of hydrogen along grain boundaries and triple junctions (short-circuit diffusion) and (ii) the enhancement of the intrinsic dislocations and vacancies density on trapping mechanisms. We use an ECR microwave sources to generate reactive plasmas. These engineered nanomaterials, submitted to cold plasma assisted hydrogen implantation should adsorb hydrogen for shorter interacting time. It was established that, ion implantation produces hydrogenated phases in nickel. In practice, thin pellets will be used for plasma treatment to be loaded in H thanks to hydride formation. Parameters of the hydrogen charging plasma has been carefully studied (ions density, energy and flux) to optimize the implantation procedure, to analyze the induced structural modifications due to hydrogen penetration, and on the aging due to cycling, which could lead to a significant variation of the hydrogen retention capability. These experiments has been assisted by the development of a new 3D numerical tool, coupling non-equilibrium kinetic hydrogen transport and trapping, mechanical field evolution, and the induced damages in material. This model enable to predict transient hydrogen inventory and embrittlement of the bulk. It will allow to simulate the total retained hydrogen; depth profiles of solute and trapped hydrogen; and the temperature distribution in the exposed material over the time.

Keywords
Plasma
Hydrogen
Storage
MicroWave
Nano-material
In the present work, hydrogenated silicon carbonitride (SiC$_x$N$_y$:H) thin films were elaborated by the mean of a hybrid process combining RF sputtering and ECR plasma, in the goal to use them as antireflective coatings and hence to increase the efficiency of PV cells. This material was obtained by sputtering a Si target under an Ar-N$_2$-CH$_4$ gas mixture, and four coaxial microwave sources while the reactive gas flow ratio $R = \frac{[F_{N_2}]}{([F_{N_2}] + [F_{CH_4}])}$ was varied. The study is conducted in order to verify the tunability of the chemical composition of SiC$_x$N$_y$:H versus R, which leads to control their refractive indices. That make them an attractive antireflective coatings for silicon PVs. The plasma was studied using OES to identify the different emitting species related to the sputtered silicon and the reactive gas decomposition efficiency. According to the performed RBS analysis, we could tune the carbon and nitrogen rates in a wide range (going from a silicon carbide like film for R=0 to a silicon nitride like film for R=1). XPS analyses were performed to identify the chemical environment of the elements forming the films and the evolution of the main bond components was studied showing a decrease of Si-C and increase of Si-N with R. FTIR was used to define bonded hydrogen contents in the films, its amount decreases with R and a preferential Si-H bonds formation instead of C-H (produced by CH$_4$ decomposition) was highlighted. Total hydrogen amount of the films was also determined by the mean of ERDA analysis. Refractive indexes of the deposited films were characterized using spectroscopic ellipsometry, a relatively large scale [1.8- 2.3] at 633 nm of $n$ values was obtained versus R, the same behavior was observed for optical band gap values measured by UV-visible spectroscopy [2- 4.5 eV].

**Keywords**
Reactive spuettingering
SiC$_x$N$_y$:H
Optical properties
XPS-RBS
Boriding of low alloy steels with powder or a paste-like precursor is well understood and has been studied for many years. The process involves boron diffusing into the material surface at temperatures above 750 °C. Very hard and wear-resistant boride layers with a larger layer thickness are formed compared to conventional hard coatings. A disadvantage of this process is the resulting residues of the precursor on the material surface, which must be laboriously removed and then disposed of. To get around this, gas boriding processes with BCL$_3$ precursor and additional plasma support were developed. However, the problem here was the formation of pores and the technology was not suitable for the successful treatment of high-alloy steels.

With a new boriding process, it was possible to produce almost non-porous boride layers on various high-alloyed steels at temperatures of 700 - 750 °C. This could be achieved by changing the process gas composition and changing the gas supply. The use of the BCL$_3$ precursor could be significantly reduced. With the new process, coating thicknesses between 10 and 20 μm with good adhesion can be achieved after a process time of two hours. Depending on the tool steel used and the process parameters, the layer hardness is between 1800 and 2500 HV. After boriding, the edge zone has a columnar structure which has disappeared after post-hardening of the steels according to the specifications of the material manufacturers. In Chromium-alloyed tool steels a fine-grained edge zone with chrome boride precipitates could be observed. Ball-on disk-tests against steel and aluminum demonstrate a very good friction and wear behavior.

**Keywords**
- plasma diffusion
- boriding
- wear reduction
- high-alloy steel
Plasma processing of metal-porphyrins and phthalocyanines for the fabrication of low dimensional metal nanostructured layers

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The development of new fabrication methods for the nanostructural control is crucial to synthesize rationally designed materials with enhanced properties.[1,2] Plasma activated deposition methods have evolved during the last decade from focus on compact thin films towards the controlled deposition of nanoscale materials.[3–4] Advantages of these vacuum-plasma methods mainly relay in their straightforward scalability, low deposition temperatures, compatibility with an ample variety of substrates and high accuracy in the composition, as well as on the control on their morphological characteristic as microstructure, texture or alignment.[3–4] However, a critical bottleneck for the application of procedures for the deposition of nanoscale materials is the limited availability of volatile metalorganic and metal halide precursors.

The present work establishes the bases for a vacuum and plasma supported methodology for the fabrication of metal or metal-oxide nanostructured layers with controlled microstructure by using metal-porphyrins and phthalocyanines as precursors.[5–7] The layers synthesized range from compact to porous films as well as low dimensional nanostructures such as 2D networks, nanowires or nanocolumns, with a wide range of applications like optic, optoelectronic, catalysis or solar cells, among others.

1 W. Xiong et al. Front. Optoelectron. 8 (2015) 351
4 A. Barranco et al. Prog. Mater. Sci. 76 (2016) 59
7 M. Alcaire. et al. Nanoscale 3 (2011) 4554

Keywords
Plasma processing
Thin films and Surfaces
Low dimensional nanomaterials
Plasma Enhanced CVD
KN2100

**Plasma Printing: Area-selective functionalization of surfaces at atmospheric pressure – Plasma sources and applications**

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The paper will give an overview on area-selective surface treatment using microplasmas at atmospheric pressure. In this so-called plasma printing process dielectric barrier discharges (DBD) are ignited inside microcavities, which are formed temporarily during the treatment by the contact of a suitably designed »plasma stamp« with the substrate surface. In the last two decades different plasma sources have been developed and patented in order to modify or coat different types of substrates for various applications. For semiconductor applications a localized plasma treatment of wafers was optimized so that wafer bonding can be performed at temperatures as low as 200 °C rather than at 1000 °C necessary in today’s standard processes. In the field of biomedical applications area-selective deposition of different coatings with specific chemical functionalities have been applied to control the adhesion of biomolecules like proteins, cells, or anti-bodies.

In recent years the stamp technology was transferred to a reel-to-reel system allowing now line speeds up to 10 m/min. One of the most promising applications is the additive electroless metallization after area-selective surface treatment of polymers. By using N₂/H₂ gas mixtures more than 10 nitrogen-containing functional groups per nm² can be grafted to the surface, forming a seed layer for the subsequent electroless processes. Flexible printed circuits and biosensors were produced using copper and palladium, respectively, with resolutions down to 25 µm. The latest development is a combined process of plasma printing and gravure printing of security products such as Guilloches or color shift devices. The wettability of different nano inks was adapted to the treated surfaces. Graphene-containing nano inks were optimized so that they contract to the plasma-treated regions on BOPP. The sharp border between plasma treated and untreated areas leads to a high-resolution gravure-printing process with resolutions below 10 µm.

**Keywords**

microplasmas
dielectric barrier discharges
surface functionalization
OR2101

A novel plasma jet with RF and HF coupled electrodes: jet characterization and effects on the surfaces

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The goal of achieving low temperatures and high plasma density is sought since many years. These requirements are needed to treat sensitive substrates from polymers to living tissues. At the same time chemical precursors used for surface functionalizations have to maintain their organic structure and keep high process efficiency. The two requirements usually are one against the other and the different solutions identified are the best achievable compromises.

Here, as a novel technical solution, we present a patented plasma jet where the coupling of RF and HF electrodes offers cold, stable and efficient conditions. The plasma is operated with argon as main process gas and it keeps its efficiency even with relatively high oxygen or precursors concentrations. Electrical, optical and temperature plasma jet characterization will be presented. In particular it will be highlighted the damping of the HF streamers by the RF plasma and the two frequencies plasma coupling like in a glow plasma. Optical and temperature measurement will highlight its low temperature processing, up to room temperature. In order to show its potential, it will be presented the deposition on a low melting substrate as polycaprolactone (PCL), the deposition of sensitive precursors using vapors of pyrrole monomer and the deposition of zinc oxide by aerosol of zinc acetylacetonate.

In order to highlight the peculiar features of the jet will be also presented the ion exchange in glass induced by the plasma jet, which allows also an easy patterning in the microscale of the ions in the glass at low temperature (about 150°C).

\textbf{Keywords}

atmospheric plasma jet
frequencies coupling
low temperature process
Non-Vacuum Plasma Nitriding with Nitrogen-Based Gases

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In contrast to the conventional nitriding techniques with low-pressure plasmas, our original nitriding utilizes atmospheric-pressure plasmas. The advantages of the atmospheric-pressure plasma nitriding include that vacuum equipment is unnecessary, that the treatment process is simple, and that the capital cost is low. We have developed a novel atmospheric-pressure plasma nitriding using the pulsed-arc (PA) plasma jet with nitrogen-based gases. The PA jet nitriding is available for a partial surface area of steels and titanium alloys. Here, we detail recent demonstration of nitriding to austenitic stainless steel.

Stainless steels are relatively difficult to perform nitriding to because of the barrier effect of passive layer against nitrogen diffusion. In the conventional low-pressure plasma nitriding, the passive layer is removed by ion sputtering. On the other hand, ion sputtering is not available in atmospheric-pressure plasmas for too short a mean free path. To overcome this issue, we control the hydrogen addition to the operating nitrogen gas to reduce the passive layer. Without hydrogen addition, the expanded austenite phase, a nitrided layer formed on austenitic steel, cannot be produced owing to the passive layer. However, adding hydrogen at the flow ratio of 1 to 5% provides the expanded austenite phase. This is the first achievement of expanded austenite formation by atmospheric-pressure plasmas. Here, the thickness of the expanded austenite layer tends to decrease with increasing the hydrogen flow ratio. In the conference, we discuss the method in which the hydrogen flow ratio is purposely changed in the middle of treatment process to provide a thicker expanded austenite layer.

Moreover, the feasibility of another atmospheric-pressure plasma nitriding with dielectric barrier discharge is also presented.

Keywords
nitriding
atmospheric-pressure plasma
stainless steel
expanded austenite
pulsed-arc plasma jet
Plasma Based Surface Finishing of 3D Printed Metallic Parts

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Since several years, the formation of three-dimensional objects with arbitrary geometry has gained growing interest, especially concerning rapid prototyping or additive manufacturing of different parts for a huge range of applications. Methods for the so-called printing of plastic parts are stereolithography, digital light processing, polyjet modeling or fused deposition modeling using typically digital data from a 3D model generating complex 3D structures.

Furthermore, the printing of metallic geometries arouse great interest due to its feasibility of generating complex parts for e.g. automotive or aerospace industry, especially for rapid realization of prototype parts. Moreover, for changing single damaged parts, e.g. blades in a turbine, the 3D printing of the needed parts are of high interest not least from a financial point of view. Typical methods for generating 3D printed metallic parts are selective laser melting and electron beam melting. In the case of printed metallic parts, the surface roughness is very high. Consequently a polishing process is needed providing the opportunity reducing massively the surface roughness of complex shaped parts, e.g. in preparation for coating deposition.

At this point, the plasma electrolytic polishing process offers the opportunity polishing complex 3D structures highly efficiently in a short time scale. The rough parts are moved into a solution of a specific electrolyte with defined conductivity and temperature biased by a positive voltage in a range of 90 to 400 V. This leads to the formation of a plasma around the part causing plasma chemically induced abrasion of the surface.

In this talk, the concept of treating metallic 3D printed parts by plasma electrolytic processes will be presented including several examples, inter alia from automotive and aerospace industry.

Keywords
plasma electrolytic polishing
additive manufacturing
rapid prototyping
Cold atmospheric plasma processes for water activation: investigating chemical selectivity and energy efficiency for agriculture and medicine applications

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The aim of our research works is to bridge plasma technology with Life Sciences applications to offer innovative plasma solutions where conventional processes fail or are limited. In that framework, the activation of water stands for a major issue first in agriculture and second in medicine.

We have developed several plasma processes based on a DBD approach, including (i) matrix configurations enabling the treatment of large volumes of water and (ii) bubbling systems where calibrated bubbles of post-discharge gases interact with the liquid to enhance its concentration in radicals species.

A complete experimental set of analytical techniques dedicated to the characterization of long lifetime chemical species has been implemented using colorimetry and acid titrations techniques considering acid-base equilibria, pH and temperature variations induced during plasma activation. 16 species are quantified and monitored, including ammonia, orthophosphates, carbonate ions, nitrite/nitrate ions, hydrogen peroxide, etc. The related consumption/production mechanisms are discussed as well as their interaction with the gaseous phase. In parallel, a chemical model of electrical conductivity based on Kohlrausch’s law has been developed to simulate the electrical conductivity of the plasma-activated water. The processes are then compared in terms of chemical selectivity and energy efficiency in order to forecast their potential in seeds biology and cancerology.

Keywords
DBD in parallel
Agriculture
Kohlrausch’s law
RO(N)S
energy efficiency
Coupling of Atmospheric Plasma Jet and Plasma Electrolytic Oxidation as potential alternative for the classical anodization of 3000 aluminum alloys

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During the past few decades, anodization of aluminum alloys is facing new challenges due to the increasingly strict environmental standards all around the globe. Therefore, a significant demand exists for more environmentally friendly alternatives to Cr(VI) baths or similar classical anodization methods. In this study, a novel alternative process for the anodization of the aluminum 3000 series is proposed. This original procedure couples two plasma-based techniques for modifying the chemical and physical properties of the aluminum substrate.

First, aluminum substrates are exposed to an extensive treatment under an atmospheric pressure plasma jet (APPJ), working through a rotating arc inside the jet body. SEM, stylus profilometry and X-Ray microtomography measurements clearly indicate an increase in the surface roughness with the treatment duration. This is due to the etching of the substrate as suggested by optical emission spectroscopy (OES) but also due to the partial melting and crystallographic rearrangement of the alloy structure during the process observed through X-ray diffraction measurements, favorizing 200 and 111 Miller plans. APPJ-treated samples are then used in a plasma electrolytic oxidation (PEO) for varying durations. This leads to the formation of a γ-Al₂O₃ layer with thicknesses dependent on the treatment duration. Stylus profilometry and SEM show a strong variation in the roughness depending on the initial substrate and the PEO treatment duration. XPS and XRD measurements show that the APPJ treatment allows a strong decrease of silicate salt grafting, which is initially present in the solution, reducing the growth of an amorphous SiO₂ phase into the plasma anodized layer. The effect of the coupling of the two plasma techniques on the electrochemical behavior of the substrates is then evaluated by potentiodynamic curves and electrochemical impedance spectroscopy.

Keywords
Anodization
APPJ
PEO
An enhancement of fracture toughness of hard nanostructured materials without compromising the strength is challenging as the ability of most hard materials to deform inelastically is rather limited. In this work, various innovative design strategies for fracture toughness enhancement of brittle materials will be presented, which rely on compositional, microstructure and mechanical property depth-distributions and dedicated grain-boundary and interface design. An example of the development of films with dedicated mechanical properties by a cross-sectional combinatorial approach will be given for a graded TiAlN system exhibiting variations of hardness and fracture toughness with the Al content. Another strategy for fracture toughness enhancement is a combination of hard and elastic constituents in a multilayer structure resulting in crack deflection and possible crack arrest at the interfaces. This approach will be demonstrated for TiN/SiO$_x$ and CrN/Cr multilayer systems with various architecture. Furthermore, in order to turn catastrophic brittle fracture into a controllable deformation process, columnar grains of polycrystalline brittle TiN films were repeatedly tilted with a zig-zag fashion, which enabled multiple crack deflection accompanied by an increase of fracture toughness exceeding the values of their monolithic counterparts with columnar microstructure by more than 150%. Further fracture toughness enhancement of the sculptured films was realized through an implementation of additional interfaces by incorporating layers well differing in their structure and mechanical properties. Crack deflection along kinks of the tilted TiN columnar grains and at the elastic SiO$_x$ interfaces was monitored in-situ by TEM revealing the role of weak grain boundaries and interfaces as effective toughening elements in analogous heterogeneous structures.

Based on these findings and results of micromechanical testing of complex multi-layered CrMnFe-based alloys varying in grain size and grain boundary network, design rules for strong and simultaneously tough structures could be established. The results will demonstrate that a dedicated compositional, grain-boundary and interface design offers great potential for the development of novel hard fracture resistant materials.

**Keywords**

grain-boundary and interface design
Sputter-deposited chromium oxynitride films for strain sensing at high temperature

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Strain and pressure sensing for the high temperature range are increasingly in demand, e.g. for use in chemical reactors and gas turbines. Different thin film materials that are stable in high temperature are subjects of research. Some have an enhanced strain sensitivity, making them particularly promising.

In this work, the properties of highly sensitive chromium oxynitride films are presented. Films are deposited on heated glass substrates by DC sputtering from a chromium target in argon atmosphere with small amounts of reactive gas (air or nitrogen). Samples are patterned using a picosecond laser.

Annealing in air above the desired application temperature leads to relatively small changes of film properties and makes films stable at high temperature. Films are characterized up to 350 °C with measurements of gauge factor and resistivity drift in vacuum and in air.

Films resistivity is about 10 times larger than in bulk chromium. Gauge factors are in the range of 15, i.e., about 5 times larger than those of typical metal films. Unlike metallic films, they are highly sensitive to transverse as well as longitudinal strain. The temperature coefficient of resistance is adjustable (0±500 ppm/K) by varying deposition parameters and annealing, but the resistivity over temperature shows anomalous changes in slope.

Grazing incidence X-ray diffraction and transmission electron microscopy reveal a nanocrystalline chromium thin film. Using X-ray photoelectron spectroscopy it is found that the films have a composition of chromium, oxygen and nitrogen with up to 10 at-% oxygen and up to 5 at-% nitrogen. They can thus be considered chromium oxynitride, Cr_{1-x-y}O_xN_y. It is possible that charge transport takes place by electron tunnelling across insulating barriers of oxide and nitride in between chromium crystallites, leading to high resistivity and strain sensitivity.

Keywords
chromium
strain sensor
piezoresistivity
high temperature
Vacancies and Thermodynamics in Al-O-N and Al-Si-N Thin Films

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Ternary Aluminum Oxynitride (Al-O-N) and Aluminum Silicon Nitride (Al-Si-N) as well as the quaternary combination Aluminum Silicon Oxynitride (Al-Si-O-N) can be fabricated as thin coatings by Reactive Unbalanced Closed Field Direct Current Magnetron Sputtering (R-UCFDCMS). They all provide attractive qualities such as full transparency and hardness, which renders them interesting as e.g. transparent protection layers. Low amounts of O and Si can be considered as dopant atoms that incorporate the AlN wurtzite lattice. O replaces N on anionic lattice sites, since both of these atoms are electronegative and thus act as electron acceptors. Si, on the other hand, exchanges with electron donating Al. The result is a crystalline solid solution. The substitutions lead to an electron excess, because both dopants contain one valence electron more than the atoms they replace. A potential mechanism to account for this electronic imbalance is the formation of Al vacancies on cationic lattice sites. As a supporting indication for voids, cell lattice parameters measured by X-ray diffraction are observed to shrink upon O and/or Si addition. To consolidate the hypothesis, ab initio DFT calculations were performed. Cell parameter changes upon solid solution formation were calculated and showed good agreement with experimental results. The solid solution was also tested for its thermodynamic state and found to be metastable. Upon raising the O and/or Si content and transgressing the solubility limit found at 6-8% O and/or Si, a nanocomposite forms. The single crystallites are continuously enveloped in an amorphous tissue of Al$_2$O$_3$ and/or Si$_3$N$_4$. At yet higher O and/or Si portions above 30%, the material develops into a fully amorphous phase.

Keywords
aluminum silicon oxynitride
sputter deposition
solid solution
vacancies
metastable
In-situ high-temperature X-ray diffraction investigations of magnetron sputtered niobium oxide layers up to 900°C

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Niobium oxide films with a thickness in the range of 1.3 µm were deposited on silicon single crystal wafers by DC powered magnetron sputtering at process pressures of 0.3-0.6 Pa utilizing a 71.6 mm diameter planar substoichiometric niobium oxide (Nb₂O₄.₈) target, which was powder metallurgically produced by hot isostatic pressing. After the deposition process, the layer material was completely amorphous. The primary crystallization of the hexagonal Nb₂O₅ phase and the subsequent transformation to the orthorhombic phase were investigated by means of in-situ high-temperature X-ray diffraction up to a temperature of 900°C under a reducing N₂/H₂ atmosphere. The precise determination of the cell parameters by Rietveld refinement enabled the determination of the anisotropical thermal expansion behaviour of the crystalline Nb₂O₅ phase. Besides, an activation energy of the primary crystallization reaction of +460(50) kJ/mol was quantitatively determined by isothermal in-situ experiments in the temperature range of 505-545°C.

Keywords
DC magnetron sputtering
niobium oxide
high-temperature X-ray diffraction
Easy measurement of the thermal conductivity of coatings with the TDTR method

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Functional coatings and thin films are applied for many purposes: To yield effects such as increased wear resistance and corrosion protection, to achieve certain sensing or optical properties and many more. Generally, it can be said that thermal properties of materials gain importance in many fields, ranging from electronics to wear protection. Indeed, an important aspect of coatings is their thermal conductivity which plays a crucial role in many applications.

However, suitable values for the thermal conductivity often cannot be taken from literature since the thermal conductivity is strongly dependent on the crystalline film structure and, mostly, only values for bulk material are given for very specific compositions. This is why special measurement methods are required for characterizing thin films.

Here, the method of time-domain thermoreflectance (TDTR) provides an efficient means of measuring the thermal conductivity of coatings with layer thicknesses spanning the entire common thickness range from single nanometers to several millimeters. The method is straightforward and only requires a minimum of easy sample preparation.

In this talk, the basics of heat conduction and the working principle of the TDTR method will be explained. It is generally found that the nano- and microstructure and atomic composition of a film strongly influence thermal conductivity. Application examples will be shown for the field of hard coatings for wear and corrosion protection, thermoelectrics and sensor technology. Of course, the measurement method is not limited to these fields but can, in principle, be applied to all kinds of coatings. The results are not only interesting with regard to applications, but also in respect of to heat conduction science, which is a subtopic of solid state physics.

Keywords
thermal conductivity
films
coatings
characterization
thermal properties
Comprehensive Thin Film Analysis by Cross-sectional X-ray Nanodiffraction

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All thin films and engineered surface layers inherently exhibit marked through-thickness property gradients. The complexity of these gradients varies greatly, ranging from the simplest case of a nucleation layer at a substrate interface, to intricately tailored multilayer architectures comprising many different materials, phases and microstructures at multiple levels of hierarchy. In order to understand the overall functional properties of these structures it is of paramount importance to characterize these through-thickness gradients, ultimately making it possible to properly attribute certain aspects of application performance to the time-dependent deposition parameters. This contribution aims to demonstrate the comprehensive analytical capabilities of cross-sectional X-ray nanodiffraction (CS-nXRD) for this purpose.

The method relies on the scanning of thin film cross-sections with sub-30nm spatial resolution, while recording the corresponding film thickness-dependent diffraction patterns. Using the example of a TiN - SiOₓ multilayered thin film, the various parameters accessible through CS-nXRD will be presented. The film was deposited using magnetically unbalanced reactive pulsed DC magnetron sputtering from one Si and two oblique Ti targets, alternately switching between them, resulting in a zigzag-like film morphology. The evolution of (I) phase composition, (II) crystallographic texture, (III) grain size, (IV) micro-stress/defect concentration and (V) macro-stress within each of the sublayers was characterized and could be attributed to various and time-dependent growth mechanisms, as well as the corresponding deposition conditions.

Complementary analysis by electron microscopy and CS-nXRD using in-situ sample environments for mechanical and/or thermal loading further enhances the analytical potential and various examples illustrating these method's possibilities will be presented.

Keywords
nanodiffraction
synchrotron XRD
residual stress
Nano-structural control of carbon-based thin films by PECVD and their surface modification

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Catalyst-free growth of carbon nanomaterials were performed by microwave plasma-enhanced chemical vapor deposition using CO as a carbon source gas. The effect of CO: H$_2$ and CO: O$_2$ ratio on the morphology of carbon films is investigated. Without an addition of hydrogen, vertically aligned CNFs were synthesized. At lower H$_2$: CO ratio carbon nanowalls were synthesized, while polycrystalline diamond films were deposited with much higher H$_2$: CO ratio. We have also investigated the effect of electric field on the structure of carbon nanomaterials and the well-parallelized carbon nanowalls were successfully synthesized by the addition of strong electric field near the substrate. We were able to parallelize CNWs with comb-shaped multi-wire-type electrode which creates electric fields to control the shape and angle of CNWs. However, when we insert the parallelizing electrode into microwave plasma zone in the waveguide position, sparking on the electrode occurs and easily metal electrodes are severely damaged. To avoid the sparking on the electrode, we inserted the parallelizing electrode with substrate into the discharge tube slightly down flow area from the wave guide position. The plasma density of this position is originally too weak to synthesize CNWs. Thus, we additionally applied the magnetic field in the microwave plasma to create dese ECR plasma. We set the resonance point outside of waveguide zone and inserted the parallelizing electrode into the resonance zone in the down flow of waveguide zone. We have investigated the effect of shapes, sizes, and location of parallelizing electrodes. We tested two types of electrode system, contacting and non-contacting electrode system. The possible mechanism for controlling the nanostructure of carbon nanomaterials is discussed. We have also studied to fabricate composite thin films by coating the carbon nanowalls layer with metal oxides and their electrochemical property was analyzed.

Keywords
PECVD
nanostructure
nanocarbon
carbon nanowall
ECR plasma
Plasma parameters measurement of microwave surfatron discharge applied in new plasma-enhanced-ALD

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In the last decades the atomic layer deposition (ALD) has proven to be almost an irreplaceable technique in many technological steps, widening both its principal variations and possible applications. Preparation of ultra-thin films or 3D objects in a nanoscale is a key task in development of cutting-edge microelectronics, optoelectronics or catalytic technologies. This necessitate deposition of thin films of a high uniformity in both vertical and horizontal direction. The leading technological companies sees the plasma-enhanced(PE)-ALD as potent solution for achieving lower temperatures and higher speed of deposition.

In this work we utilized a Langmuir probe for two-dimmensional measuring of plasma density, electron temperature and plasma potential of a microwave surfatron plasma for development and implementation of plasma ALD system for low-temperature deposition of thin dielectric films with possibility of application of the atomic layer etching (ALEt). We investigated the plasma parameters for various combinations of surfatron nozzle geometry, gas pressure in a chamber, gas flow and gas mixture. We studied the possibilities of deployment of the multi-nozzle systems for achieving a sufficient level of homogenization of the plasma parameters, leading to production of a large area homogenous ALD thin films for industrial application. Obtained results proved that radial homogeneity of the plasma density can be improved when lower mass flow rate of working gas is used. On the other hand, for higher pressure in the chamber the plasma density rapidly decreased in axial distance from the nozzle outlet.

The authors appreciate the financial support of Technology Agency of the Czech Republic nr. TF03000025.

Keywords
microwave surfatron
ALD
plasma density
electron temperature
Langmuir probe
**Time resolved tunable diode-laser induced fluorescence measurements of titanium neutral atoms sputtered in reactive Ar/N2 HiPIMS discharge**

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This work is dedicated to study the transport behavior of the Ti neutral atoms sputtered in reactive high power impulse magnetron sputtering (R-HiPIMS) device used for TiN coating deposition which is interesting in many industrial applications. Time resolved tunable diode-laser induced fluorescence TR-TDLIF ($\lambda_0=398.17$ nm) measurements were performed to probe the atoms velocity distribution functions. Several parameters such as pressure, target-probe volume distance and gas mixture (Ar/N$_2$) have been investigated, at fixed discharge power (350 W.cm$^{-2}$) and discharge time ($T_d=10$ µs, $f=1$ kHz). It was found that the TR-TDLIF signal has to be fitted using three Gaussian distributions. They correspond to the energetic (EN), thermalized (TH) and quasi-thermalized (TH$_{GV}$ : TH atoms with a group velocity) atoms populations. From the fitting, deposited fluxes and energies were estimated and in order to obtain local quantitative measurements, the TR-TDLIF signal was calibrated using laser absorption spectroscopy. The measurements, performed at 20 mTorr and 3 cm from the target, indicate that the metallic Ti target undergo a strong nitridation process (transition from metallic mode to compound mode) after inserting only 1% of N$_2$ in the gas mixture. This is inferred from the reduction of the impulse flux values of EN, TH and TH$_{GV}$ sputtered atoms that have been found to be respectively 1, 2 and 0.6 ($*10^9$.part.cm$^{-2}$) in the case of 1% N$_2$ compared to the corresponding values 4.3, 8.5 and 2.5 ($*10^9$.part.cm$^{-2}$) in the case of pure Ar. From the energy point of view, at 5 mTorr and 5 cm, it was detected that the mean energies of EN and TH$_{GV}$ atoms decrease drastically in the temporal post-discharge from 8.5 eV and 0.5 eV to 1 eV and 0.2 eV, respectively. Furthermore, the TiN coatings have been analyzed by several means (like SEM, XRD and EDS) and correlations with the TR-TDLIF results have been investigated in order to understand the underline physics of sputtering and atoms transport behaviors, and to study their influences on TiN coating properties. In the same line, a comparative study with reactive direct current magnetron sputtering process (R-dcMS) has been performed.

**Keywords**
HiPIMS, Reactive sputtering (Nitrogen), LIF, Diode laser
Simultaneous determination of sheath parameters in an rf-plasma by common and non-conventional diagnostics

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For a better understanding of the plasma-wall interaction in a capacitively coupled rf-plasma the combination of different diagnostics is used to determine energy flux to the surface, ion energies bombarding the surface and forces acting on the surface in dependence on different plasma conditions. For the determination of the plasma conditions such as electron density and temperature in addition to plasma and floating potential, a Langmuir probe with rf-compensation is used. A specially designed setup of two parallel electrodes with integrated probes are installed in the reactor. The lower electrode is driven by a 13.56 MHz rf-voltage. The upper grounded electrode has different openings in which a passive thermal probe (ptp), a retarding field analyser (rfa) and a force probe (fp) are embedded, respectively. Their surfaces are parallel to the surface of the upper electrode.

The ptp allows the measurement of the overall heat flux to its surface, the rfa determines the ion energies coming to the surface via a scanning grid and the force probe measures the force exerted on the surface by the plasma species. The setup of the four diagnostics allows a simultaneous investigation of energy and particle transport governing the sheath of an rf-plasma.

Keywords
sheath
diagnostics
non-conventional
plasma-wall-interaction
Dual rotatable magnetron sputtering sources are state of the art in large area coating technology and are nowadays also being used for deposition of precision interference coatings. For the latter, a precise uniformity control on flat as well as on curved moving substrates is mandatory. The design of optimized deposition setups including uniformity masks and specialized substrate holders usually requires time consuming experimental iterations. Thus, a simulation tool capable of predicting the film thickness distribution and optimizing the geometrical setup is desirable.

Based on known erosion profiles on the sputter targets, the angularly resolved particle flux profile close to the substrate can be obtained via Direct Simulation Monte Carlo (DSMC) method. This enables subsequent computation of the film thickness profile on curved substrates in different positions. However, in a bipolar pulse magnetron discharge a uniform plasma density distribution cannot always be presumed and a proper determination of the sputter erosion profiles is not trivial.

In order to get a more detailed picture on possible plasma non-uniformities in dual cylindrical magnetron discharges, we present 3D Particle-in-Cell Monte-Carlo (PIC-MC) simulations of the plasma discharge in Argon. Due to numerical constraints, the PIC-MC simulations are performed at lower plasma density compared to real discharges but nevertheless represent the relative plasma density profile in a reasonable approximation. The impact of different parameters such as total pressure, magnet tilting angle and electrical pulse shape on the plasma distribution is shown, and the results are compared with experimental findings.

Keywords
plasma modelling
magnetron sputtering
bipolar pulsing
OR2305

**Numerical Simulation of the Gas Flow in a PECVD Reactor**

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PECVD processes are often optimized empirically by adjusting parameters like power, pressure and gas flow rates. This work shows how numerical models can be applied to complement experimental investigations and to obtain a detailed understanding of the processes taking place in a RF plasma device. Besides the complex chemical processes determining the growth and the composition of deposited films, special attention should be paid to the gas flow. Since its properties influence pressure and residence time of the reactive species at the interface between gas volume and surface of the substrate, it is crucial to analyse and adapt the gas flow to improve the deposition process.

The main objective is to adjust the gas management in a way so that uniform gas flow conditions all over the substrate can be realized in order to achieve a homogeneous film growth over a large area. Depending on the considered pressure and the dimension of the geometry, the necessity for an appropriate theoretical description of the gas flow is discussed (continuum flow vs. molecular flow). A numerical model is then presented which describes a laminar continuum gas flow. It is shown how geometrical characteristics of the plasma device and variations of the gas flow rate cause local pressure changes which in turn affect the residence time of the gas on the substrate surface. These parameters are compared with experimentally obtained spatial profiles of the film thickness to set a benchmark for subsequent simulations. The attained information about the influence of the gas flow on the deposition rate is used to further optimize the geometry of the plasma device including the gas management and the positioning of the substrate. To that end, variations of geometrical parameters are carried out in the simulation model in order to identify optimal deposition conditions.

**Keywords**

numerical simulation
CFD
PECVD
capacitively coupled plasma
modelling
In the present study, efficient metal-ion-irradiation during film growth, and at the same time, reduction of gas ions irradiation, is demonstrated for high-power impulse magnetron sputtering (HiPIMS) by the use of synchronized, but delayed, pulsed substrate bias. In this way, the growth of high-quality polycrystalline W thin films at low substrate temperature (unheated) is demonstrated for both Ar and Kr atmospheres. The time evolution of ion and excited neutral densities in the pulsed sputtering process was characterized by the use of optical emission spectroscopy (OES) measurements. Here, the HiPIMS conditions used were a peak current density of 0.8 A/cm\(^2\) a pulse width of 100 μs, and a frequency of 100 Hz. Based on the OES investigations, time delays of the negative substrate bias pulse of 50 V were selected to 30, 60, 90 and 120 μs. X-ray diffraction and scanning electron microscopy analyses revealed that the as-deposited W films consist of the alpha-phase with a preferred orientation of (110) and with a grain size ranging from 100-120 nm for the Ar process. In particular, with the delay time of 60 and 90 μs, higher crystallinity was confirmed in comparison with the other delay time conditions. Room-temperature electrical resistivity measured by four-point probe method could be correlated to the microstructural properties, which shows the lowest resistivity of 33.1 μΩ cm for a delay time of 60 μs. For the Kr process an even better results were obtained with larger grains (250 nm) and lower resistivity (14.2 μΩ cm).

**Keywords**
HiPIMS
synchronized pulsed substrate bias
tungsten
electric resistivity
optical emission spectroscopy
Controlled reactive HiPIMS – effective technique for low-temperature deposition of functional oxide films

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Reactive high-power impulse magnetron sputtering (HiPIMS) with a feedback pulsed $O_2$ flow control and to-substrate $O_2$ injection into a high-density plasma in front of the sputtered metal (Hf or V) target was used for high-rate deposition (up to 230 nm/min) of densified, highly optically transparent, stoichiometric HfO$_2$ films onto floating substrates at the substrate temperatures $T_s$ below 140 °C, and for low-temperature ($T_s = 300$ °C) deposition of VO$_2$ films with a pronounced semiconductor-to-metal transition onto conventional soda-lime glass substrates without any substrate bias voltage and without any interlayer. The HfO$_2$ depositions were performed using a strongly unbalanced magnetron with a planar Hf target of 100 mm diameter in argon-oxygen gas mixtures at the argon pressure of 2 Pa. The deposition-averaged target power density was close to 30 Wcm$^{-2}$ at a fixed repetition frequency of 500 Hz. The voltage pulse duration ranged from 50 µs to 200 µs (duty cycle from 2.5% to 10%). The target-to-substrate distance was 100 mm. The HfO$_2$ films were nanocrystalline with a dominant monoclinic phase. They exhibited a hardness of 18 GPa, a refractive index of 2.12 and an extinction coefficient of $5\times10^{-4}$ at the wavelength of 550 nm. The high deposition rates of the films are explained using a simplified formula and model calculations. The VO$_2$ depositions were performed using an unbalanced magnetron with a planar V target of 50.8 mm diameter in argon-oxygen gas mixtures at the argon pressure of 1 Pa. The deposition-averaged target power density was close to 13 Wcm$^{-2}$ at a fixed duty cycle of 1% with a peak target power density up to 5 kWcm$^{-2}$ during voltage pulses ranged from 40 µs to 100 µs. A high modulation of the transmittance at 2500 nm (between 51% and 8% at the film thickness of 88 nm) and the electrical resistivity (changed 350 times) at the transition temperature $T_r = 56$-57 °C was achieved for the VO$_2$ films synthesized using 50 µs voltage pulses when the crystallization of the thermochromic phase was supported by the high-energy (up to 50 eV relative to ground potential) ions.

Keywords
Controlled reactive HiPIMS
Optically transparent HfO2
Thermochromic VO2
Comparison of atmospheric pressure radio frequency plasma slit-jet with glide arc

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Non-thermal atmospheric pressure plasma jets represent a simple versatile technology for the modification of material nanostructure and surface chemistry. We have compared, by plasma diagnostics and analysis of plasma-modified polypropylene, two different atmospheric pressure plasma jets, a novel radio frequency (RF) plasma slit-jet with the plasma width of 150 mm (scalable to 300 mm) operating in argon and the commercial glide arc jet (plasma width of 10 mm) from SurfaceTreat operating at 50 Hz in flowing air. Both systems were studied also with additives, gaseous or volatile compounds, enabling to tune the conditions of plasma treatment or plasma enhanced chemical vapor deposition (PECVD). Optical emission spectroscopy revealed that glide arc system was producing much more dissociated reactants and the plasma treatment of polypropylene in dry air or with additives like ethanol or isopropanol produced surfaces with more functional groups. The advantage of the RF plasma slit-jet can be seen in its larger width, a better treatment uniformity and less dissociated added compounds, i.e. higher retention of the precursor structure in the case of PECVD.

Keywords
plasma jets
atmospheric pressure
plasma treatment
PECVD
OES
Controlling plasma properties of reactive HIPIMS process using novel combined control technique

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While reactive HIPIMS processes are more and more adapted in industrial plasma applications, the need for reliable and stable control techniques becomes more important for effective production. In HIPIMS plasmas the degree of ionization is one main factor for layer density while layer stoichiometry is ruled by the plasma composition of metal and reactive gas species. Changing either parameter will affect also the other parameter. Thus, controlling both degree of ionization as well as stoichiometry simultaneously can only be realized by combining different measuring and controlling methods.

In standard reactive sputtering processes the plasma stoichiometry is determined by the reactive gas flow and spectroscopic plasma monitoring of emission lines of metals and reactive gas is commonly used to monitor and control the composition of plasma species. This works well for applications where the degree of ionization plays a minor role, however, at higher ion densities the emission lines are affected considerably by the degree ionization which is the case in HIPIMS plasma. A deconvolution of the impact of these effect to the emission lines is quite complex by using only spectroscopic plasma monitoring technique. Thus, a second measurement method is required to provide an additional indicator for the parameters.

By combining the measurement of peak current and peak voltage with the spectroscopic plasma monitoring technique and implementing a common evaluation and control algorithm, a reliable and stable process control of both plasma parameter can be realized in HIPIMS applications.

Examples of Al₂O₃ and TiO₂ applications showing the novel combined control technique are presented and discussed.

Keywords
reactive HIPIMS
process control
plasma monitoring
pulsed plasmas
HIPIMS-Deposited Nanoscale Multilayer Coatings to Improve the Quality of Friction Stir Welds in Aluminium Alloys

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Friction stir welding (FSW) is a joining technology whereby the two counterparts are mechanically intermixed by a probe which is plunged and rotated into the solid material. The appearance of the welds is improved significantly if material flow to the periphery of the probe is constricted using a stationary non-rotating shoulder. However, due to the extreme forces required to rotate through a solid piece, the material of the joint is brought close to the melting point and reacts aggressively with the shoulder material and builds up causing a rough surface finish and fast wear of the probe.

In this work, coating formulations have been tested on H13 probes and shoulders in order to reduce the friction coefficient and hinder reactions with the shoulder material, reduce sticking and improve the surface finish of the weld. High Power Impulse Magnetron Sputtering (HIPIMS) was used to produce TiAlN/VN nanoscale multilayer coatings with an engineered interface to provide good adhesion to the substrate and a smooth surface of the coating. The tests extended to DLC produced by a plasma-enhanced chemical vapour deposition process (PACVD), AlTiN by pulsed cathodic arc evaporation, TiB₂ by chemical vapour deposition (CVD) and TiBN by CVD. The best weld finish was found for TiAlN/VN and DLC coatings with low weld roughness and limited buildup on the shoulder. The lowest wear on the probe was found for AlTiN, TiB₂ and TiAlN/VN. The wear initiated at the sharp edges of the probe.

The microstructure, texture, hardness and wear rates of the coatings are discussed. There was no intermixing zone between the coating and the workpiece material. The performance in weld tests correlated well with high-temperature tribological performance both in air and vacuum.

Keywords
HIPIMS
friction stir welding
microstructure
**Tuning the HiPIMS sputtering process of C target for the deposition of DLC coatings**

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The use of HiPIMS technology for a variety of applications is continually expanding in the last decades. The higher flux of ionized particles reaching the substrate and the ability to tune their energy represent major advantages, differentiating the HiPIMS process from classical magnetron sputtering. In this contribution we present experimental results on the development of C sputtering process using HiPIMS, aiming for the deposition of dense, thick and well adherent DLC coatings. The process optimization and tuning of the ion flux to the substrate is achieved by using a few key parameters, aiming to improve the stability of the process and increase the deposition rate. The first type of parameters refer to the pulse characteristics where the peak voltage and peak current are used for controlling the type of sputtering regime and the pulse width for controlling the stability of the process. The second type of parameters are related to the gas composition, using Ar and a mixture of Ar/Ne as sputtering gases, use of Ne being known to produce higher electron temperature and deliver correspondingly higher ionization degree. Moreover, the reactive version of the process using both C₂H₂ and CH₄ as gas precursors is also investigated for DLC deposition. The use of these parameters enables the tuning of the process in a wide process interval, going from low current DC-like sputtering, passing through transitory regimes prone to instabilities, to finally reach stable high power sputtering in usually narrow process intervals and being bounded by a micro-arcing regime. Typical DLC coating properties for selected conditions will also be presented, establishing a link between process conditions and film properties.

This work was supported by M-ERA Net project TANDEM through the Romanian Ministry of Research and Innovation, UEFISCDI, project No 56/2016, and National CORE Project 2018.

**Keywords**
carbon sputtering
high power impulse magnetron sputtering (HiPIMS)
diamond like carbon (DLC)
HiPIMS voltage reversal: widening the process window - tailoring the coating properties.

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HIPIMS (High Power Impulse Magnetron Sputtering) is a magnetron sputtering technology devoted to produce thin film coatings with enhanced properties. The technology offers advantages such as enhanced ionization that gives rise to denser coatings, higher hardness values and smoother surfaces. This paper presents studies of the role the HIPIMS discharge, as well as an added positive voltage reversal pulse right after the negative HIPIMS pulse, have on coating properties and productivity in industrial applications.

The instant advantage is that the magnetron surface will be immediately discharged, which will reduce the tendency to arcing. However, there are several other effects observed, such as enhanced high energetic positive ion bombardment towards the substrate. Measurements of the deposition rate, coating hardness and crystallinity have been performed for different metallic coatings (Ti, Al) as well as nitrides (TiN) and oxides (TiO₂) deposited in reactive mode and more recently the effects that HIPIMS and positive voltage reversal plays on DLC coatings, in terms of adhesion as well as the functional layer.

Keywords
hipims
positive pulses
hard coatings
ionized
Tuning the ion energy by bipolar HiPIMS to control of the Mg thin film microstructure

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High power impulse magnetron sputtering is a method renowned for the high ionization degree of the sputtered metal atoms. Traditionally, a high negative voltage pulse is applied and is followed by a long off time. Eventually, the energy of the bombarding metal ions is controlled during unipolar HiPIMS by applying a negative bias voltage on the substrate.

In this work, we use a power supply capable of applying a positive pulse after the negative one to control the ion energy, or stated differently bipolar HiPIMS as a tool to control the ion energy is studied. Both the influence of the delay time between the negative and positive pulses as well as the applied positive voltage is investigated by means of energy- and time-resolved mass spectrometry located at the substrate position. It is found that applying the positive voltage allows to significantly increase the energy of the bombarding ions. The observed changes as compared to a classic HiPIMS pulse can be successfully described. The technique is used to deposit Mg thin films. Film microstructure and texture were measured by X-Ray diffraction (XRD) and scanning electron microscopy (SEM). The film texture changes from random to a (002) fiber texture with increasing the positive pulse amplitude while a clear change of the surface morphology is observed. To benchmark these results, a comparison is made with conventional DC magnetron sputtering and unipolar HiPIMS.

\textbf{Keywords}

HiPIMS
Mg
thin films
microstructure
mass spectrometry
Characterisation of magnetron sputtered SnZnOx by means of spectroscopic ellipsometry

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Transparent conductive oxide (TCO) films are a vital part of a large part of modern technology. The production of TCO materials has sparked much development in plasma coating technology. Quality control measurements of these layers are therefore important in many fields of optics and electronics such as high efficiency thin film photovoltaics. In this presentation, we report on optical measurements of ZnSnOx layers generated by DC/RF magnetron plasma co-sputtering. By changing the respective power on two different targets, the overall power, the gas composition and post-treatment, the properties of this type of layers can be varied in a number of parameters. The optical, electrical, and chemical properties of TCO layers are the technically most important properties together with the layer thickness. The dielectric function of layers is accessible by means of spectroscopic ellipsometry, which also yields the very important value for the layer thickness at the same time. It would be a significant step forward in quality control to use this non-destructive method also as a fast test for electrical properties. Therefore, we report on the optical properties connected to the production parameters, and also on our preliminary results connecting the optical dielectric function (in the visible and near infra-red) to the electrical conductivity of the layers. We discuss the effect of deposition parameters on the optical properties of the layers and present an approach for correlating optical and electrical properties. Further, we discuss the question of accuracy of optical properties gained from model-fit-based optical methods and the use of different parameterised models for the dielectric function to achieve this.

\textbf{Keywords}
Mixed Oxides
TCO
Quality Control
Ellipsometry
Optical Constants
In-situ micromechanical testing reveals the influence of droplets on mechanical properties of a multi-layered AlCrN/AlCrSiN arc-evaporated coating in as-deposited and annealed state

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Experimental determination of mechanical properties is a key task for the development of nanostructured functional materials. It is also essential to understand the behaviour of these materials upon thermal loading in terms of the evolution of metastable phases, microstructure and mechanical properties. Recently, in-situ micro-cantilever bending tests have been established for the mechanical testing of magnetron sputtered coatings. In the case of arc-evaporation, a possible influence of macro-defects on the mechanical properties of the coatings is of demanding scientific interest. In this contribution, a multi-layered arc evaporated hard protective coating composed of equally thin hexagonal AlCrN and metastable cubic AlCrSiN sublayers, with a bilayer period of ~65 nm, was investigated using micromechanical bending tests in a scanning electron microscope (SEM) in the as-deposited state and after annealing at 1100°C. SEM on the cross sections of the coating before and after annealing showed a stable multi-layered architecture, whereas the bilayer period increased after annealing to ~73 nm, which is associated with the phase decomposition of the metastable constituents. Young’s modulus E, fracture stress σ_F and fracture toughness K_{IC} were evaluated by bending of focused ion beam milled micro-cantilevers, both in as-deposited and annealed states. The measured properties indicated that elastic properties (E) change during annealing due to the phase transformation, whereas fracture properties (σ_F, K_{IC}) are nearly unaffected. Furthermore, a set of micro-cantilevers including macrodefects was prepared and investigated, where a reduction of elastic and fracture properties of ~40% was revealed. In summary, the micro-cantilever bending method, already known for the testing of magnetron sputtered coatings, was, for the first time, successfully applied for testing of arc-evaporated protective coatings, providing information on the influence of macrodefects on the coating’s mechanical properties.

Keywords
AlCrN
micromechanical testing
droplet influence
Multiscale elemental analysis of buried interfaces in multilayered structures

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Elemental analysis of buried interfaces in multilayered structures (for instances conversion layers under organic coatings or hybrid organic/inorganic solar cells) and encapsulated materials is extremely challenging. Two analytical techniques offering quick insight into materials – Micro XRF and Glow Discharge Optical Emission Spectrometry - can help to optimize and control the manufacturing process and understand failure causes.

Micro XRF offering both transmission and fluorescence images directly permits to measure encapsulated electronic components without preparation as the probing beam consists of X Rays that could penetrate deeply in polymers, and not electrons. At the same time the lateral resolution of micro XRF can be as good as 10µm but depth resolution is limited.

On the other hand Glow Discharge Optical Emission Spectrometry relies on a plasma to sputter the material of interest and excite the sputtered species offering fast elemental depth profiles. The technique measures all elements (including H, Li, C, O, N) with nanometre depth resolution but it has no lateral resolution. Ultra Fast Sputtering of organic layers is achieved by adapting the plasma gas nicely revealing embedded layers. Synergies and complementarities of the techniques will be described and examples of applications presented.

Keywords
GDOES
µ XRF
buried interfaces
elemental analysis
lateral and depth resolution
A MEMS nanoindentation system for quantitative nanomechanical characterization of soft materials

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A MEMS-based nanomechanical measurement system for quantitative nanomechanical characterization of soft materials with low uncertainty is hereby presented with the aim of bridging the capabilities of nanoindentation instruments and those of AFMs. The MEMS nanoindenter is developed on basis of an electrostatic comb-drive actuator, featuring a force resolution better than sub-nN and a maximum indentation depth of up to 10 µm. For material testing, a Berkovich-like indenter tip directly is formed out of the end of the transducer’s main shaft by means of focused ion beam (FIB) fabrication.

Quantitative approaches for the characterization of the MEMS nanoindenter are explained in detail. Nanomechanical measurements of typical soft materials using this MEMS nanoindenter are reported in the manuscript.

Keywords
- micro-electro-mechanical system
- soft materials
- nanoindentation
- nanomechanical characterisation
Microstructural characterization of plasma nitrided γ and γ’ phases in nickel-based superalloys

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Nickel-based superalloys are used in extreme conditions and nitriding is investigated as a way to improve their properties. In previous works, nitriding at moderate temperature (400°C) was performed in a RF plasma based reactor at the floating potential on various Ni-based superalloys to determine the specific nitriding behavior of γ/γ’ phases and the role of microstructural parameters such as grain size, crystallographic orientation, volume fraction of γ’ or chemical compositions. It was shown that plasma nitriding leads to the incorporation of nitrogen in γ with the formation of expanded austenite, known as the S-phase or γN, with around 25% at. of N in solid solution, as well as nitrides (CrN). Regarding the γ’ precipitates, incorporation of nitrogen is strongly dependent on its composition and higher Ti/Al ratio results in deeper N diffusion. The present study has been conducted to provide more information, at the submicrometric/nanometric scale, about the chemical and structural modifications of the γ/γ’ phases induced by nitriding. Scanning and transmission electron microscopy (combined with EDS, EELS and EFTEM), as well as tomographic atom probe characterizations have been performed on two representative superalloys: Udimet 720Li and single crystal MC2. Inhomogeneous distribution of N has been revealed in the γ matrix and γ’ precipitates. Nitrided γ matrix is composed of coherent γN, CrN precipitates and a third FCC phase resulting from the decomposition of the expanded austenite associated with N and Cr depletion. In nitrided γ’, formation of the expanded phase was not observed but coherent nanometric nitrides were evidenced as well as larger precipitates at the surface resulting from Ni extrusion when N is incorporated in γ’. Further investigations are performed to identify the nitrides in γ’ which could differ depending on the superalloy studied (TiN, AlN, …)

Keywords
Plasma nitriding
Ni-based superalloys
Transmission electron microscopy
Coatings used in tribological applications often exhibit high hardness and stiffness to achieve a high wear resistance. One film characterization method frequently used is nanoindentation which allows the determination of indentation hardness and indentation modulus among other material properties. The indentation modulus describes the elastic surface behavior during indentation and for coating characterization is mostly relevant due to its indication of wear resistance. To obtain the true indentation modulus of a coating, the indentation modulus of the coated sample must be measured with varying load and then extrapolated to zero load. Current recommendation of the standard ISO 14577-4:2016 is a linear extrapolation, which fits poorly for non-linear curves. Such curves are commonly found for hard coatings on soft substrates, for example steel substrates with superhard tetrahedral amorphous carbon coating (ta-C).

In this study we present a new empirical fit model named "sigmoid". This fit model is compared to several existing fit models described in literature by means of goodness of fit and stability of fit, using nanoindentation measurements on ta-C coatings with wide ranges of indentation modulus and coating thickness. This is done by employing a user-independent and model agnostic fitting methodology. It is shown that the sigmoid model outperforms all other models in both goodness of fit and stability of fit. Furthermore we demonstrate that the sigmoid model's fit parameter directly correlates with coating thickness and thus allows for a new approach of determining ta-C coating thickness from nanoindentation.

**Keywords**
Nanoindentation
DLC
ta-C
films
thickness
Influence of nanolayer thickness on the performance properties of multilayer composite nano-structured modified coatings based on nitrides of Ti, Zr, Al and Nb for carbide metal-cutting tools

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The paper considers multilayer composite nano-structured modified Ti-TiN-(Ti, Al)N, Zr-ZrN-(Zr,Al)N and ZrNb-(Zr,Nb)N-(Zr,Al,Nb)N coatings for metal-cutting tools. The coatings under the study have identical elemental composition and thickness (4 μm), but differ in the thicknesses of the nanolayers (20-100 nm). The mechanical characteristics of the coatings were studied, and the tool life tests were carried out for carbide tools with the above coatings for dry turning of steel at $v_c = 300, 350, \text{ and } 400$ m/min. A tool with a coating characterized by a lower thickness of sub-nanolayers showed the longest tool life at all cutting speeds. Microstructural studies (using SEM) of the nature of wear and failure of metal-cutting tools with the coatings under the study were conducted. The microstructural studies have shown a marked difference in the mechanisms of wear and failure for the cutting tools with coatings under the study. For the cutting tool with coatings with a smaller thickness of nanolayers (20-50 nm), at lower cutting speeds, the balanced wear is typical with the formation of small longitudinal cracks and delaminations, while at high speeds ($v_c = 400$ m/min), the brittle fracture "as a whole" with the formation of a network of longitudinal and transverse cracks is typical. The cutting tool with coatings with a greater thickness of nanolayers (60-100 nm) at a speed of $v_c = 300$ m/min already shows active delamination between nanolayers with elements of brittle fracture. At a cutting speed of $v_c = 400$ m/min, it shows extensive delamination, both between sub-nanolayers and between intermediate and wear-resistant coating layers, with separation of large segments of coating. The mechanism of wear and failure of the cutting tool with coatings with a smaller thickness of nanolayers, especially at high cutting speeds, is more favorable in terms of the overall performance of coated tools.

\textbf{Keywords}

nanolayer thickness
multilayer composite nano-structured modified coatings
metal-cutting tools
filtered cathodic vacuum-arc deposition (FCVAD)
Influence of the surface roughness on hydrophobic behaviour of Cr based coating

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The most of the recent research combine the influence of chemical composition on surface energy with convenient surface topography which should form composite interface with air pockets in the valleys between asperities. These pockets cause lowering of the real surface of contact between water and a solid in comparison with the plain projection of the wetted area, thus reducing wettability.

In general, wide spectrum of works focused on this approach often uses polymer-based nanocomposite materials. Many of these materials contain silicon and/or fluorine, since addition of these two elements further reduces wettability. However, several articles focus on hydrophobic properties of pure metallic coatings. Regarding that approach, we used magnetron sputtering method to prepare 20 µm thick coatings of pure chromium with resulting contact angle up to 107.5° (thus hydrophobic) as a model. The reason for this was to induce crystal growth resulting in specific surface roughness. Another of the tested systems was CrN/Cr showing the value of contact angle of 111°. Observation of the fracture surface of the Cr coating has proven the presence of the columnar crystals growing at the expense of their neighbors because of the prolonged deposition times. The resulting surface morphology is then formed by almost perfectly developed crystals in the shape of hexagonal pyramids providing a suitable surface roughness conditions for hydrophobicity.

The focus was to prepare convenient surface topography of the Cr coating which could serve as a substrate for additional technique altering chemical composition in order to further enhance hydrophobic properties by decreasing surface energy.

Acknowledgement: Authors acknowledge support from the ESIF, EU Operational Programme Research, Development and Education, and from the Center of Advanced Aerospace Technology (CZ.02.1.01/0.0/0.0/16_019/0000826), Faculty of Mechanical Engineering, Czech Technical University in Prague.

Keywords
chromium, coating, hydrophobic, roughness, thickness
**Growth and performance of durable smart optical coating systems obtained by energetic reactive sputter deposition**

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Optical coating (OC) applications represent a multibillion dollar market worldwide. As the range of applications of OCs continuously broadens and the need for an increased performance and versatility increases, it is becoming important to develop thin film materials with novel nanostructures based on unconventional approaches to supply them with multifunctional properties.

In our present work we investigate the growth of passive and active metal oxide coatings suitable for large area smart windows based on thermochromic and electrochromic materials, as well as on the performance enhancement of glass and plastics. Specifically, we apply low duty cycle pulsed DC magnetron sputtering (LDMS) and High Power Impulse Magnetron Sputtering (HiPIMS) in a reactive atmosphere, as well as ion bombardment during the film growth in order to obtain passive hard transparent AlN and Al₂O₃ coatings, and high-quality thermochromic VO₂ films, and durable electrochromic WO₃ systems.

We demonstrate that an appropriate control of the surface reactions offers attractive opportunities for tailoring switchable transmittance, reflectance and emissivity, as well as the mechanical, tribological and environmental durability for various applications such as advanced glazings for architectural glass, active color shifting security devices, smart radiators for the thermal control in satellites, performance of displays, and others.

**Keywords**
Electrochromic WO3, thermochromic VO2
glazing, pulsed reactive sputtering, ion bombardment
micro/nanostructure
smart windows, optical security devices, smart radiators, durability
Elaboration of thermochromic LaCoO\textsubscript{3} thin films using semi-industrial sputtering machine

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In the past, we demonstrated the feasibility of a thermochromic solar collector based on VO\textsubscript{2} and commercialized it under the name ThermProtect\textregistered. The present work concerns the elaboration and the optimization of a new generation of solar collectors based on large LaCoO\textsubscript{3} coatings. Thermochromism is the aptitude of some materials to reversibly change their electrical, optical and magnetic properties versus temperature due to structural modifications. Such change occurs at a specific temperature called metal-insulator transition temperature (T\textsubscript{MI}) and thus, thermochromic materials are IR transparent (insulator) below T\textsubscript{MI} and IR reflective (metal) above. Perovskite-type oxide LaCoO\textsubscript{3} exhibits complex and temperature dependent behavior. It is known, that LaCoO\textsubscript{3} undergoes successive spin-state transitions as a function of temperature resulting in thermochromic effect and unsharpened transition from these two states accompanied by a drastic change in emissivity which makes it an excellent candidate for passive thermal regulation applications. However, due to the structural and chemical complexity of such system, the synthesis of this material at semi-industrial scale is challenging. For this work, we investigated deposition and annealing conditions and performed structural and optical characterization of deposited coatings.

The films were synthesized on Al substrates by magnetron co-sputtering of two pure metallic targets (99.95\%) using an in-line semi-industrial coating machine especially designed for depositing on A4-size substrates. The films were deposited in elemental (ESM) and compound (CSM) sputtering modes. To obtain the perovskite structure, annealing in air of as-deposited films was performed between 500 and 580°C. The SEM topographical analysis shows that dense and homogeneous films were obtained. The annealing conditions leading to crystalline perovskite structures were confirmed using XRD analysis. The evaluation of IR emissivity variations by infrared camera clearly shows a strong increase in emissivity for temperatures higher than 200°C and the emissivity variation (Δε) reaches 50%.

Keywords
thermochromic perovskite coatings
Iron doped tetrahedral amorphous carbon thin films by filtered cathodic vacuum arc for electrochemical sensing applications

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The development of new electrode materials for in vivo and in vitro detection of neurotransmitters and active pharmaceutical ingredients, such as opioids, is becoming increasingly important. Here, pulsed filtered vacuum arc process is used to investigate the effect of iron doping in tetrahedral amorphous carbon (ta-C) thin films, to be used as electrodes in the electrochemical detection of drugs.

As of yet unreported iron-doped ta-C thin films (Fe/ta-C) are co-deposited with 2, 5 and 10 at% iron using a dual-source filtered cathodic vacuum arc process at room temperature. The versatile dual-source vacuum arc setup enables control over the metal content in the carbon or metal matrix, providing the means for the tailoring of application-specific thin films for different sensor applications. Deposited films are examined extensively using physical film characterization methods combined with electrochemical techniques.

Tetrahedral amorphous carbon thin films have been shown to perform well in these electrochemical detection applications, and although facile electron transfer has been achieved for ultrathin 7 nm thick ta-C electrodes, such films commonly suffer from pinholes on various electrode surfaces. On the other hand, thicker ta-C films can be too resistive for sensor applications. Here, even the smallest addition of 2 at% iron in 30 nm ta-C thin films is found to dramatically decrease sheet resistance and re-enable this facile electron transfer, while preserving the desired sensor properties. Overall, significant improvements to the electrical and electrochemical properties of the material are achieved by iron doping. As a result, Fe/ta-C films outperform reference ta-C films in the drug detection application.

Keywords
iron/ta-C composite
PVD
sensor
electrical
electrochemical

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In this work the transparent conductive oxides indium oxide (In$_2$O$_3$), tin oxide (SnO$_2$), titanium oxide (TiO$_2$), and zinc oxide (ZnO) are reviewed. While In$_2$O$_3$, SnO$_2$, and ZnO are already commercially used on a large scale in flat panel displays, thin film solar cells and low emissivity window glass coatings, TiO$_2$ is currently still under development. These TCO materials are n-type, wide bandgap semiconductors that can be doped up to high carrier concentrations (N > 10$^{21}$ cm$^{-3}$) making it degenerate semiconductors, i.e. metal-like. The lowest resistivities (>1·10$^{-4}$ Ωcm) are achieved with doped indium oxide, mostly doped with tin.

The maximum carrier concentrations that can be achieved in these TCOs is about the same. The significantly different resistivities of these four oxides are due to their different electron mobilities $\mu$; the highest values being reported for ITO ($\mu > 100$ cm$^2$/Vs). The physical processes, limiting the mobility at such very high carrier concentrations (>5·10$^{20}$ cm$^{-3}$) are not yet fully understood. The main scattering processes are discussed for every of the oxides.

All TCOs are highly transparent from the UV to the NIR spectral range. In the IR spectral range, depending on the carrier concentration, absorption by free electrons takes place. By using hydrogen as a dopant, indium oxide with very high electron mobility can be deposited, thus reducing the free carrier absorption in the IR.

Research and development is going on to replace In$_2$O$_3$ by ZnO, which is much cheaper (abundance $\approx$ 120 ppm). SnO$_2$ is already used on a large scale for window glass coatings and also for thin film solar cells, based on CdTe. SnO$_2$ and TiO$_2$ are chemically very resistive, a property that is still awaiting a wider application.

Keywords
transparent conductive oxides
wide bandgap semiconductors
charge carrier transport
carrier scattering
Design and high-temperature durability tests of solar-selective coatings based on aluminium titanium oxynitrides $\text{Al}_y\text{Ti}_{1-y}(\text{O}_{x}\text{N}_{1-x})$

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Aluminium titanium oxynitrides were studied as candidate materials for high temperature absorbers in solar-selective coatings (SSC) due to their excellent stability and their tuneable optical behaviour. A set of individual $\text{Al}_y\text{Ti}_{1-y}(\text{O}_{x}\text{N}_{1-x})$ layers with different oxygen content was prepared by cathodic vacuum arc (CVA) deposition. A comprehensive analysis of the sample microstructure and morphology allowed an accurate modelling of the optical constants in the whole wavelength range of solar interest (190 nm - 25 µm). The optical properties of these films can be controlled from metallic to dielectric character by adjusting the oxygen content. Complete multilayer SSC, including a TiN layer as IR reflector, were designed by applying optical simulations, obtaining excellent optical selective properties ($\alpha = 94.0\%$ and $\varepsilon_{RT} = 4.8\%$). The design concepts were validated by an excellent agreement between simulated and experimental stacking order, composition and optical properties. The durability of two multilayers was studied under conditions simulating realistic operation of central receiver power plants. Both SSC stacks were stable in single stage tests of 12 h at 650°C in air. During cyclic tests, the coarser microstructure of multilayer 1, was found to be more resistant against oxidation than multilayer 2 constituted of four oxynitride layers with a graded oxygen content. Multilayer 1 fulfilled the performance criterion of $\text{PC} \leq 5\%$ for 300 symmetric, 3 h long cycles at 600°C in air confirming that the designed SSCs are exciting candidate material for concentrated solar power applications at high temperature. Financial support by the EU, grant No. 645725, project FRIENDS$^2$, is gratefully acknowledged.

Keywords
Solar-selective coatings
CSP
Optical simulation
Thermal test
Spectral Properties and Thermal Stability of Mo/ZrSiN/ZrSiON/SiO₂ Solar Selective Absorbing Coating

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Abstract:
The Mo/ZrSiN/ZrSiON/SiO₂ solar selective absorbing coating, which can be used for photo-thermal conversion in solar absorber, is fabricated on stainless steel (SS) substrate by magnetron sputtering. The deposition parameters, composition and layer thickness are optimized experimentally. High solar absorptance of 0.95 and low thermal emittance of 0.06 are obtained in the coating. On the other hand, it also exhibits an excellent thermal stability up to 600 °C both in vacuum and air. The evolution of the structure, surface morphology and optical properties of the coating with temperature are carried out using XRD, AFM, spectroscopy, etc. The elemental diffusion at the interface of the multilayer films after aging at 700 °C for 100 h is analyzed by Rutherford backscattering spectroscopy (RBS). The results show that this coating can be a good candidate for concentrated solar power (CSP) project in high temperature

Keywords
magnetron sputtering
solar selective absorbing coating
solar photo-thermal conversion
IR emissivity
thermal stability
Towards anatase promotion in Cr (co-)doped TiO2 sputtered films

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Many applications of TiO₂ partially rely on its good performance as solvent for impurities [1]. In particular, metal (cation) dopants can functionalize or enhance TiO₂ as catalyst [2], diluted magnetic semiconductor [3] or transparent conductor [4]. Special attention has been devoted to TiO₂ photoactivity where doping has been extensively studied towards band-gap narrowing to achieve visible-light (VISL) response [2]. Metal doping (Cr,Mo,V…) can increase VISL absorption but introduces severe structural distortions that additionally result in carrier recombination centers [4]. Our research seeks for processing routes to improve the structural quality of Cr (co-)doped films produced by magnetron sputtering with emphasis in phase selectivity. Namely, the promotion of anatase is preferred due to the superior photoactivity of this phase or phase mixtures with high anatase content [5]. Recently [6], we have reported the impact of non-contact flash-lamp annealing (FLA) on monolithic TiO₂(:Cr) films. By tuning the energy flux, FLA yields customized TiO₂ phases but, in doped structures, phase formation only takes place for low Cr contents (< 5 at.%) and the rutile structure is mostly favored. On the contrary, modulated film architecture has shown promising results for anatase growth [7]. In this paper, such scheme, in conjunction with FLA, is explored in detail to optimize the film structural quality and growth design.


Keywords
TimO₂
magnetron sputtering
flash-lamp-annealing
photocatalysis
Vacuum and in-air thermal stability studies of SnO$_2$-based TCO for concentrated solar power applications

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In concentrated solar power plants the receiver tubes are one of the key components for increasing the energy efficiency. Absorber materials of those tubes have to exhibit high-temperature and air stability, high optical absorption in the solar region and low thermal emittance. In state of the art central tower plants black paints (i.e. Pyromark 2500) are used as absorber material but the high emissivity of those paints leads to high radiative energy losses. Moreover, these paints undergo a temporal degradation and performance loss during the lifetime of the plant.

Here, an alternative concept for high-temperature stable solar-selective coatings is presented. It consists of a transparent conductive oxide (TCO) deposited as solar-selective transmitter on a black body absorber. For this purpose, SnO$_2$:Ta thin films were reactively sputtered on fused quartz substrates. Their vacuum and in-air stability up to 800°C were studied by in situ Rutherford backscattering spectrometry (RBS), Raman spectroscopy and spectroscopic ellipsometry (SE). The correlation between structural, optical and electric transport properties was analyzed by RBS, SE, UV-VIS spectrometry, and Hall Effect measurements. Solar selective properties are demonstrated as proof of concept for the TCO deposited on a silicon substrate.

Financial support by the EU, grant No. 645725, project FRIENDS$^2$, and the HGF via the W3 program (S.G.) is gratefully acknowledged.

Keywords
Sputtering
Thin Films
Nanomaterials
High-Temperature Stability
Solar Energy
In the sense of environmental sustainability, the application of ultra-stable material systems comes more and more into the focus of academia and industry. Ta-C is one of these highly attractive materials, exhibiting extreme thermal stability ($\geq 3000^\circ$C), highest hardness ($\geq 40$ GPa) and strength, accompanied by strong chemical inertness. Nevertheless, a wide use of Ta-C is intriguingly limited by its unique covalent-metallic bonding character being responsible for the relatively low ductility and strong affinity to oxygen, leading to the formation of partly volatile oxides already in the range of 400 $^\circ$C (representing $0.1 \cdot T_m$).

Therefore, we applied an ab initio guided approach (Density Functional Theory using VASP) to select alloying elements ($X = \text{Zr, Si, Al}$), which represents the best compromise between increased oxidation resistance, solubility in the preferred face-centred structure, as well as enhanced ductility (fracture toughness). In addition, the influence of carbon vacancies, which can be phase stabilizing in TMCs, is also consider. To verify our theoretical predictions, we deposited the most promising ternary $\text{Ta}_{1-y}X_y\text{C}$ compounds by non-reactive physical vapour deposition process and oxidized the coatings up to 1600 $^\circ$C. The kinetic of the oxide scale growth is investigated by HR-TEM, APT, as well as XRD.

**Keywords**

Ultra-High Temperature Coatings  
Ta-X-C  
Oxidation Resistance  
Super Hardness  
DFT
Kinetic Monte Carlo simulations of thin film growth deposited by reactive magnetron sputtering and evaluation of morphological properties of the film.

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A three dimensional kinetic Monte Carlo (kMC) model has been developed in order to simulate the growth of oxides thin film by vacuum deposition methods. The model takes into account simultaneous deposition of metallic and reactive species. Both metallic and reactive fluxes may consist of atoms as well as ions, each flux is characterized by its own energy and angular distributions.

During the simulation of deposition particles (metallic and reactive atoms and their ions) are considered to be randomly thrown towards a substrate with the velocity according to given energy and incident angle distribution functions. Metallic atoms are supposed to be attached with the sticking probability equals to 1. Sticking coefficient of reactive species depends on the local stoichiometry around the location where the reactive atom hit the film. Reactive atoms are supposed to be attached only if the local composition of the film is under stoichiometric. Effects of momentum transfer from the energetic particles to the film are also taken into account.

The presented kMC model has been applied to the growth of TiO$_2$ film deposited by a magnetron sputtering on a curved substrate. The properties of the film have been studied at different locations at the substrate. It has been showed that the morphology of the film is the function of the position on the substrate. Depending on the position the film can either exhibit tilted columnar growth or not. Also it has been shown that the roughness of the film is not uniform across the substrate but depends on the location. The simulation results have been compared with the experimental data and the good agreement between them has been found.

Keywords
kinetic Monte Carlo simulations
film growth
reactive sputter deposition
Titanium oxide
Optimisation of PVD and PECVD thin film deposition on 3D objects

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Plasma assisted deposition technologies are efficient methods for developing innovative surface functionalities and adding high value to a large range of materials. Especially magnetron sputtering and Plasma Enhanced Chemical Vapor Deposition (PECVD) are widespread techniques allowing the deposition of thin films on substrates at different scales, and with various geometries from flat to 3D shapes. Ensuring a good coating homogeneity in term of thickness and properties can become difficult when considering tridimensional objects or complex surfaces with high roughnesses such as those arising from the highly expanding additive manufacturing sector. However it is a main factor of product quality for most applications involving mechanical and tribological properties, aesthetics, corrosion resistance, optical properties … The control of thin films deposition requires then a suitable understanding of the different elements involved in the deposition process, such as substrate position and movement, gas injection, pumping, cathode specificity, and their effects on the final properties.

This study aims at a better understanding of coatings characteristics obtained from magnetron sputtering and PECVD on static and moving samples, in order to prepare the implementation of such deposition processes in a large 3D vacuum coater. It is in a preliminary step based on an experimental approach at lab scale, using a specifically designed substrate holder allowing the characterization of samples placed at different positions. Thin layers of Ti, TiO₂ and SiO₂ are characterized in term of thickness, morphology and roughness. A Numerical simulation approach is furthermore considered using NASCAM (Nano SCAlE Modelling) software for predicting some of the thin films properties.

Keywords
3D
Sputtering
PECVD
Simulation
Nondestructive Characterization of Heterogeneous Coatings Based on Ultrasonic Reflection and Scattering Mechanism

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The characterization of coatings features, such as thickness, elastic modulus, and interfacial morphology, especially in a nondestructive way, is significant to ensure manufacturing quality of coatings as well as the high performance of the components in service. However, it is still difficult to achieve an accurate nondestructive measurement of these coating features, especially for heterogeneous coatings, using conventional ultrasonic technique, due to the coupled material and geometry constrains including ultra-thin thickness, multiple interfaces, and coating material heterogeneity that cause recorded ultrasonic signals in complicated interfered, scattered, and distorted forms. In this work, a characteristic response is clarified to solve such a problem by exploring the ultrasonic reflection mechanism in coatings of four layers and three interfaces and the scattering mechanism on tiny scatterers from the heterogeneity. Using the wave-mode conversion analysis, phase-screen approximation theory, and acoustic scattering self-consistent theory, the ultrasonic reflection coefficient amplitude spectrum (URCAS) is identified as a characteristic response. Therefore, the quantitative relationships between the coating features and the URCAS can be established to derive the coating thickness, elastic modulus, interfacial roughness, and porosity from the resonant frequency, phase and amplitude of URCAS. It is demonstrated that, a novel ultrasonic small angle incidence scheme is developed by utilizing the identified characteristic response for characterizing of WC-Ni coatings thermally sprayed on steel components. The thickness measurement is less than 10% error for 300-400 μm thick coatings, in comparison with the destructive characterization on optical microscopy. The measured elastic moduli are in the range of 315-351 GPa, and the Poisson's ratios were during 0.221-0.245, in good agreement with published data. Moreover, the interfacial roughness of the coatings can be measured as decoupling the effect of the attenuation coefficient $\alpha(f)$ in the URCAS, with less than 1.4 μm absolute error and 11.0% relative error for an interface roughness of 13.1 μm.

Keywords
Heterogeneous coating; Reflection mechanism; Scattering mechanism; Ultrasonic reflection coefficient amplitude spectroscopy
Interface model and characterization for nanoscale ReB$_2$/TaN multilayers with desired modulation period and ratios: First-principles and experimental investigations

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ReB$_2$/TaN multilayers were prepared using magnetron sputtering. Extensive measurements were employed to investigate the structure and mechanical properties of the multilayers. In order to explore the properties of TaN/ReB$_2$ multilayers or nanocomposite, we calculated the structure of TaN/ReB$_2$ system by density-functional theory (DFT).

The results demonstrated that the hardness of multilayers reaches a maximum value of 38.7 GPa at $\Lambda=10$ nm and $t_{\text{ReB}_2}:t_{\text{TaN}}=1:1$ then decreases with $\Lambda$ increases or $t_{\text{ReB}_2}:t_{\text{TaN}}$ decreases further. Almost all multilayers exhibit lower residual stress than the average value of monolithic ReB$_2$ and TaN coatings. We believe that periodic insertion of TaN into ReB$_2$ layers suppresses its grain growth, which releases stress build in the ReB$_2$ layers. The interfacial stability of a system can be measured by its adsorption energy. The higher the interfacial energy is, the more stable the interfacial structure will be. The adsorption energy of B-Ta interface is higher than that of others. So the results showed that the B-Ta interface was the most stable interface. Microstructure evolutions in ReB$_2$/TaN multilayers are carefully investigated by differing modulation periods and modulation ratios. Clear coherent interface structure forms between epitaxial layers at the optimal modulation period of 10 nm, modulation ratio of 1:1. The fine nanocrystallities with small grain sizes are also kept stably in individual layers at the optimal modulation condition.

Keywords
ReB$_2$/TaN multilayer
magnetron sputtering
density functional theory
interfacial stability
modulation
Characterization of a-SiC:H thin films prepared by PECVD from the point of adhesion

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Thin films characterization from the point of adhesion is mainly done by nanoscratch test. Possibilities of application can be determined by adhesion between substrate and thin film prepared e.g. PVD or CVD. In this case, adhesion of thin films of amorphous hydrogenated silicon carbide (a-SiC:H) to the silicon wafer substrate was studied. Industrial applications of this research could be in the field of composites without interface and protective coatings. Thin films were deposited from pure tetravinylsilane monomer (TVS) by plasma-enhanced chemical vapor deposition (PECVD). The substrates were pretreated with argon plasma (10 sccm, 5.7 Pa, 5-200 W) using continuous wave for 10 min to clean the surface from adsorbed gases and reach reproducible adhesion of thin films. Plasma depositions of films were done in two regimes - pulsed plasma and continuous wave (3.8 sccm, 2.7 Pa). Range of the power during the depositions was between 2 and 150 W for pulsed plasma and 10 and 70 W for continuous wave. Prepared films were evaluated by nanoscratch test with maximum peak load up to 10 mN and the length of 10 μm. Scratch testing was done by diamond indentor (90 °) with radius 1 μm. One thickness series and two power series were tested. The thickness series deposited at a constant power of 2 W shown that values of critical load linearly increased from 1.3 mN to 9.2 mN with increasing thickness in range 33 nm – 666 nm. Because of this fact, the thickness of the film from power series was around 100 nm. We revealed for pulsed plasma that the critical load increased with enhanced power from 1.6 mN (2 W) up to 4.6 mN (75 W) and it was invariable for higher power, i.e., 4.4 mN (150 W). The samples which were prepared in continuous wave shown also increasing trend from 1.8 mN (10 W) up to 4.0 mN (50 W) and 3.9 mN for 70 W. It means that higher values of critical load are for continuous wave in range 20 W – 50 W and 75 W and 150 W for films prepared by pulsed plasma. The adhesion of the films was observed for 1500 days without aging effect.

Keywords
adhesion
scratch test
PECVD
thin films
Computational study of pulsed depositions of metal films

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When depositing metal films on dielectric substrates, a three-dimensional growth occurs. The complete mechanism involves a number of atomic scale parameters, the basic being substrate temperature and deposition rate. Besides them the kinetic energies of impinging atoms, state of the substrate and the duration of the evaporation process are important physical parameters. This idea of variable deposition times is applied in the pulsed laser deposition and pulsed plasma deposition technologies. The type of deposition technique influences profoundly the composition and energies of impinging particles.

For the study of initial growth stages the combination of experimental and computational approaches is very useful. The contribution is devoted to the analysis of main physical processes taking place during nucleation and early stages of film growth. For this purpose two methods of computational physics were applied - atomistic computer simulation and image processing of micrographs of resulting films.

In the atomistic modelling of metal film growth the combination of two techniques was used: the nucleation process and the initial island growth were simulated by the molecular dynamics approach, while the simulation of further growth stages was performed by the kinetic Monte Carlo method. The combined molecular dynamics & kinetic Monte Carlo approaches were used both for the preparation of simulated structures and for their analysis. The further approach of computational physics was the image analysis, applied both on the results of simulation and on experimental data. The main purpose of this study was to analyse the influence of basic mechanisms of the initial stages of film growth in both continuous and pulsed regimes. The main differences in laser deposition or vacuum evaporation and plasma deposition techniques are included into the molecular dynamics part of the complete atomistic model.

Keywords
pulsed plasma deposition
pulsed laser deposition
atomistic computer modelling
image processing
Monte Carlo simulations of charge transport and strain sensing properties of co-sputter deposited granular metal thin films

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Thin films made by sputter-depositing metal and ceramic materials have a large resistivity and high strain sensitivity with large transverse sensitivity. We develop a model based on sphere packings to investigate the influence of the disorder of diameters and distances on the piezoresistive properties. Several ceramic-metal (cermet) films are fabricated, e.g. films of platinum and aluminum oxide or platinum and boron nitride. Their resistivities vary over many orders of magnitude. Strain sensitivity is in the range of 5 to 25. Their sensitivity to transverse strain is typically 70 % of the longitudinal sensitivity. Using x-ray diffraction and transmission electron microscopy, it is found that the films consist of roughly spherical metal crystallites with a mean size of a few nanometers, separated by the amorphous ceramic. A model for the composite materials is build based on morphology and analytical descriptions of charge transport. The latter is characterized by thermally activated electron tunneling and a Coulomb blockade due to the small crystallite size. For a simulation of the system's global transport characteristics, a representation of the disordered array of nanocrystallites (NCs) with a certain size distribution is required. Sphere packing algorithms are utilized to create randomly arranged 3D structures with spherical NCs of a defined size distribution with a defined distribution of next-neighbor distances. Due to the random disorder, charge transport does not occur straight through the film, but along convoluted paths. Total conductivity if found by evaluating all next-neighbor conductivities; conductivity in unstrained and strained states leads to gauge factors. Systems with various sizes, distributions and values of metal content are simulated and compared to the measurements. The elastic moduli of the components and the particle sizes have a large effect on the gauge factor. It is found that the achievable maximum of the gauge factor is reduced by disorder in the film.

Keywords
cermet
granular metal
piezoresistivity
Reduced atomic shadowing in HiPIMS: role of the thermalized metal ions

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Traditionally, the most influential deposition parameters regarding both bombardment and shadowing effect in magnetron sputtering-based deposition processes are the deposition pressure and substrate biasing. Decreasing the process pressure results in an increased discharge voltage and less collisions with gas atoms and molecules and thus it increases the average energy of the sputtered species. On the other hand, the high-angle component of the angular distribution of the impinging species also decreases thus weakening of the shadowing effect. Substrate biasing allows us to bombard the growing film with ions extracted from the plasma with an energy proportional to the applied voltage (and ion charge state). This triggers re-sputtering if a high enough voltage is used. However, the vast majority of the sputtered species in magnetron sputtering are neutrals, not ions, and thus mostly Ar ions are involved in re-sputtering.

Additional control of the bombarding flux can be obtained by ionizing the sputtered flux. In the last decade, High-Power Impulse Magnetron Sputtering (HiPIMS) has been popularized for this purpose. In a previous paper it was shown that Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS, allowed us to overcome the shadowing effect and, thus, to deposit Cr thin films with much smoother surfaces and densely packet columns even at relatively high pressure. The main objective of the present work is to identify the mechanisms which effectively decreases the shadowing effect in DOMS. For this purpose, the deposition conditions and properties of two Cr films deposited by DOMS at higher pressure and DCMS at lower pressure were studied and compared. In both cases the energy distributions of the energetic particles bombarding the substrate were evaluated by energy-resolved mass analysis and the angular distribution of the Cr species impinging on the substrate was simulated using Monte Carlo-based programs. The microstructure, structure and mechanical properties of the films were characterized by SEM and AFM, XRD and nano-indentation.

Keywords
Shadowing
HiPIMS
DOMS
Characterization of the Ti/Al adhesion layer in thin films of Au for applications in biomedical sensors

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Gold is often used for manufacture devices due to its high electrical conductivity and optical reflectivity. On the other hand, silicon has high capability of absorb oxygen on its interface. When put together, as bilayer, the bond of gold into silicon substrate can be poor requiring an adhesion layer. Typically, oxidative metals such as chromium and titanium are used in this sense as intermediate layers, enhancing the gold adhesion. In contrast, due their oxidation and diffusion to the gold surface the electrical, structural and morphological properties can be affected substantially. Herein, we present a characterization study of a more resistant and reliable adhesion layer, composed of Ti/Al. The effects of the adhesion layer on thin film of Au/TiAl/Si deposited by magnetron sputtering are analyzed through a couple of measurements. The XRD results indicated that the films are preferentially oriented in the (111) plane exhibiting a crystal structure. A four point probe technique was used to acquire the resistivity ($\sim 10^{-9} \, \Omega\cdot m$), at room temperature, for the Ti/Al alloy, showing good conductivity. The thickness of the films was estimated with Rutherford backscattering spectrometry showing a Ti/Al alloy of 60 nm with varying thickness around of 200, 300 and 900 nm for the gold top layer for different sets of films. In order to determine the Au implantation profile in Ti/Al, we calculated the Ti/Al ratio and the ion energy loss of H, He and Au in the films, also using RBS, and the results were compared to simulations obtained. Other measurements as FEG and GD-OES showed that the morphology of the film are very smooth and the interface between the films and substrate are abrupt. The set of results suggests that the Ti/Al interface could be a good alternative as adhesion layer for applications in biomedical sensors, due to its excellent conductivity, low oxidation and good durability.

Keywords
Biomedical sensors
Gold thin film
Ti/Al adhesion layer
Influence of aliphatic side chain on the near atmospheric pressure plasma polymerization of 2-alkyl-2-oxazolines for biomedical applications

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Recently, the plasma polymerization of 2-oxazoline monomers has been studied for the deposition of coatings with potential use in biomedical applications, as they were reported to exhibit antifouling properties which were also present for the parent polymers.1 In this work, the near atmospheric pressure plasma polymerization of a range of 2-alkyl-2-oxazoline monomers (methyl, ethyl, n-propyl and n-butyl) is explored and the effects of a growing aliphatic side chain on the properties of the obtained coatings are investigated using a variety of analytical techniques (WCA, FT-IR, XPS and NMR). The antifouling capacity of the deposited coatings are examined by cellular, bacterial and protein adhesion tests. With the growing aliphatic side chain, stable coatings are obtained at lower input powers and the coatings become more hydrophobic, while the side chain does not have an influence on the chemical groups deposited in the coating. It also became apparent that the composition of the plasma polymerized coatings significantly differs from the parent polymers. The cellular, bacterial and protein adhesion tests indicated that fouling occurred for all coatings, which may be ascribed to the difference in chemical composition between the 2-oxazoline plasma polymers and the conventionally synthesized poly(2-oxazoline)s. Despite this deviation in terms of antifouling capacity, the obtained coatings show promise as cell-interactive coatings and could find applications in tissue engineering.


Keywords
Plasma polymerized 2-oxazolines
Near atmospheric pressure
Parallel plate dielectric barrier discharge
Cell-interactive coatings
Anti-fouling coatings
Development of Microplasma Spraying Technology for Applying Coatings from Biocompatible Materials onto Medical Implants

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There are numerous ongoing researches in the area of manufacturing of the medical implants. One of the technologies for increasing the biocompatibility of implants is special surface treatments using microplasma spraying of biocompatible coatings. It has been shown by several previous research studies that hydroxyapatite (HA) is a good candidate as a bioactive and biocompatible material. Therefore we have chosen HA as the candidate material for the coating. It assists with the promotion of bone growth into the implant and facilitates the integration of the bone and implant. It is our objective in the current study to optimize the parameters of microplasma coating of hydroxyapatite onto endoprostheses of the hip joint in order to obtain the coatings with optimal structure phase composition and properties. The study was carried out on the pilot robotic industrial site for microplasma treatment of materials at the East Kazakhstan State Technical University. A sublayer of porous titanium with a thickness of 200-300 \( \mu \text{m} \) and a porosity of around 150 \( \mu \text{m} \) was sprayed onto the surface of a titanium based implant. Subsequently, a layer of HA with a thickness of the order of 200 \( \mu \text{m} \) was deposited over the porous titanium layer. The impact of the main process parameters of micro-plasma spraying such as the amperage, plasma gas consumption, spray distance, HA powder or titanium wire consumption on the quality of the coatings was investigated. X-ray diffraction analysis and transmission electron microscopy were used for studying the structural-phase composition of coatings and substrates. The coatings morphology and porosity were investigated using scanning electron microscopy via ZAF PB, MicroCapture, Atlas software for Image processing. The adhesion strength of coatings made of HA with a titanium sublayer has been determined. The technological recommendations for applying bilayer microplasma coatings of titanium/HA onto hip implants were developed. Acknowledgements: the study has been conducted with state funding of the Republic of Kazakhstan by the project “Production of titanium products for further use in medicine”

Keywords
microplasma spraying
hydroxyapatite
titanium
Modification of graphen-like coatings by plasma and vacuum ultraviolet radiation for biomedical applications.

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Hemo- and biocompatible properties, along with high strength, chemical inertness and durability provide graphene–like materials with an edge over most antithrombogenic coatings for biomedical implants and devices. However long term interaction of proteins or living cells with the implant surface can finally lead to a strong immunological response and the ensuing cascade of biochemical reactions can adversely affect the device functionality. Therefore, it is necessary to control the long term interactions between the biomedical implant and its surrounding biological environment. Plasma and vacuum ultraviolet modification of graphen-like coatings could be employed to mitigate these adverse physiological responses to the implant material. In this investigation plasma chemical treatment in atmospheric DBD discharge and monochromatic vacuum ultraviolet irradiation was used to modify surface composition, wettability, durability and conductivity of graphene oxide films deposited on medical polymers. Chemical composition, surface energy and structure of the surface layer before and after modification were characterized by contact angle measurements, XPS and FTIR spectroscopy. It has been shown that irradiation by vacuum ultraviolet radiation result in the detachment of the C−O polar groups accompanied by an increase in the conductivity and a decrease of wettability and surface energy of the reduced graphene oxide film. On the other hand atmospheric plasma treatment leads to the formation of oxygen containing groups and increase of graphene oxide surface energy.

Keywords
graphene oxide
DBD plasma
vacuum ultraviolet
XPS
ATR FTIR
High Efficiency Antimicrobial Coatings for Infection Control Applications

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Microbial infections on surfaces found in hospitals are routinely measured at levels far exceeding safe limits. This is a major cause of Hospital Acquired Infections (HAIs), which have a significant economic and social impact. Reducing the probability that surfaces could transfer harmful microbes to patients and hospital personnel has the potential to lower the level of HAIs. In addition densely populated areas present areas where cross infection could rapidly spread by surface contact. Most surfaces in an aerated environment exhibit a certain degree of antimicrobial efficacy, for example stainless steel surface could kill 90% of bacteria (Log 1). However in order to control disease propagation higher levels would be necessary, ideally at a 99.9% (Log 3) level or higher.

A series of new PVD coatings have been developed in order to achieve Log 3 (99.9% of bacteria kill) to Log 6 (99.999% of bacterial kill) on surfaces. Novel methods for the evaluation of the antimicrobial performance have been developed. Results will be presented.

Keywords
antimicrobial
bactericide
biofilm
antimicrobial coatings
Radical-functionalized plasma polymer films: Multi-functional interfaces for bone implant applications

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A large number of orthopaedic surgeries fail due to poor bone integration or biofilm formation; leading into revision surgeries in extreme cases. In 2016, there were more than 400,000 knee and hip replacement surgeries undertaken in Germany alone, with the estimated price of about EUR 6000 per replacement. Application of bio-functionalized coatings on bone implantable devices is a promising approach to drive rapid bone-implant integration and to eliminate infection, dramatically reducing the need for revision surgeries. Here we report the development of highly reactive and stable, radical-functionalized plasma polymer (RFPP) films for bone implants using a combination of plasma polymerization and plasma immersion ion implantation. A custom-made plasma polymerization reactor consisting of a radio frequency (RF) electrode and a pulsed voltage source connected to the titanium substrate was utilized to deposit RFPP films from mixtures of argon, acetylene, and nitrogen gases. We provide new insights into the role of energetic ion bombardment on the growth mechanisms of plasma polymers by measuring the hydrogen content of the films using elastic recoil detection analysis. Nano-indentation and nano-scratch tests, as well as stability studies in simulated body fluid (SBF) at 37°C suggested a strong correlation between the degree of energetic ion bombardment and physico-chemical stability of the coatings. The effectiveness of RFPP films to regulate osseointegration is confirmed by covalent attachment of fibronectin followed by quantifying primary osteoblast attachment, spreading, and proliferation. The bio-functionalized interfaces enhanced the interaction of primary osteoblasts, suggesting the bioactive presentation of fibronectin and the potential to improve bone cell interactions with implants treated in this manner. The RFPP films functionalized with antimicrobial peptides Mel4 and caspofungin prevented biofilm infection caused by S. aureus and C. albicans, respectively. Deposition of RFPP films via this technique holds great promise for the fabrication of modern real-world biomaterials, in particular bone implantable devices such as hip prosthesis and dental implants.

Keywords
Plasma polymerization
Bone implants
Physical-chemical and biological characterization of ZrN/Ag thin films deposited by reactive magnetron sputtering for biomedical applications

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The research for new biomaterials has been widely performed in order to solve problems such as infections that can occur in implants. This work brings the use of thin film coatings of zirconium nitride with silver nanoparticles as a solution to this problem. Zirconium nitride has several properties that give it an ideal character for use in bioapplications, such as high hardness, excellent chemical resistance, high resistance to corrosion and biocompatibility. In addition, metallic silver in the form of nanoparticles is effective against a broad spectrum of bacterial and fungal species, including strains that are resistant to antibiotics. Silver nanoparticles are considered to be even more active due to their high surface area to volume ratio. In order to combine the ZrN and Ag properties, these were co-deposited by magnetron sputtering on titanium and AISI 304 steel substrates. The physical-chemical characterization proved that ZrN thin films are stoichiometric (condition in which they exhibit the best tribological properties) through RBS analysis. The existence of Ag on the surface was also demonstrated by the GD-OES technique, and the effective formation of ZrN was observed through Raman spectroscopy. Hardness measurements were obtained through nanoindentation and the result obtained (15 GPa) is in accordance with the literature. For the biological characterization, two tests were performed. The first consisted of a visual analysis through Petri dishes with nutrient agar to attest the bactericidal activity against Escherichia coli through the formation of halos around the samples. The second test, a quantitative approach, had the objective of evaluating the percentage reduction of microorganisms’ adhesion to the samples with surface treatment. The test was done with the bacteria Listeria and Salmonella. It was observed that there was a maximum percentage reduction of microorganisms’ adhesion of 53.33%.

Keywords
Reactive magnetron sputtering
Antimicrobial action
Zirconium nitride/Silver thin films
Owing to medical titanium alloy (Ti-6Al-4V) has relatively poor hardness, corrosion resistance and antibacterial activity, it is essential to take some surface modification treatments on the medical titanium alloy. In consideration of the excellent mechanical, cell adhesion, and antibacterial properties of implant materials, titanium nitride coatings combined with Ag and Cu ion implantation become the preferred choice for the surface modification of medical titanium alloy.

TiN coatings were synthesized by multi-arc ion plating system, with medical titanium alloy (Ti-6Al-4V) as substrates. To obtain good cell growth antibacterial property, Ag and Cu ions were implanted to the surface of TiN coatings at different fluences via ion implantation system. The structure was observed by TEM and SEM. The hardness and elastic modulus of TiN coatings before and after ion implantation were surveyed using a Nanoindenter XP system. Cytocompatibility and antibacterial property of TiN coatings at different Ag and Cu ion fluences was evaluated by osteoblast and Escherichia coli (E. coli, DH5α) in vitro.

The hardness and elastic modulus increase with the increasing Ag and Cu contents, and the maximum value achieves 35 GPa and 330 GPa when the Ag+Cu fluence reaches $5 \times 10^{17}$ ions/cm$^2$. In the cell proliferation experiment, compared with the group without ion implantation, the number of living cells grown on the surface with Ag+Cu implantation was more and had no downward trend in seven days. The antibacterial property of TiN coatings at $5 \times 10^{17}$ ions/cm$^2$ was extremely ideal and almost no E. coli growth.

**Keywords**

ion implantation
TiN coatings
multi-arc ion plating
antibacterial property
cytocompatibility
Antibacterial Coatings on PET Films and Non-wovens by Aerosol-Atmospheric Pressure Plasma

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Polyethylene terephthalate (PET) can be used for a variety of purposes, e.g. for food and beverages photographic films, or as fibers/non-wovens. Each application requires particularly high demands on material surfaces with inhibiting effects on bacterial or fungal growth. Preventing the microbial colonization on the technical surfaces is important to preserve the product quality of packaged goods, film resolution quality and well-being when wearing functional clothing (odor formation) or general hygiene requirements. Nowadays, the bulk properties (e.g. mechanical, optical) of materials in the specified applications have been optimized. Antibacterial thin coatings, which do not affect bulk properties, have therefore become a very active field of research, due to identifying alternatives to the traditional application of biocides. Currently there are three major strategies for tailoring antibacterial coatings: antibacterial agent release, contact-killing, and anti-adhesion/bacteria-repelling.

The aim of this study is to reduce the microbial growth on PET films and also non-wovens by deposition of nm-thin antimicrobial coatings applying the aerosol-atmospheric pressure plasma technology. Depending on process parameters (current and velocity), plasma polymer-like coatings of octenidine, chitosan, chloro-hexidinbis (D)-gluconate and sulfobetaine methacrylate were prepared on a PET-GAG type film (150 µm, Folienwerk Wolfen GmbH). The surfaces were characterized spectroscopically (FTIR, XPS), morphologically (profilometry, REM) as well as concerning their surface energy. The microbiological properties were tested based on standardized microbiological tests and compared to a commercial PET film with antimicrobial properties designed by Ag Nanoparticles. Additionally the studies focused on the evaluation of a fast test procedure to characterize the antimicrobial efficiency on the basis of fluorescence intensity of Pseudomonas fluorescens (GFP) bacteria.

Keywords

aerosol-atmospheric pressure plasma
antimicrobial coating
PET
Titanium and ITO surface modification with Protein: evaluation by Non-contact and Non-destructive Kelvin probe technique

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Titanium and its alloys are widely used for bio-medical implants due to their high strength, remarkable biocompatibility, resistance to corrosion, conduciveness to Osseo integration etc. Tin doped indium oxide (ITO) is a bio-compatible thin film. The tissue-metal or metal oxide surface interactions are fundamentally important in assessing the functionality of the implants. Kelvin probe is a non-contact and non-destructive technique to measure the surface work function of the metals; even after the measurement, the surface remains in this technique. The surface work function is very sensitive to any charge transfer process from proteins (a major constituent of tissues) to the surface of the metal. In the present study, piranha solution cleaned Titanium surfaces (10 mm x 10 mm) and freshly coated ITO thin films are immersed in different proteins: (i) lysozyme (14 kilo Daltons, kDa), (ii) carbonic anhydrase (30 kDa), (iii) bovine serum albumin (66 kDa) and (iv) human immunoglobulin (150 kDa). The surface work function of the virgin and protein treated Titanium and ITO surfaces have been measured. The surface work function results show substantial evidence of surface modification of Titanium and ITO with the proteins. Even after thorough washing steps, the protein dipped Titanium and ITO surfaces show significant modification. The surface work function results are being analysed to correlate the protein concentration to the surface modification.

Keywords
Kelvinprobe
Surface Workfunction
ITO
Protiens
Surface functionalisation, nanoroughness and drug delivery by atmospheric plasma jet on scaffolds

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Advances in tissue engineering have highlighted how roughness and surface chemistry in the scaffolds can affect cells growth and differentiation. Moreover the new generation of scaffolds focuses also on smart functions such as the delivery of growth factors or anti-inflammatory drugs and on the possibility to make gradients of the different properties or functions within the same scaffolds.

Here we present an innovative way to control nanoroughness, chemistry and drug delivery just by depositing them locally by spraying smart or inert nanoparticles and fixing them mechanically on the surfaces by an atmospheric plasma coating encapsulation. The size and quantity of the nanoparticles deposited allows a control of the roughness. The biodegradable nanoparticles allows the introduction of the smart functions or drugs and the plasma coating assures the desired surface chemistry. Since the whole process is in open-air, fast and localized, it is compatible with 3D-printing and allows gradients designs.

The new process has been evaluated on titanium alloys for dental implants for osteoblasts growth and on polycaprolactone (PCL) for fibroblasts growth. Silica and fluorescent PLA nanoparticles of 200nm in diameter have been used to induce the roughness. The fixing and the carboxylic and ammine groups surface functionalities have been obtained by atmospheric plasma coating around 150nm thick. The surfaces have been characterized by AFM, SEM and FT-IR, while cells growth have been evaluated by viability assay, protein absorption, proliferation and focal adhesion. All the parameters have been improved, cells adhesion has been increased of 20% relative to commercial large grits and acid etched (SLA) titanium alloys and of a factor 10 compared to smooth PCL. The possible drug release has been simulated quantifying the fluorophore coming from the PLA nanoparticles in the cells growing media.

\textbf{Keywords}

nanostructures
cells growth
A bi-layer formation of plasma films over QTF surface for improving the stability of amine-rich layer

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Plasma polymerization (PlzP) method is a common way to control the thickness of film growth with a uniform coating over the substrate materials. Especially, adjustable chemical composition of the thin film achieved by plasma modification has become vital over the years, that directly influence the performance and the functionality of the polymers for desired application. At this point due to their positively charged property, amine-rich thin films step forward for biotechnological applications. They can provide covalent bonding with negatively charged biomolecules such as enzymes, DNA or living cells. However, high amine concentration affects the thin films’ stability negatively because of the magnitude of the surface energy. To overcome this problem two different hydro-carbon groups which are n-Hexane(HEX), and n-Heptane(HEP) were applied to the surface by PlzP before amine-rich coating. The main reason of selecting hydrocarbon group is; pre-coating can be a key tool since this coating has high degree of cross-linking as well as having thermal and chemical stability compared to other polymer thin films. These different films examined from first day to the thirtieth day by using Contact Angle, Frequency and Resistivity measurements.

After completing the surface functionalization step, Glutheraldehyde (GA) [25% (v:v)] applied to the thin film surfaces for activating amine groups with aldehyde. To check GA performance a model protein, Bovine serum albumine (BSA), was used to control the binding performance of modified and activated surfaces. This work showed that, two steps PlzP samples are more stable than single step PlzP samples, this mean; the surfaces which contain hydro carbon groups, effects directly the performance and long-term stability of amine-rich surfaces. This study leads a potential development of a biosensor platform for detection of antibody, toxins etc. in all types of environment.

Keywords
Plasma polymerization
thin films
amine rich thin films
hydrocarbon thin film
thin film stability
Polycrystalline Co$_3$O$_4$ thin films grown at different substrate temperature by pneumatic spray

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Abstract

Cobalt oxide thin films have attracted substantial research effort in recent years because their potential application in various technological areas. In general, cobalt oxide exists in three different crystalline forms; namely CoO, Co$_2$O$_3$ and Co$_3$O$_4$, but the latter stoichiometry is largely reported for the above cited applications because of its chemical stability and desired electrochemical properties. In this work, Cobalt oxide (Co$_3$O$_4$) thin films were deposited onto glass substrates using a (homemade) pneumatic spray pyrolysis technique (SPT) using perfume atomizer from aqueous solution of hydrated cobalt chloride salt (CoCl$_2$·6H$_2$O) as source of cobalt. The films were deposited at various substrate temperatures ranging from 250 to 450 °C in steps of 50 °C, the effect of substrate temperature on structural, electrical and optical properties was studied.

The characterization of samples was carried out by X-Ray diffraction, UV-VIS spectroscopy, scanning electron microscopy (SEM) and four probe points measurements. The X-ray diffraction study showed that all the films were polycrystalline spinel type cubic structure. The preferred orientation of the crystallites changed from (311) to (111) when the substrate temperature increases. The calculated grain sizes were in 25 to 40 nm range. The optical transmittance and the band gap energy increases with the increase of substrate temperature indicating an improvement of the crystallinity of the films. The electrical conductivity of Co$_3$O$_4$ is in the order of $10^{-2}$ (Ωcm)$^{-1}$.

Keywords

thin film
pneumatic spray
Cobalt oxide
substrate temperature
properties
Flexible and printed photovoltaics can contribute greatly to increasing global access to cheap energy. Dye-sensitized solar cells (DSSC) and perovskite solar cells, in which the photo-electrochemical system relies upon a mesoporous crystalline TiO\(_2\) layer, have emerged as a promising low-cost photovoltaic technology and constitute a notable application field for semiconducting photoanodes. Fine mesoporous TiO\(_2\) films are usually cured at high temperatures by means of a slow convection heating procedure (at least 30 min above 350 °C) in order reliably to remove all organic components present in the coating formulation. The high sintering temperature, however, precludes the use of such a procedure for thermally sensitive and flexible substrates and results in performance deterioration in transparent conducting oxide substrates.

We prepared hybrid mesoporous titania/silica electron-generating and transporting layers using wet coating with a dispersion consisting of prefabricated titania nanoparticles and a methyl-silica binder. Titania/methyl-silica wet layers were deposited by inkjet printing on ITO/PET flexible foils and further mineralized by low-temperature (70 °C) atmospheric-pressure air plasma using diffuse coplanar surface barrier discharge (DCSBD) to form a titania/silica hybrid nanocomposite coating. The plasma mineralization process provides production performance superior to the previously-considered processes (thermal sintering and UV curing), taking only a fraction of the time required for them at far lower temperatures. The coating can be applied on flexible polymer which makes the application suitable for fast roll-to-roll fabrication units. The reported method could constitute a major step forward in the large-scale manufacture of low-cost flexible functional coatings.

**Keywords**
- plasma treatment
- flexible and printed electronics
- roll-to-roll
- mesoporous coating
- ambient air diffuse plasma
Structure optimization of Ta-O-N films prepared by reactive HiPIMS for more effective water splitting

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The TaON material is a promising candidate for application as a visible-light-driven photocatalyst splitting water into H₂ and O₂ and thus converting solar energy into chemical energy. The photo-generated electron-hole pairs act here as the active water splitting species. In order to work as a water splitting photocatalyst, the material must satisfy certain conditions: (i) band gap of proper width (preferably corresponding to visible light absorption) and (ii) suitable alignment of the band gap with respect to the water splitting redox potentials. The subsequent transport of the charge carriers through the material (particularly across the films thickness) plays an important role in the effectiveness of the process.

In this work we first demonstrate that using reactive high-power impulse magnetron sputtering (HiPIMS) as the deposition technique followed by post-annealing of the deposited film at 900°C in a vacuum furnace, allows us to prepare a polycrystalline (non-textured) film exhibiting a pure TaON phase. Such film satisfies the above mentioned conditions for a water splitting photocatalyst (band gap of ~2.6 eV). In addition, the film exhibits a lower electrical resistivity as compared to the amorphous as-deposited film, allowing easier transport of the charge carriers in the film. As the monoclinic TaON phase exhibits anisotropic charge carrier conductivity, tailoring the texture of the film can further improve the charge carrier transport in a desired direction. In this work, we therefore also investigate the possibilities of the following approaches: deposition at elevated substrate temperatures (up to 850°C), deposition at high power densities in a pulse (up to 4 kW/cm²) and/or deposition onto suitable substrates providing proper seeding layers (e.g., Pt, Ta, ZrO₂) to prepare textured TaON film allowing enhanced charge carrier mobility across the film thickness.

**Keywords**
Reactive HiPIMS
TaON
Water splitting
Photovoltaic property of ZnO:Al/n-ZnO/p-Si structures fabricated by pulsed laser deposition

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ZnO material has been extensively utilized in semiconductor device technology due to its unique electrical and optical properties. ZnO has wide direct band gap (3.37 eV), n-type conductivity, which are a promising as photodiode material. Also, Al-doped ZnO (AZO) thin film is particularly attractive for an electron transporting layer of solar cell because of its high optical transmittance, good thermal stability, high conductivity, and low cost of fabrication.[1] In this study, we fabricated ZnO/p-Si substrate with and without AZO as electron transporting layer by using pulsed laser deposition (PLD) [2,3], and the performance of these devices were analyzed by current density-voltage (J-V) characteristic and spectral responsivity. The ZnO thin films were deposited on p-Si substrates under different oxygen pressure from 40 mTorr to 70 mTorr by using pulsed laser deposition (PLD). In x-ray diffraction analysis, ZnO thin film grown under oxygen pressure of 60 mTorr showed the highest intensity of (002) diffraction peak and highly c-axis oriented. At room temperature, all ZnO thin films grown at different oxygen pressure showed near band edge emissions about 385 nm, and good rectifying behavior under dark condition. The n-ZnO/p-Si device grown at oxygen pressure of 60 mTorr showed better photovoltaic properties. When Al-doped ZnO (AZO) deposited on the surface of n-ZnO/p-Si structure, the power conversion efficiency of the device under Air Mass 1.5 Global solar simulator was much enhanced from 0.61% to 1.5%. By measurement of spectral responsivity, it appeared that the AZO layer as an electron transporting layer affects to the photocurrent enhancement in all solar spectral range.

References

Keywords
photovoltaics
pulsed laser deposition
In this study, LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ and Li(Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$)O$_2$ thin film were selected to research. The low electronic conductivity and Li$^+$ diffusivity of LiMnPO$_4$ severely limits its electrochemical activity room for maneuver, especially under high current density. On the other hand, Li(Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$)O$_2$ can exhibit a promising electrochemical performance among currently working cathode materials. However, the Ni/Li mixing and growth of preferred orientation seriously affect the capacity and rate capability. To overcome these drawbacks, DC/RF magnetron sputtering approach will be incorporated. Through intrinsic modification of LiMnPO$_4$ cathode with Fe and C, a better electrochemical performance could be demonstrated in half lithium-ion battery. For layered type material, the Li(Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$)O$_2$ is deposited on various buffer layer substrate by reactive magnetron sputtering using single NMC target in an argon/oxygen atmosphere. It is expected that the development of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ and Li(Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$)O$_2$ would exhibit a great potential to meet the demand of next-generation high power Li-ion battery.

Keywords
Li(Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$)O$_2$
LiMn$_{0.8}$Fe$_{0.2}$PO$_4$
Thin Film battery
Cathode
Lithium-ion battery
Cr/C multilayers coating for proton exchange membrane fuel cells bipolar plate

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The bipolar plates of Proton Exchange Membrane Fuel Cells (PEMFC) are key components of the cell; instead of using graphite, for weight and cost consideration, research is currently made in order to replace graphite by coated stainless steel. This coating must resist to drastic conditions in terms of corrosion, but also has to ensure a good conductivity and a low interfacial contact resistance (ICR), and present a reasonable price. These target values are fixed by the Department of Energy (DOE) but, in the industrial production process, the coating must also tolerate a high deformation if the plate is stamped for designing its channels after the coating deposition.

Among the promising processes, PVD deposition of coatings such as CrN, CrNC, TiN, and CrC are in agreement with the target values (below 10mΩ.cm² for ICR and 1µA.cm⁻² for corrosion), but the deformation tolerance of these coatings are limited. In our work, we investigate the synthesis and the characterization of new coating layers. In particular, the synthesis of a Cr/C multilayer coating on stainless steel sheet by magnetron sputtering is currently under study and shows many promising results. The process, monitored by plasma emission spectroscopy (PEM) offers an accurate control of the coating characteristics (layer composition, layer thickness, interfaces). The number of layers, and the carbon and chromium content in each unit layer have a strong influence on the key properties (ICR, corrosion and deformation) that have been investigated through a set of experiments. Assemblies of 4, 10, 20 and 40 layers with different chromium and carbon content (from 30 to 70%), but a similar total thickness (≈800nm) have been studied and exhibit corrosion current below 0.1µA.cm⁻², a deformability up to several % and ICR values in the range from 40 to 100 mΩ.cm². SEM cross-section and XPS depth profiling characterization have been performed before and after ICR and corrosion tests to link the coating characteristics and its electrochemical behaviour.

Keywords
PEMFC
multilayer coating
Nanostructured Metal-Oxide Based Hydrogen Gas Sensor Prepared by Magnetron Sputtering

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Hydrogen is an inexhaustible and transportable source of energy. It consists of a potential begins to be a restorative for clean energy generation. In various areas of industry, more accurate, faster and more selective detection of hydrogen gas is needed. It can be used for monitoring and control hydrogen concentration. The safe transportation, storage demand, reliable and fast hydrogen gas sensors are required. Nanostructures/nanoclusters of metal oxides are suitable candidates for gas sensors due to their large surface volume ratio. This approach provides a practical and direct access to detect the gases.

The sensitivity responses of tungsten oxide nano-structured thin films prepared by reactive DC magnetron sputtering from metallic target were studied. Various metallic oxide clusters (CuO, WO₃) were deposited on the top of the prepared thin films using a gas aggregation chamber cluster source. We demonstrated that sensitivity was enhanced by these clusters. Various deposition parameters were applied (time, temperature, Ar/O₂ ratio) in order to improve the sensitivity. Crystal Structure and surface morphology of as-deposited films were studied by XRD, SEM, and AFM. The sensor response to hydrogen gas in an atmosphere with controlled composition (synthetic air/H₂) was studied at various temperatures for a variety of deposition parameters.

Keywords
Sensitivity
Hydrogen
Tungsten Oxide
Nanoclusters
Sputtering
Reactive magnetron sputtering gadolinia-doped ceria diffusion barriers for anode ceramic substrate of solid oxide fuel cells

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PVD by plasma emission monitoring (PEM) was employed to synthesize GDC (10%Gd doped ceria) thin films on anode-grade ceramic substrate and steel AISI340. Reactive magnetron sputtering deposition technique was used for formation of gadolinium doped ceria (GDC) 5-10μm thin films. Material characteristics and chemical compositions of GDC films were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). By optimization of preparative parameters of PEM and modification of surface of anode ceramic substrate. An Alcatel SCM650 sputtering chamber was used for synthesizing the dense GDC layers. A Ce-Gd metallic target (90 10% at) was powered by a pinnacle + pulsed current generator from Advanced Energy. Gadolinine ceramics (GDC10) were made from a metal target of Ce-Gd in a reactive atmosphere. Working in a reactive condition allows better control of the process and higher deposition rates compared to the use of a ceramic target. The microstructural morphological surface features of the half-cell complete cell were analyzed by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD). The chemical states of the surface of the prepared sample were analyzed by X-ray photoelectron spectroscopy (XPS) and 3D profilometry and was employed to nos-destructively quantify the craking and behavior observed before and after different annealing. Finally, the EIS (Electrochemical Impedance Spectroscopy) measurements were performed on NiO-GDC/GDC half-cells under 60 sccm nitrogen by the means of a Solartron SI 1260 impedance / gain analyzer from 20 MHz to 0.1 Hz with 11 points per decade.

Keywords
SOFC
Magnetron
GDC10
Coatings
Electrochemical
A Study of in-situ plasma nitrocarburizing-PEMOCVD duplex-treated thin coating films for metallic bipolar plate of PEMFC

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Metallic bipolar plate for PEMFC (Polymer Electrolyte Membrane Fuel Cell) are becoming lighter and thinner in terms of power density, specific power and cost. Such metallic bipolar plate needs various properties and reliability required in a fuel cell stack, and therefore it is urgent to develop new surface treatment technology that can be satisfied requirements.

In this study, new duplex-treatment which are consisted with plasma nitrocarburizing and PEMOCVD processes are investigated for stainless steel 316 plate. Very thin carbon-based metal coating films are performed on the substrate in two steps in-situ. Plasma nitrocarburizing process penetrates nitrogen and carbon on the substrate surface to form a diffusion layer, so-called S-phase. The carbon-based coating films are deposited by MOPECVD process from acetylene and MO-precursor (Metal Organic Precursor) mixed gas. The S-phase and thin carbon-based metal films are observed using TEM, FE-SEM. The thickness of films is under the several tens of nanometer size and the grains are 5 ~ 40 nm. The interfacial contact resistance (ICR) and corrosion resistance of carbon-based metal films are compared with gold coatings. ICR and corrosion resistance results are closely related to grain size of films. The best ICR and corrosion resistance of carbon-based metal films are 13.3 mΩ·cm² and 0.387 uA/cm² respectively and these results are equivalent to or better than gold coatings.

Keywords
Carbon-based metal film
PEMOCVD
Duplex treatment
Metallic bipolar plate
PEMFC
Nanostructured carbon bio-cathodes for enzymatic biofuel cells with direct electron transfer

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Among the new sources of renewable and sustainable energy under development, biofuel cells which convert chemical energy into electrical energy using enzymes as catalysts show a clear acceleration of research for 10 years(i). However, several challenges have still to be faced before such devices can get close to become a commercial reality, including the increase of the power output for more demanding electronic devices. Two main parameters of the biofuel cell design are crucial: the overall available surface for enzyme immobilization and the wiring of the biocatalyst on the electrode in order to optimize the transfer between the electrode and the active site of the enzyme(ii). Carbon nanotubes deposited on graphite and graphene have been extensively investigated in the field(iii). We propose an alternative and innovative method leading to a considerable increase of the surface area of graphite: synthesis of carbon nanowalls (CNWs) described as self-assembled, vertically standing, few-layered graphene sheet nanostructures(iv) by plasma-enhanced chemical vapor deposition in a CO/H2 microwave discharge. CNWs were then functionalized by atmospheric plasma to ensure efficient enzyme grafting. Design of experiments methods have been performed to optimize the plasma functionalization parameters as well as the immobilization conditions of laccase. The controlled immobilization of laccase on the surface of the electrode involving its amine or aldehyde groups (after oxidation of the glycoside groups) made it possible to reach currents greater than 1 mA/cm2, which makes this approach competitive by compared to the best performances achieved to date. (i) M. Rasmussen et al Biosens. Bioelectron. (2016), 76, 91-102, (ii) S Cosnier et al J Power Sources, (2016), 325, 252-263, (iii) AA Babadi et al, Biosens Bioelectron, (2016), 79, 850-860, (iv) S. Mori et al, Diamond Relat. Mater., (2011), 20, 1129.

Keywords
biofuel cell
Lanthanum cobaltite LaCoO$_3$ layer for thermal solar collector

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LaCoO$_3$ shows a metal-insulator transition associated to an interesting change in optical properties. Deposited on aluminum and silicon substrates, the material acts as a smart selective layer due to the variation of emissivity ($\Delta\epsilon$). LaCoO$_3$ was synthetized by magnetron sputtering in order to make an easy upscaling and the temperature of metal-insulator transition (TMI) was lowered using nitrogen-doping in order to use it as a thermal-control coating on solar panels. A two-steps process was employed: the first step is the co-sputtering of cobalt and lanthanum in poisoned regime followed by a crystallization step in a furnace. Samples are characterized with a scanning electron microscope, X-ray diffraction, secondary ion mass spectroscopy. The optical properties of the samples have been studied, using an infrared or UV-visible reflectance versus temperature to investigate their ability to regulate temperature. Transmission electron microscopy analysis shows a globular micro-structure. Crystallization’s kinetic has been studied by observing the evolution of (110) planes. Reflectivity versus temperature gives a variation of emissivity ($\Delta\epsilon$) over 50% at $\lambda=8\mu$m between 573K to 773K.

**Keywords**
Perovskite
Oxynitride
Magntron Sputtering
thermochromic
thin film
Heat flux investigation of the low temperature oxidation of a titanium thin film freshly deposited by magnetron sputtering

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Understanding the mechanisms of oxide thin films formation is of high interest for various applications (catalysis, dielectrics,...) and there have been numerous experimental and theoretical efforts from mid-20th century [1] to nowadays [2,3]. At ambient temperature and low O₂ pressure, the oxidation mechanism are well-described by the Cabrera-Mott models. The oxide growth rate is high initially due to the O₂ chemisorption at the surface and the Mott potential formation. As the oxide thickness rises, the effect of the Mott field decreases and the oxidation diminishes down to a limited thickness (few nm). But, the metal oxidation is also influenced by the metal properties (morphology, defects,...) and the understanding of these factors is still unsatisfactory.

Because the chemisorption/oxidation process releases an energy (enthalpy of the oxide formation), we investigated the chemisorption/oxidation mechanisms of a freshly deposited thin film by the measurement of the energy flux \( \varphi \) with a thermopile [4]. Ti thin films have been firstly deposited by sputtering and secondly submitted to O₂. The thin film thickness has been varied between few nm and 1 µm and the O₂ pressure has been changed from 0.1 to 15 Pa. \( \varphi \) displayed a rapid increase right after the O₂ introduction. This peak was followed by a logarithmic decrease. Such measurement is in accordance with the Cabrera-Mott models. Moreover, it has been observed that the energy was strongly dependent to the Ar pressure fixed during the Ti deposition step (between 0.5 and 5 Pa). The released energy increases when the Ar pressure decreases which means that porous thin film leads to thicker oxide formation. Finally, this study showed that in situ flux measurement can help to better understand of the chemisorption/oxidation mechanisms.


Keywords
low temperature oxidation
magnetron sputtering
PO1052

**Study on the correlation of process parameters and plasma density in PIAD employing active plasma resonance spectroscopy**

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Most applications in photonics greatly rely on optical components which ensure specific spectral properties. In this context, optical interference coatings (OIC) of high quality are key elements, enabling for the refining of optical components with functional coatings like anti-reflectives, high-reflectives or filters. A versatile method for the manufacturing of OICs is plasma ion assisted deposition (PIAD), which is commonly understood as the combination of electron beam evaporation and the densification of the growing film by means of a plasma ion beam. Present concepts of process control only affect the operating parameters and deposition parameters, while there is no access to gain insight on plasma conditions. Fluctuations and deviation of plasma conditions due to long term drifts cannot be detected with common monitoring techniques of thin film properties but affect the quality, reproducibility and yield of PIAD processes.

A promising diagnostic tool for monitoring of the plasma state is active plasma resonance spectroscopy (APRS). The recent implementation of a multipole resonance probe (MRP) offers a process compatible approach to measure electron density ($n_e$) during deposition. In this contribution, we present an installation of a pair of MRPs in an industrial box coater, allowing access to both, magnitude and changes in lateral distribution of $n_e$ near the substrate plane. The sensitivity of the MRP has been evaluated and the impact of various operating parameters on $n_e$ has been assessed appropriately. The interdependency of lateral distribution of $n_e$ and homogeneity of layer properties across the radial coordinate of the box coater at nominally constant level of plasma assistance is discussed based on single layer experiments of TiO$_2$ and Ta$_2$O$_5$.

The work is based on funding by the German Federal Ministry of Education and Research (BMBF) under grants 13N13208, 13N13212 and 13N13213.

**Keywords**

PIAD

APRS
In situ TEM techniques for coatings investigations

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Over the past decades, the applications of transmission electron microscopy (TEM) have shifted from observation of static illustrations to in situ measurements of mechanical properties and structural changes. It provides the chance to observe at the atomic level materials responses to an external impact, discover transient states during chemical or structural transformations, and correlate materials structure to their functionalities. In present study in situ TEM techniques were employed in investigations of hardness, adhesion, crack resistance as well as diffusion processes and thermal stability of hard nanocomposite and multilayer coatings. Using FIB method different shapes of samples were fabricated and size-properties relationships were evaluated and compared with common micro- and macroscale techniques. This research brings about mechanical properties and behavior of coatings at high temperatures which impact the reliability and performance of special modern nanodevices and opens new data about well-known materials.

The authors acknowledge the financial support from the Russian Scientific Foundation (Agreement 14-19-00273-П).

Keywords
in situ TEM
mechanical properties
adhesion
thermal stability
multicomponent coatings
Atmospheric pressure plasma processes: Correlations of in-line analytical investigations with surface analysis

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In foil producing industries, the dielectric barrier discharge (DBD) is established to chemically modify the outermost polymer surface and improve wetting or adhesion properties. By introducing defined process gases, aerosols or precursors within a carrier gas tailor-made surface properties will be achieved. But these processes need high effort of process control to maintain good product qualities. Therefore, there is a general interest to correlate plasma parameters with the resulting surface properties and find parameters for inline process control \cite{1, 2}.

The aim of the presented investigations is to find correlations between the reactions in the gaseous phase and the resulting surface properties and evaluate the gained information as a process controlling tool. First, DBDs with various treatment atmospheres are compared and evaluated concerning their efficiency of surface activation onto low density polyethylene (LDPE). Simultaneously, optical emission spectroscopy (OES) is applied to study the reactive species in the plasma. The surface modification of the polymer surfaces is analysed in particular by the determination of the polarity by contact angle measurements. Additionally, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) are applied to investigate and evaluate the plasma modified surfaces.

Beside the high intensity of the $N_2$ atomic emission, the intensity of the weak $O_2$ emission peak can be used as parameters for plasma characterization and it can be correlated with surface properties like oxygen content determined by XPS and the polar component of surface tension. Therefore, the peak intensities can be used for inline monitoring of the plasma parameters and is suitable for industrial application. \cite{1, 2}


Keywords
DBD
OES
Surface Analysis
In situ FTIR-ATR monitoring plasma-activated hydroxylation of silica using
dielectric barrier discharges, vapor-phase amino-silanization, and amino-group
derivatization

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In situ monitoring of thin film growth and surface modification is helpful for the
elucidation of physico-chemical process mechanisms and for studies of the nature
and chemical reactions of surfaces and coatings before they come into contact with
the environment. FTIR-ATR spectroscopic monitoring of the modification of
polyethylene surfaces in the afterglow region of dielectric barrier discharges (DBDs) in
N$_2$/H$_2$ mixtures, for example, has recently been used to provide indications of the
non-selectivity of aldehyde derivatization for primary-amine detection.[1,2]

Previous experiments performed at IOT and IST were limited to studies of the
interaction of relatively stable active species in outflows from DBDs such as oxygen or
nitrogen atoms, and nitrogen molecules in the N$_2$(A) state, with polymer surfaces.
Multi-ATR elements made from electrically conductive materials like Si or Ge may,
however, be used as the ground electrode in asymmetric DBD arrangements.

FTIR-ATR monitoring of a surface or a growing thin film and its interaction with
reactive neutral and charged species as well as energetic photons from a DBD is
possible. The present contribution reports about plasma-assisted surface
hydroxylation of silicon oxide layers thermally grown on Si multi-ATR crystals. The
discharge is generated within a fused quartz flat DBD reactor, enabling a gas flow
parallel to the crystal surface and transverse to its long axis. Argon with admixtures of
H$_2$, O$_2$, and H$_2$O, respectively, was applied as plasma gas to find the optimum DBD
treatment conditions for a subsequent vapor-phase silanization process, using
aminopropyl trimethoxysilane (APTMS). Information about process kinetics and
chemical nature of the surfaces could be gained from the in-situ experiments.


Keywords
FTIR-ATR spectroscopy
in-situ monitoring
silanization
Vacancies in MONTAN – a mechanism for tuning hardness–toughness relationship

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The cubic-structured nitrides of Mo and Ta exhibit excellent tribo-mechanical and electrical properties and are often used as alloying components to improve, for instance, materials resistance against wear and oxidation. The outstanding properties both materials owe to their inherent driving force to form vacancies. Fusing Mo–N¹,² with Ta–N² experimentally and theoretically – we investigate a novel material system and present here the evolution of structure and mechanical properties of »MoNTaN« coatings triggered by varying the chemical potentials. The insights into the origin of the observed phenomena allow us to tune the hardness–toughness relationship and hence to design materials for applications requiring tailor-made properties.

References:

Keywords
MONTAN
Magnetron sputtering
Vacancies
Mechanical properties
Ab initio
The (in)stability of process control mechanisms in reactive DC sputtering deposition

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The RSD model is currently the most advanced model to describe process curves during reactive DC magnetron sputtering deposition. It tries to implement the most essential chemical and physical processes to understand the most of the reactive sputtering process. The considered operation parameters in the model are the reactive/inert gas flow, the pumping speed, the discharge current/voltage/power and the target/substrate geometry. Together with the material dependent parameters like sputter yields, reaction coefficients, secondary electron emission yields,… they define the outlook of the process curves and especially their intrinsic instability properties which may manifest in hysteresis behavior. Indeed the RSD model is now capable in simulating a more broader range of process curves.

Getting control on the process and handling the possible hysteresis is one of the main concerns to obtain a desired thin film at an economical high deposition speed. Removing the hysteresis to establish stable process control is one way in obtaining these favorable deposition conditions. However, the approaches for hysteresis removal like increasing pumping speed/inert gas pressure or reducing target area, are either hard to establish or induce unfavorable working conditions. Another way is getting along with the hysteresis and access the unstable transition regime by feedback control which may make the process control more complex. However, it has been shown that this unstable transition regime can sometimes be operated stable when a right choice of controlling parameter is made. Its success depends basically on the material/reactive gas combination at hand and is primarily defined by the mutual difference in secondary electron emission yields of the metal and the formed compound. Such stabilization can for example be obtain for the Al/O₂ system while this is not the case for the Ti/O₂ system. Here the proposed solutions are investigated by the RSD model, with an emphasis on the origin why some material/reactive gas systems are intrinsic harder to control than others.

Keywords
reactive sputtering
modelling
hysteresis
On the growth of TiO\textsubscript{x} coatings by reactive magnetron sputtering from metallic and ceramic targets: a joint modelling and experimental story

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This work reports the study of the growth mechanisms involved in TiO\textsubscript{x} thin film deposition by magnetron sputtering. An Ar-O\textsubscript{2} plasma chemistry obtained by dual magnetron setup operating in DC mode is used. Growth from both metallic and TiO\textsubscript{1.8} targets are compared. Isotopic \textsuperscript{18}O\textsubscript{2} is used as reactive gas for all different configurations. The aim is to differentiate oxygen coming from ceramic targets and oxygen coming from the gas phase. Indeed, using ion beam analysis techniques such as Rutherford Backscattering Spectroscopy it is possible to precisely analyze Ti, \textsuperscript{16}O and \textsuperscript{18}O content of the samples. Other investigation techniques such as AFM, SEM … are also used to fully characterize deposited coatings. In order to study the effect of energetic ions bombardment of samples during deposition, 70° and normal incidence samples are compared. In addition to sample’s characterization, Langmuir probe, energy-resolved mass spectrometry and energy flux probe are used to obtain plasma phase properties.

In a second part, simulations tools are used to predict both discharge and coating’s properties. In order to simulate the complete plasma process, three different software are used. Each one is handling a defined step of the process (i) neutral particle motion, (ii) charged particle motion and (iii) film growth. We will discuss the comparison between simulation predictions and experimental investigations. Those two approaches allow us to achieve a better understanding on the growth of oxide layers by reactive magnetron sputtering and how plasma parameters influence coating properties.

Keywords
Reactive Magnetron Sputtering
Simulation
TiO\textsubscript{2}
film growth
Two main driving forces influence the thin film microstructure and texture during reactive DC magnetron sputtering: the thin film composition and the mobility. The latter is mainly defined by the available energy per arriving atom, and can be modified by the deposition conditions. In this study, the impact of these driving forces is studied during the growth of copper oxide thin films. The thin film composition was modified by a change of the oxygen partial pressure, and the pumping speed. The deposition rate drops a function of the oxygen fraction due to a change of the target sputter yield. The latter was independently quantified based on gas consumption measurements. The discharge current affects both the thermal flux towards the growing films, and the deposition rate, and permits in this way to modify the energy per arriving atom. The film texture was characterized by X-ray diffraction. From our measurements it became clear that the oxygen fraction defines the crystallographic phase which is hardly influenced by the average energy per arriving particle.

Keywords

- copper oxide
- fraction of oxygen
PO2005

**Comparison of mechanical behavior of TiN, TiNC, CrN/TiNC, TiN/TiNC films on 9Cr18 steel by PVD**

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TiN, TiNC, CrN/TiNC and TiN/TiNC films were deposited on 9Cr18 steel using magnetron sputtering technique. The morphology, composition, chemical state and crystalline structure of the films were observed and analyzed by X-Ray photoelectron spectroscopy (XPS), X-Ray diffraction (XRD) and scanning electron microscopy (SEM). Hardness and adhesion force were tested by nanoindentation and scratch tester, respectively. The friction and wear behavior of TiN, TiNC, CrN/TiNC and TiN/TiNC films sliding against GCr15 balls were investigated and compared synthetically using ball-on-disk tribometer. It was found that Ti-N, Ti-C, Ti-N-C and C-C bonds were formed. The TiN/TiNC film was composed of TiN, TiC and TiNC phases. Hardness and adhesion force results indicated that although the TiN film possessed the highest hardness, its adhesion force was lowest among all the films. Tribological test results showed that the friction coefficient of TiN/TiNC was much lower than that of TiN and the wear rate decreases remarkably from $2.3 \times 10^{-15}$ m$^3$/Nm to $7.1 \times 10^{-16}$ m$^3$/Nm, which indicated the TiN/TiNC film has better wear resistance.

**Keywords**
TiN films
structure
friction
wear
Black aluminium thin films prepared by magnetron sputtering

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Black aluminium thin films were prepared by means of pulsed DC magnetron sputtering. The films were deposited from pure aluminium target and their properties modification is reached by proper variation of deposition conditions, such as adding nitrogen to argon working gas of partial pressure from $5 \times 10^{-4}$ Pa to $2 \times 10^{-2}$ Pa. The total pressure varied from 0.1 Pa to 10 Pa. The deposited black aluminium thin films exhibit, due to specific surface micro-nanostructure, excellent absorptivity in UV-VIS-IR electromagnetic radiation spectral regions. The evolution of the film properties with thickness and temperature was examined. The film properties were characterized by spectrophotometry, AFM, SEM, XRD, photoelectron spectroscopy and positron annihilation spectroscopy.

The deposition method allows effective, low cost fabrication of the coating on several kinds of substrates (eg. glass, fused silica, quartz, copper and stainless steel) and it is also suitable for large area substrates coating. The coating could find application as absorbers of electromagnetic radiation, plasmonics, detectors and chemical sensors.

**Keywords**
magnetron sputtering
black aluminium
nitrogen
absorptive coating
Hard (Zr,Ti) alloy films with small amount of oxygen resistant to cracking

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The poster reports on the effect of the addition of small amount of oxygen into Ar sputtering gas on the microstructure, mechanical properties and macrostress of the (Zr,Ti) alloy films prepared by DC magnetron sputtering. It was found that the addition of small amount of oxygen into Ar sputtering gas makes it possible to sputter nanocrystalline (Zr,Ti,O) alloy films with high hardness $H > 10$ GPa, high ratio $H/E^* \geq 0.1$, high elastic recovery $W_e \geq 60\%$ and enhanced resistance to cracking; here $E^*$ is the effective Young's modulus. The main result of the presented investigation is the demonstration that the incorporation of a small amount of O into a (Zr,Ti) alloy film is a very effective way to form the flexible (Zr,Ti,O) alloy films with enhanced resistance to cracking. [1]


Keywords
(Zr,Ti,O) alloy films
Structure
Microstructure
Mechanical properties
Resistance to cracking
Photoactive TiO\textsubscript{2} and Ta doped TiO\textsubscript{2} 1D nanotubes grown by electrochemical anodization of Ti and TiTa films deposited by DC pulsed magnetron sputtering on FTO transparent substrates

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The self-organizing electrochemical anodization yielding 1D nanostructures such as nanotubes of various metal oxides and their doped versions is relatively well-established process. These nanoarchitectures are being increasingly utilized for photonic applications such as photocatalysis and photoelectrochemistry due to very high specific surface area enhancing the solar harvesting efficiency and superior charge transfer performance. In this work we describe a novel approach to obtain 1D TiO\textsubscript{2} nanotubes directly grown on FTO glass, which represents suitable transparent substrate for aforementioned photonic applications. In this two-step approach we first deposited pure Ti and TiTa layers by a DC pulsed magnetron sputtering. These films were next transformed to the nanotubes by an electrochemical oxidation process. We investigated the correlations among deposition plasma parameters (deposition pressure, temperature of substrate, applied power, and a plasma activation of FTO substrate prior to the deposition), properties of the deposited Ti and TiTa films (crystalline structure, density, adhesion to the substrate, density of pinholes, etc.), and structural (crystallinity, adhesion to the FTO substrate, density of defects, etc.) and particularly functional (photoelectrochemical characteristics) properties of the grown TiO\textsubscript{2} based nanotubes. The films prepared were described by a broad portfolio of characterization techniques involving XRD, Raman spectroscopy, SEM, HRTEM, XPS, tribology measurements, etc. The functional properties were examined based on PEC measurements involving linear sweep voltammetry, chronoamperometry, OCP, IPCE, impedance spectroscopy, and hydrogen evolution.

Keywords
Magnetron sputtering
Nanotubes
Anodization
Thin films
Photoelectrochemistry
Tunable optical and electrical properties of IGZO thin films prepared by reactive HiPIMS

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We report on the tunable optical and electrical properties of transparent semiconducting amorphous indium gallium zinc oxide (IGZO) thin films prepared by high power impulse magnetron sputtering (HiPIMS). Transparent semiconducting amorphous IGZO films have attracted great attention due to their excellent electrical properties and possible utilization in thin film transistors or in photovoltaic applications. It is known that the properties of IGZO films are highly sensitive to process parameters, especially to oxygen partial pressure. In order to reach tunable properties of transparent IGZO films we have employed HiPIMS which is very suitable and progressive method for preparing high-quality oxide layer. This is mainly due to a high degree of ionization of target material particles in the discharge plasma and associated high ion-to-atom ratio in particles flux toward the substrate. These features lead to formation of very dense films structure. Moreover, enhanced kinetic energy of particles impacted onto growing film deliver significant amount of energy promoting the growth of the films and is very important especially in the case of deposition on heat sensitive substrates. In this paper we show the use of reactive HiPIMS is an effective way to produce IGZO films, and that the value of pulse-averaged target power density being in the range of 100-1020 Wcm\(^{-2}\) (which is two orders of magnitude higher compare with the conventional dc or RF magnetron sputtering) and the repetition frequency are suitable parameters for controlling the optical and electrical properties of the IGZO films. Correlation between plasma discharge parameters and electrical and optical properties of deposited films will be discussed and explained in details.

Keywords
HiPIMS
IGZO
tunable properties
reactive sputtering
Optical and electrical properties changes induced by cation size in rare-earth vanadates REVO3 (RE : La, Pr, Nd and Sm)

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Conventional solar cells have limited energy conversion efficiencies because photons with energy lower than the band gap are not absorbed by the system and those with higher energies are inducing phonons. A possible way to improve the efficiency of solar cells consists in using multi-junctions with several layers, covering the largest range of the solar spectrum. In this way Mott Insulators have been proposed as solar-absorbers because their property of carrier multiplication could be efficient [1]. LaVO₃ is among those which could be interesting, with an indirect forbidden band gap of 1.1 eV and a good absorption coefficient [2] which seems optimal according to the Shockley-Queisser limit [3]. In the same view other rare-earth vanadates (REVO₃, where RE: Pr, Nd or Sm) could be interesting.

Usually crystallized rare-earth vanadates films are deposited by ALD, MBE or obtained with powder reactions. After studying the conditions of co-sputtering for each system (metallic and poisoned regimes) we propose a two-step method to obtain REVO₃ thin films. Thin films of REVO are first sputtered and both RE/V atomic ratio and film thickness are evaluated by a Scanning Electron Microscope (SEM). Then to get crystallized REVO₃ we use an external annealing in a reducing atmosphere composed of a mix of Ar and H₂.

Films are analyzed by the use of X-Ray diffraction (XRD), X-ray Photoelectron Spectrometry (XPS), Fourier Transform InfraRed spectroscopy (FTIR) and finally resistivity measurements to know what the cation size effect on the obtained properties is.

Keywords
solar perovskite
solar material
oxides
vanadate
thin films
Deposition of Oxyfluoride Thin Films by Cold Plasma Process for the Energy and Environment Domain

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Thin films are important because they offer the potential for low-cost processing with minimal material usage while fulfilling application requirements. One of the most significant applications is the production of renewable energy such as solar energy conversion and water splitting (photocatalysis). Recently, layered bismuth oxyhalides BiOX (X: Cl, Br, I, F), a family of semiconductor photocatalyst materials had attracted significant interest for use in environmental remediation. Compared to the other bismuth oxyhalides, BiOF had been scarcely reported. Therefore, our challenge is to master the synthesis of oxyfluoride thin films by sputtering bismuth target in Ar/O₂/CF₄ radiofrequency magnetron plasmas. By plasma sputtering, interesting materials are obtained due to the possibility of tailoring their optical and electrical properties by changing the stoichiometry of the deposit. However, the major disadvantage during the reactive sputtering process is due to target poisoning. Hence, in a first step, the reactivity of oxygen and fluorine gas on the bismuth target as well as the change from elemental to compound sputtering mode were studied by optical emission spectroscopy which is a powerful technique to study the composition of the sputtering atmosphere. Nature of bonds between Bismuth and other elements have been determined from different techniques (IR and Raman spectroscopies, XPS) whereas the elemental composition was confirmed by Rutherford backscattering spectroscopy (RBS). Moreover, the optical properties, such as the refractive indices and the optical band gap, were deduced from UV-visible spectroscopy and ellipsometry. Finally, to go further, the photocatalytic activity of the deposited films will be presented upon degrading universal organic pollutants.

Keywords
reactive sputtering
thin films
bismuth oxyfluoride
energy
photocatalysis
PO2012

**Sputtering and evaporation mechanisms in magnetron process using a hot target**

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Disconnecting the target from the water cooled-magnetron is known to enhance the deposition rate especially for oxide thin film [1]. This also leads to the improvement of the thin film quality [2] that could come from the infra-red light emitted by the hot target [3]. Bleykher et al have recently proposed a model of heat and erosion processes [4-5]: they showed that the growth rate increase at high temperature is due to the evaporation of the hot target. In this model, the ions accelerated through the plasma sheath transfer kinetic energy to the target leading to its temperature rise. The target power is mainly released by radiative emission $P_{\text{rad}}$ and species ejection (sputtering $P_{\text{sput}}$ and evaporation $P_{\text{evap}}$). We improved this model to take into account the temperature dependence of the sputtering mechanism/yield (issued from a molecular dynamic simulation [6]). The poster will present the whole model and the influence of the process parameters (as the power) on different parameters: temperature, $P_{\text{rad}}$, $P_{\text{sput}}$, $P_{\text{evap}}$, atomic flux leaving the target and global power transferred to the substrate $P_{\text{sub}}$. Four metals will be investigated (Cu, Zn, Ti, Ni) having different saturated vapor pressures, sublimation temperatures, surface binding energies, heat capacities and thermal conductivities. Finally, the results will be compared to the experimental ones regarding the deposition rate and $P_{\text{sub}}$.


**Keywords**
Magnetron
hot target
Mechanical properties of sputter deposited (Zr,Y)N thin films

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Transition metal nitrides (TMN) coatings have been deeply studied for their mechanical properties and oxidation resistance over several tens of years. Great achievements have been obtained those last 20 years, by the synthesis of nanocomposite films by adding a third or more elements to TMN. More recently, new applications of TMN coatings in the field of solar energy and plasmonics have been proposed and give rise to new interesting investigations. This poster aims to study the effect of Y doping on the structural and mechanical properties of ZrN-based films devoted to plasmonic purposes. Zr-Y-N films with different Y contents, up to Y/(Zr+Y) = 50 at.% have been elaborated by co-sputtering Zr and Y targets in reactive mixtures of Ar+N\textsubscript{2}. It was observed that the NaCl B1-type structure of ZrN was conserved in the whole range of Y contents showing a linear increase of lattice parameter of the (Zr,Y)N solid solution. Variations of Young’s moduli values E and hardness H of the films were estimated based on the Oliver and Pharr method by using a CSM ultra-nano hardness-tester (UNHT) equipped with a Berkovitch indenter tip working at ultralow loads in the range of 200-1000 µN. Young’s moduli were also assessed by using scanning acoustic microscopy (SAM) as a complementary technique. The results showed the necessity of using a more stringent criterion that the Bückle’s law used for hardness assessments and that E slowly decreased with Y content in the whole range of Y contents.

Keywords
Reactive Sputtering
Films
Mechanical Properties
Zr-Y-N
UNHT
Effect of tantalum addition on Cu-Zr binary glass metallic thin films properties.

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Bulk metallic glasses (BMGs) have attracted considerable attention due to their high strength, superior elasticity, and high corrosion resistance. However, the poor room-temperature deformability and fatigue properties of these alloys make their applicability restricted. Tantalum addition seems to reduce the density of free volume and the formation of shear band which lead to the enhancement of the mechanical properties of metallic glasses thin films [1]. Therefore, the aim of this work is to investigate the effect of tantalum addition on the mechanical properties and thermal stability of Cu-Zr binary metallic glass thin films.

Cu-Zr-Ta ternary metallic glass thin films were successfully deposited by magnetron sputtering. The effects of tantalum addition on the microstructure, morphology and mechanical properties of these coatings are reported. Nanoindentation tests were performed in order to determine hardness and Young modulus. X-ray diffraction XRD and EDS electron dispersive spectroscopy analysis were also used to investigate the chemical composition and structure of coatings. A particular attention has been paid to the ductility of the deposited thin films by carrying out of compressing micro-pillars, obtained by FIB, test.

Keywords
metallic glasses
thin films
PVD
magnetron sputtering
Effect of substrate bias on the growth behavior of iridium on A-plane sapphire using radio frequency sputtering at low temperatures

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As for many other noble metals, the electronic structure, surface energy, and catalytic activity of the iridium surface strongly depend on its crystallographic orientation. However, it is often elaborate and expensive to manufacture single crystal surfaces with specified crystallographic orientations. One approach to overcome this problem is the heteroepitaxial growth of metal films on dielectric substrates. The heteroepitaxial growth of such films usually requires deposition conditions close to the thermodynamic equilibrium, i.e. deposition at high substrate temperatures and very low deposition rates [1,2].

In this study we present results on the investigation of the substrate bias effect on the growth behavior of iridium films deposited on A-plane sapphire by radio frequency (rf) sputtering at low substrate temperatures. Iridium thin films deposited without substrate bias were compared to films deposited with simultaneous application of a second rf-plasma on the substrate. The morphology, crystallinity, and crystallographic orientation of the resulting films were characterized by scanning electron microscopy, X-ray diffraction, and electron backscattering diffraction. We find that the application of an additional substrate bias leads to the generation of ordered nuclei with preferential crystallographic orientation and thus strongly affects the growth behavior of iridium (001) on sapphire (11-20). In this way, the fabrication of well-ordered thin films of Ir with large (100)-domains becomes feasible even at high deposition rates and at substrate temperatures as low as 350 °C [3].


Keywords
Bias-assisted rf-sputtering
Iridium
heteroepitaxy
ion assisted film growth
low temperature
Influence of reactive oxygen species during deposition of iron oxide films by high power impulse magnetron sputtering.

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Iron oxide films were deposited using high power impulse magnetron sputtering (HiPIMS) of an iron cathode in an argon/oxygen gas mixture at different gas pressures (0.5 Pa, 1.5 Pa, and 5.0 Pa). The HiPIMS system was operated at a repetition frequency f = 100 Hz with a duty cycle of 1 %. A main goal is a comparison of film growth during conventional and electron cyclotron wave resonance-assisted HiPIMS. The deposition plasma was investigated by means of optical emission spectroscopy and energy-resolved mass spectrometry. Active oxygen species were detected and their kinetic energy was found to depend on the gas pressure. Deposited films were characterized by means of spectroscopic ellipsometry and grazing incidence x-ray diffraction. Optical properties, stoichiometry, and crystal structure of as-deposited films were found to depend on the deposition conditions. Deposition of hematite iron oxide films with the HiPIMS-ECWR discharge is attributed to the enhanced production of reactive oxygen species.

Keywords
HiPIMS
iron oxide
optical emission spectroscopy
mass spectrometry
XRD
Electrical and optical properties of hydrogen- and niobium-doped TiO$_2$ electrodes

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Hydrogen-doped titanium oxide (THO) and niobium-doped TiO$_2$ (TNO) films are of interest for various applications which require transparent conductive electrodes, i.e., photovoltaics [1], light emitting diodes [2], display technology [3], and solar water splitting devices [4]. The films were prepared by reactive magnetron sputtering from metallic targets (titanium and titanium-niobium alloys) as well as from ceramic targets (TiO$_x$ and TiO$_x$:Nb) in different sputter gas mixtures (argon/oxygen, argon/oxygen/hydrogen, and argon/H$_2$O vapour) onto unheated substrates. The as-deposited films were amorphous, as shown by Raman spectroscopy and X-ray diffraction, and exhibited a high resistivity in the order of 10 to 10$^5$Ωcm. By a subsequent annealing in vacuum at 460 °C for 2 min, the films became polycrystalline with large crystallites (> 10 µm; anatase phase), accompanied by an increase of the optical transparence and the electrical conductivity. The niobium-doped as well as hydrogen-doped films on borosilicate glass stand out due to their low resistivities ($\approx$1-6·10$^{-3}$Ω cm), high carrier mobilities ($\approx$8-12 cm$^2$V$^{-1}$s$^{-1}$) and low optical absorption (k < 0.008) at a wavelength of 550 nm). In this study, the influence of the dopant element concentration (Nb, H) in polycrystalline anatase films on the electrical characteristics (Hall and conductivity measurements) as well as optical properties (UV/VIS/NIR) were investigated in detail.


Keywords
TiOx
TCO
Hydrogen
Water
Niob
E-beam evaporation vs. rf-sputtering: Comparing the growth behavior, crystallinity, and morphology of heteroepitaxial iridium (001) films on sapphire (11-20)

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Many characteristics of the metallic surface i.e. the electronic structure, surface energy, and catalytic activity, strongly depend on the crystallographic orientation. To control and define the crystallographic orientation of a metallic surface is thus important in applications ranging from electronic device fabrication to catalysis. (100)-oriented iridium films are of economic interest for the growth of single crystalline diamond substrates or ferroelectric PZT-films [1]. A possible synthetization route is the heteroepitaxial growth of iridium thin films on single crystal oxides. This is often done by e-beam-evaporation [2] at high substrate temperatures (> 600 C°-800°C) and low deposition rates (< 1nm/min). However, regarding e.g. industrial production processes, an alternative deposition technique with significantly lower substrate temperatures and higher deposition rates would be desirable. When compared to e-beam-evaporation, it is expected that e.g. sputtering allows for an enhanced control of microstructure and intrinsic stresses in the deposited films even at relatively low substrate temperatures but also leads to a higher number of growth defects. In this study we therefore compared the growth behavior, crystallinity, and morphology of e-beam evaporated iridium films with bias assisted rf-sputtered iridium films. For e-beam-deposition, we varied the substrate temperature and the evaporation rate, for sputtering, we varied also the substrate temperature, the deposition power and working pressure. XRD revealed in both cases a strong preferential (100)-orientation whereas SEM and EBSD-investigations confirmed large (100)-grains with small mosaic spread.


Keywords
Bias-assisted rf-sputtering
e-beam evaporation
growth behavior
Bismuth vanadate (BiVO$_4$) thin films were prepared by radio frequency (RF) plasma sputtering in reactive Ar/O$_2$ atmosphere using two separate targets of Bismuth oxide and Vanadium. The coatings were deposited both on silicon, soda-lime glass and FTO glass. The as-grown films were converted from amorphous to crystalline by a post deposition annealing in air at 400 °C for 2h.

The samples were characterized by X-ray diffraction, scanning electron microscopy, UV-Vis and energy dispersion spectroscopy. The characterization of the specimens showed a crystallized monoclinic structure and a good light absorption in the visible range. In fact the optical band gap deduced from the reflectance spectra was 2.5 eV. Preliminary tests demonstrate that BiVO$_4$ thin films are photocatalytically active and able to inactivate bacteria.

Keywords
Magnetron Sputtering
BiVO4
Photocatalysis
Antibacterial
High deposition rate magnetron sputtering

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Among all PVD technologies, magnetron sputtering stands out with high quality and versatility of the produced coatings. Recent advancements in high-power impulse magnetron sputtering improved sputtering process and coating properties even further, making it highly desirable for many applications. However, most common disadvantage of the magnetron sputtering — low coating deposition rate — in many areas inhibits technology transition to mass-production due to low cost efficiency. Main cause of slow coating deposition is low discharge power density — conventional magnetron sputtering operates at power density in the range 1 — 50 W/cm$^2$, and, while HIPIMS peak power density can reach several kW/cm$^2$, average power rarely exceeds 50 W/cm$^2$ resulting in low deposition rate of 1 — 2 µm/h per cathode in 1-D rotation.

High deposition rate magnetrons [1] can withstand average power densities much more than HIPIMS in continuous mode due to special design and effective cooling system, which leads to significant deposition rate increase up to 20 µm/h per cathode for metallic coatings and 10 µm/h per cathode in 1-D rotation for composite and complex composition coatings, making magnetron sputtering technology feasible for mass-production in almost any area. Moreover, equalization of sputtering rates for different materials is observed at power densities exceeding 50 W/cm$^2$ in multi-component targets. Thus, multi-element coating composition can be easily controlled via target design.


Keywords
high deposition rate
magnetron
mass production
mosaic targets
**The trajectory of the secondary electrons in the magnetic field and this determines the form of the erosion race track in a magnetron cathode**

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Magnetron sputtering involves the collision of gas ions from a magnetically confined plasma with the surface of the cathode target, with this resulting in the emission of atoms from the target towards the substrate. The shape of the racetrack in the target is dependent on the distribution of the ions incident on the target, and this depends on a combination of the strength and configuration of the magnetic field. In this study we have measured the spatial distribution of the magnetic field of different diameters and types of magnetron cathodes, each of different maximum magnetic fields. We compared that magnetic field data with the geometry of the erosion racetrack in the corresponding targets. The results showed that the inner and outer edges of the racetrack correspond to given value magnetic field vectors. We report the relationship between the configurations of the racetrack profile and the magnetic field. We have also simulated the trajectories of the secondary electrons emitted from the cathode surface and relate these to the form of the plasma and the lateral distribution of the energy of the ions incident on the target.

**Keywords**
Magnetron sputtering
racetrack
magnetic field
Morphology and thermal emissivity study of multilayer PVD metal-oxide/diacrylate polymer onto different plastic substrates/parts for automotive industry

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The automotive sector has made efforts to obtain high-quality chrome-like coatings that might replace metal parts in the vehicle interior. Chromium-free solutions are a demand in the last years due to European requirements regarding the removal of hazardous substances in vehicles production. Currently, alternative solutions without hexavalent chromium can be found. Nevertheless, there’re still gaps, particularly related to the industrial manufacturing process but also on the chromium-like brightness effect and metallic cool touch. Plastic interior components, used in automotive industry, do not present the same cool touch as metals at room temperature. Therefore, we expect to develop a multi-thin coating thru Physical Vapour Deposition (PVD) to enhance the thermal and aesthetical properties of chromium-free plastic parts for automotive interior.

In this work, we present a comparative analysis of metal-oxide/diacrylate polymer multilayer (PML) coated onto injected plastic parts for automotive interior, specifically compositions of acrylonitrile butadiene styrene (ABS) with polycarbonate (PC), and polyamide (PA). For characterization, planar set injected structures and injected 3D plastic parts were considered. Morphology and microstructure of the films and surface topology of the metal-oxide and PML films were studied using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Contact angle, energy surface (ES) and Adhesion (ASTM D3359 7) tests were also performed. As an evaluation of the performance of the coating, a thermal emissivity study was performed (ASTM C1371 - 04a) for the different plastic parts.

With these results we expect to deliver innovative sustainable and high-performance chromium-like, and chromium-free, plastic components for the automotive interior.

Keywords
Metal-Oxide/Diacrylate Polymer Multilayer
PVD
Metalized Parts/Substrates
Thermal Emissivity and Morphology
Chromium-Like
Zr and Mo thin films with reduced residual impurities’ uptake under high vacuum conditions at room temperature

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In recent years, refractory metals, such as molybdenum (Mo) and zirconium (Zr), have been studied as infrared (IR) reflectors in solar absorber applications [1, 2]. The sputter process parameters are very important for depositing a high-quality thin film achieving the necessary low emittance. IR reflectance of the metal film is influenced by the film microstructure, presence of residual impurities and surface roughness. The main objective of the present study is to prepare Mo and Zr metallic thin films with improved optical properties by high-power impulse magnetron sputtering (HiPIMS) at room temperature under high-vacuum conditions. In comparison to the Mo and Zr thin films deposited by direct current magnetron sputtering (dcMS) at the same average power, thin films deposited by HiPIMS exhibit a dense microstructure without voids, grow preferentially in out-of-plane direction, have smooth surface and are free of residual contaminants. Compared to the dcMS films, we observed an element-specific reduction of impurities measured by elastic recoil detection analysis (ERDA) by a factor of 4 or 8 for N, 3 or 4 for H and 9 or 14 for O for Mo and Zr thin films, respectively. The compositional effects are correlated with differences in the film morphology and microstructure revealed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis.

Financial support by the EU, grant No.645725, project FRIENDS2, is gratefully acknowledged. This work was supported by the SRDA under the contract No.APVV-15-0168. [1]H.Liu et al., Optimization of AlCrO-based absorber with Mo infrared reflector for solar selective applications, Vacuum128(2016)27 [2]B.Usmani et al., Optimization of sputtered zirconium thin films as an infrared reflector for use in spectrally-selective solar absorbers, Thin Solid Films627(2017)17

Keywords
refractory metallic thin films
HiPIMS
residual impurity
Growth of porous thin films by reactive magnetron sputtering using particle collimators

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In this paper we have analyzed the influence of particle collimators to selectively deposit species with preferential directionality in the magnetron sputtering deposition of thin films. Using wisely-designed collimators, tilted nanocolumnar morphologies are grown in a ballistic deposition regime, i.e. when most deposition species arrive at the film surface along well-defined oblique preferential directions, and also in a thermalized deposition regime, when these species follow an isotropic momentum distribution in the plasma gas. The obtained results suggest that the use of particle collimators may promote the growth of porous thin films even in the classical magnetron sputtering configuration, when the target and the substrate are parallel. General insights are given on this approach and, as a proof of concept, its principles applied for the synthesis of nanostructured films in a laboratory-size reactor. Evidences of this possibility have been obtained for a series of TiO₂ thin films prepared with this methodology. These results have allowed the extension of this technique to other plasma-assisted deposition methods, such as Plasma Enhanced Chemical Vapor Deposition (PECVD).

Keywords
Porous Thin Films
Magnetron Sputtering
Particle Collimators
Directionality Control
Nanocolumns
Enhanced ion assistance during the deposition of hard metal nitrides with HiPIMS voltage reversal – 30% increase of deposition rate.

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This paper demonstrates the benefits of combining positive reverse pulses in HiPIMS plasmas for the deposition of hard metal nitrides. The higher ion bombardment to the growing films, gives rise to higher ion incorporation into the growing film, i.e. higher deposition rate, as well as enhanced coating microstructural and mechanical properties. Two different industrial coating systems were used for the deposition of both titanium Nitride and Tantalum Nitride. Thickness, microstructural and compositional studies were performed for the coatings deposited with and without voltage reversal. In all cases, the coating deposition rate is higher when the positive voltage reverse is applied. It significantly increases up to 30% which is associated to the enhanced ion incorporation to the growing film. Changes in the microcrystalline structure as well as increased coating nanohardness are observed with the positive pulse application.

Keywords
enhanced dep rate
hipims
metal nitrides
hard coatings
We analyze an undesired phenomenon that takes place when growing porous/compact multilayer systems by alternatively using the oblique angle and the classical configuration by magnetron sputtering. We show that compact layers develop numerous fissures rooted on the open porous structures of the layer below, in a phenomenon that becomes amplified when increasing the number of stacked layers and that might cause the loss of structural control. An undesired phenomenon found in thin films and multilayers intended for photonic applications (e.g., antireflective coatings, 1D- Bragg mirrors and microcavities, etc.) is the condensation of water within the pores that makes the optical behaviour of the systems unpredictable and may lead to their accelerated degradation. In this work we propose a strategy to minimize this phenomenon by growing a thin and continuous accommodation layer on top of the porous film under the impingement of plasma ions, where the compact layer may subsequently grow homogeneously. This approach has been tested in practical situations by growing compact TiO$_2$/porous SiO$_2$ and porous SiO$_x$/porous SiO$_2$ multilayer systems intended for advanced photonic, optofluidic and near-IR mirror applications, from which preliminary results will be also presented. In these system a precise control over the microstructure and optical properties of the films/multilayers has been achieved using the said accommodation layer strategy.

**Keywords**
Porous Film
Multilayer Structures
Photonic Crystals
Humidity Tightness
OAD
Avoiding Target Poisoning in Reactive Magnetron Sputtering Depositions at Oblique Angles

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Target poisoning in reactive magnetron sputtering (rMS) deposition of thin films is an undesired phenomenon that leads to a significant drop of the process efficiency and the growth rate. It is also responsible for the appearance of hysteresis phenomena and reactor instabilities that may lead to quite different growth conditions upon fluctuations of process parameters. In this presentation we show a versatile and easy to implement method that, relying on the oblique angle geometry, overcomes the aforementioned drawbacks and enables the growth of stoichiometric and sub-stoichiometric materials by rMS in the non-poisoned mode of the target. The possibility to operate in non-poisoned conditions permits to achieve growth rates that outmatch those found when the classical approach is followed, i.e. when using a higher flux of reactive gas and a poisoned target. This method can also be exploited in rMS depositions to tune the film stoichiometry. We have employed amorphous TiO\textsubscript{x}, although the presented results can be easily extrapolated to other materials and conditions. It is found that the proposed method improves 400\% the growth rate of TiO\textsubscript{2} thin films.

Keywords
Reactive Magnetron Sputtering
Porous Thin Films
Stoichiometry Control
Oblique Angle Deposition
Target Poisoning
Structural and optical characterization of Cr\textsubscript{1-x}Al\textsubscript{x}(O)N films prepared by HiPIMS

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Cr\textsubscript{1-x}Al\textsubscript{x}(O)N coatings were deposited by reactive magnetron sputtering on different substrates using high power impulse (HiPIMS) and DC sources. Different experimental conditions like nitrogen fluxes and pulse parameters were investigated in order to obtain variable chemical compositions and microstructure. Elemental compositions of these films were assessed by electron probe microanalysis and electron energy-loss spectroscopy (EELS). Scanning electron microscopy revealed a columnar film growth with variable topography depending on the synthesis parameters. X-ray diffraction and high-resolution electron microscopy studies allowed determining the crystalline phases present in the films while EELS spectroscopy gave information about the nature of the amorphous phases. Optical characterization of the films has been performed in the UV-VIS-NIR wavelength range. The oxidation resistance and long term thermal stability in air has been evaluated at 700°C on stainless steel. Different optical and thermal behaviours are obtained depending on the stoichiometry. The absorptance is also calculated in order to explore the use of these films as components for high temperature solar absorbers and solar selective tandem absorbers.

Keywords
CrALN(O)
Magnetron Sputtering
HIPIMS
Microstructural characterization
Thermal stability
Optimization of plasma assisted reactive sputter deposition processes for optical coatings

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In order to meet the challenging requirements of optical coatings for modern applications, advanced methods of process optimization and state of the art deposition tools must be used. Besides other thin film coating technologies such as evaporation and PECVD sources, the Evatec AG develops innovative reactive sputter deposition sources. These sources are often combined with plasma sources for an additional plasma treatment of the growing film, altering the film properties. Here, the effect of an additional capacitively coupled radio frequency plasma on both the deposition process and the resulting thin film is presented. The sputter plasma and the plasma source are active at the same time in the same vacuum environment, allowing for an effective interaction. Hence, the substrates, which are loaded on a rotating turn table, are repeatedly exposed to both the sputter source and the plasma source. Depending on the conditions, the additional treatment by the plasma source may affect the deposition process physically by the energetic ions generated as a significant part of the quasi-neutral plasma beam, that bombards the surface, and chemically by generating reactive species such as atomic oxygen. A significant interaction is observed between the auxiliary rf plasma and the dc pulsed sputter plasma, where an active process control of the reactive gas flow is utilized to optimize the overall sputter conditions as well as the process rate. The plasma source and its interaction with the sputter source are characterized utilizing various diagnostic approaches, such as voltage and ion energy measurements as well as optical emission spectroscopy. Finally, the benefits in the properties of thin films grown in such processes with additional plasma treatment are highlighted. It is demonstrated, that optical single- as well as multi-layer systems of silicon dioxide and amorphous hydrogenated silicon with excellent uniformity at very low levels of stress, roughness, and absorption in a reproducible way.

Keywords
reactive sputtering
plasma assisted deposition
capacitive radio-frequency plasmas
pulsed discharges
optical coatings
Increasing the thermal stability of thin films by incorporating co-sputtered nanoparticles

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A new class of nanocomposite materials is created by PVD sputtering a matrix and simultaneously co-sputtering nanoparticles at ambient temperature, enabling the incorporation of nanoparticles into a material in any combination that can be magnetron sputtered.

Current nanoparticle addition methods are limited by the material combinations, thermodynamic considerations and distributions which can be produced. In addition, nanoparticle agglomeration, size and concentration characteristics are often difficult to control.

Using the combination of a classical PVD sputtering magnetron and a nanoparticle source, free control in size and distribution is demonstrated for any choice of sputterable material. The nanoparticle generator operates based on an adaptation of classical magnetron sputtering by forcing agglomeration of the sputtered ions into particles via terminated gas condensation. A quadrupole mass filter is incorporated into the system to measure nanoparticle size distribution and flux during a process, in-situ optimization of process parameters, and a filter to obtain desired size.

To successfully integrate the nanoparticles into the matrix, the pressure set points of various regions of the vacuum system were optimized. These include the nanoparticle aggregation, the substrate zone, the magnetron sputtering the matrix material, and the trajectory of the particles starting from the aggregator exit aperture travelling via the mass spectrometer.

In this work, W nanoparticles were co-deposited into a magnetron sputtered Cu matrix. A random distribution of particles and a 4 nm average diameter was observed by transmission electron microscopy. The spatial distribution can be controlled by varying the deposition parameters. By vacuum annealing we showed that the nanoparticles stabilized the Cu grains up to 500 ºC; while the Cu film without nanoparticles underwent substantial grain growth. The introduction of less than 1 vol.% of nanoparticles was sufficient to keep the nanocrystalline structure of the Cu film unaffected.

Keywords
nanocomposite
nanoparticles
Titanium coating of ceramics for vacuum chambers for PSB RF system

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In the framework of the Large Hadron Collider Injectors Upgrade (LIU), CERN is replacing the RF cavities of the Proton Synchrotron Booster (PSB). The vacuum chambers of the RF system are composed of stacks of 6 ceramic rings, separated by stainless steel tubes, for a total length of about 1 meter. In order to prevent charge build-up on the inner walls of the ceramics during operation and to reduce electron multipacting, a high resistivity titanium thin film is needed on the internal surface of the ceramic rings.

A two-step coating process was developed. First, before brazing the stainless steel tubes to the ceramic rings, a low resistivity Ti coating (in the range of 50-100 Ohm) is applied to the chamfered extremities of the ceramic rings by planar magnetron sputtering. The role of this first coating is to ensure a good electrical contact between the stainless steel tubes and the high resistivity film (10 MOhm / square) to be deposited in the second step, once the mechanical assembly of the chambers is finished. In this second step, each ceramic ring is coated individually by a movable cylindrical post magnetron-sputtering source to guarantee the specified electrical resistivity.

In this work, we describe the two-step coating process, the coating system and the status of the production of 28 PSB RF vacuum chambers.

Keywords
magnetron deposition
particle accelerator
cylindrical configuration
**Growth Morphology of AlN Thin Films Deposited by Reactive DC Magnetron Sputtering and its Influence on the Piezoelectric Properties**

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Aluminum nitride (AlN) is a piezoelectric material and is widely used in microelectronics, electroacoustic and optoelectronics. AlN thin films are commonly deposited by magnetron sputtering, which readily allows their integration into, for example, MEMS devices. Control of the microstructure and microchemistry is essential to achieve a good performance. In magnetron sputtering ions impacting on the growing film can be used favorably for this purpose. In this work we study the AlN thin film growth morphology and its correlation to piezoelectric properties under the influence of low energy ion bombardment.

Our setup includes an electromagnetic coil that allows varying the ion to neutral ratio by more than one order of magnitude. A change in the residual stress of AlN thin films from tensile to compressive is observed for an increasing ion flux. This goes along with a transition in the growth morphology from open grain boundaries towards dense films. The impact of these changes on the piezoelectric properties of AlN thin films is discussed and possible applications for scanning probe microscopy are presented.

**Keywords**
Magnetron Sputtering
Thin Films
Aluminium Nitride
Magnetic Configuration
Piezoelectricity
**Physical and tribological properties of sputtered silicon-containing carbon coatings at high temperatures**

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Sputtered carbon coatings have excellent tribological properties, such as high wear resistance and low friction at room temperature. In a number of end-use applications, there is a need to extend these properties to higher temperatures. It has been shown that inclusion of silicon in the coating can extend the working temperature of sputtered carbon coatings [1,2]. This work focuses on evaluating the high temperature performance of carbon coatings with varying silicon contents. Differential scanning calorimetry was used to study the transition temperatures in the coatings, hence establishing the working temperature range for each coating. High-temperature tribological tests evaluated the mechanical performance. The effect of silicon addition on the structure of coating was investigated using Raman spectroscopy. Increasing the silicon content improved the thermal stability of the coatings and shifted the oxidation to higher temperatures. It also affected the wear properties. The optimum silicon content and deposition parameters were established to obtain the required performance. The optimum coating showed excellent low friction properties at 325 °C.

References:

Keywords
Magnetron sputtering
Graphitic carbon
Tribology
High temperature
The double glow plasma surface metallurgy technology, or Xu-Tec, has been continuously developing into many applications with the deeper and wider coverage. With the advancement of our modern industry, high demands for surface engineering technology have been put forward. The research and application of the Xu-Tec process of modern surface metallurgy technology in many non-ferrous materials have opened very broad development space in the future. This article introduces the research achievements in the surface alloying by the Xu-Tec process on non-ferrous materials, such as copper and its alloys, niobium, molybdenum, tungsten.

**Keywords**
double glow plasma
non-ferrous
surface alloying
Gradient metal films on ceramic surface have very important application prospects in the material engineering development. This article introduces the research achievements in the surface alloying by the Xu-Tec process on ceramic materials. In addition, the experimental device, processing procedure, and technological parameters of ceramization and metallization are described. Their mechanical properties of the formed surface ceramic and metal layer, such as surface hardness, wear and abrasive resistances, and adhesion enhancement, are presented.

**Keywords**
Xu-Tec
ceramic surface
Gradient metal film
High speed gear hobbing with customized AlCrBN coatings

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In 2017 the automobile production and therefore also the transmission production exceeded 90 million. With automobile gearboxes containing 20 or more single gears, this adds up to nearly two billion manufactured gears per year, alone in this industry sector. Further advancing fields of high performance gear application are aero-engines and wind turbines. Regarding green manufacturing gear hobbing processes are applied most often in these kinds of larger batch productions. Within this process, cutting conditions regarding chip thickness and cutting length change continuously with every generated chip. Hence, the load on the cutting edge varies critically too and affects abrasive and crater wear on the tool. Dry cutting is state of the art in gear hobbing. This intensifies the thermal process load and thus the wear phenomena.

To examine the performance of different coatings, cutting tests were performed using the well-established fly-cutting analogy test. Subsequently the worn out single hob teeth were examined by REM and confocal 3D microscope to evaluate the wear phenomena.

To reduce crater wear and to extend the performance of gear hobs a range of AlCr-based coatings were deposited in industrial π411 and π1511 arc sputtering PVD units. Significant performance differences between the chemically and structurally modified coatings were found. The addition of Boron into AlCr-based layer enables the reduction of internal stress of the coating system. Furthermore an substantial increase of tool life was achieved by doping the coating top layer with titanium in combination with an optimized nanolayer structure.

Keywords
gear hobbing
coating development
PVD
AlCrBN
arc evaporation
PO2037

**Chemical, mechanical and stability of air annealed cathodic arc evaporated CrAlON coatings**

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This study reports the synthesis and characterization of ternary and quaternary and multilayered Cr-Al-O-N coatings deposited by cathodic arc physical vapour deposition, as a function of the nitrogen and oxygen mass flow ratios during the process. The composition, microstructure, indentation hardness and modulus of the films have been characterized by scanning electron microscopy, electron probe micro analysis, x-ray diffraction, and nano-indentation techniques. The thermal stability of the coatings in ambient air at 1100ºC have been investigated, and their evolution with the annealing temperature. As the oxygen to nitrogen mass flow increases, the coatings as-deposited exhibit lower hardness, higher roughness, lower crystallinity and a more marked columnar structure. At oxygen to nitrogen mass flow ratios bigger than 10/90, the coatings exhibit a stoichiometry \((\text{CrAl})_{2+e}\text{O}_{3-e}\). Only the coatings with oxygen to nitrogen mass flow ratios smaller than 10/90 presented nitrogen in their compositions. In all cases, the coating developed cubic fcc lattice structures. After the annealing at 1100ºC the resulting microstructure showed a clear dependency upon the initial composition and architecture of the films. The evolution of the microstructure for the temperature series as well as the analysis of the indentation hardness, composition and thickness also provided valuable information about the thermal stability of the deposited coatings. Both the oxide pristine coatings and the multilayered architectures exhibit an outstanding mechanical stability up to 1100ºC.

**Keywords**
Cr-Al-O-N  
ar evaporation  
PVD
The new Hybrid LACS® Technology (Lateral ARC and Central Sputtering by Rotating Cathodes)

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The flexible PVD hard coating unit π⁴¹¹⁺ is able to operate with ARC, sputtering and PACVD. While the ARC technology brings highest performance for cutting tools, the sputtering achieves very smooth surfaces. The combination of both technologies in one coating unit enables the advantages of both worlds.

We would like to present the new LACS® technology (Lateral ARC and Central Sputtering by rotating cathodes). The novelty of this hybrid technology is the simultaneously use of Arc evaporation and sputtering, to evaporate non-alloyed metallic (Ti,Al,Cr,W, etc) and magnetron sputtered ceramic (TiB₂, B₄C) targets, resp. cathodes.

LACS® allows to deposit different high-performance coatings, like AlCrN/BN, AlTiN/BN, TiWN, TiCNWCC or TiB₂. On the other hand, the supplementary electron injection provided by ARC discharge can improve the microstructure and performance of the plasma-enhanced magnetron sputtered coatings.

On the example of BN-containing coatings we would like to illustrate how is it possible to optimize mechanical parameters of the coating by tuning of the process parameters. We will also present industrial applications of Boron doped coatings.

Keywords
Hybrid LACS®
Lateral ARC
Sputtering
Rotating Cathodes
Platit PVD
Surface morphology and mechanical analysis of nanolaminate (TiAlSiY)N/ZrN and (TiAlSiY)N/MoN condensates deposited by vacuum-arc

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(TiAlSiY)N/ZrN and (TiAlSiY)N/MoN coatings are a system composed of alternating multielement and binary nitride layers of a nano-sized scale. The laminated structure allows to vary the number of interfaces and to influence the fine-grained structure of functional coatings, which in turn leads to a change in the values of hardness and longitudinal elasticity modulus. Nanolaminate condensates were deposited using the upgraded Bulat-6 device. The pressure of the working atmosphere in the deposition chamber (P_N) was P_N = 4×10⁻³ Torr. A constant negative bias potential (-U_b = -110 V) was applied to the substrate while the substrate temperature (T_p) was about 250°C. The presence of a droplet fraction and cathode particulates is detected on the surface, which is typical for most vacuum-arc condensates from non-separated plasma flows. The size of the droplet fractions is in the range from 1 to 10 μm, while on the surface of (TiAlSiY)N/ZrN coating, it is possible to detect enlargement of the droplet fraction and tendency to agglomeration, which is probably related to the coefficient of Zr erosion and with the change of the top layer of the laminated condensate. Based on the individual sections of micrographs of the molybdenum-containing coating, the corresponding numerical surface models were constructed. These models are designed for the surface visualization and will be used for calculation of the numerical characteristics of surface morphology. The highest values of nanohardness and longitudinal elasticity modulus are 35.9 GPa and 406.8 GPa, respectively, were obtained for the (TiAlSiY)N/MoN coating. The corresponding parameters for the (TiAlSiY)N/ZrN composition are significantly lower and are equal to 22.1 GPa and 271 GPa, respectively.

Keywords
structure
nanolaminate condensates
nanohardness
longitudinal elasticity modulus
morphology
PVD and CVD are versatile techniques to deposit high quality coatings on tools and parts. They provide coatings of a wide variety of compositions and structures, including nitrides, carbides, oxides and also complex compounds. For the coating of parts, i.e. non-flat substrates, the arc evaporation and the magnetron sputtering techniques are established in typical batch coating devices, where substrates rotate during coating processes of typically several hours duration. Electron beam evaporation opens up the possibility of highly productive coating processes also for 3D-shaped substrates.

NOVELLA, a novel laboratory equipment for the coating of three-dimensional parts is a platform that integrates the electron beam evaporation technology. High rate evaporation using an axial beam gun, assisted by a powerful hollow cathode plasma source enables deposition of high quality coatings. Including a load lock and a versatile substrate transport system, it allows establishing direct process sequences of different deposition techniques including magnetron sputtering and PECVD. By the example of titanium nitride, we describe in detail the used technology. The coating experiments were carried out with deposition rates up to 180 µm/h. This rate number illustrates the productivity potential of the electron beam evaporation and represents the precondition for a cost effective coating technology. The properties of the layers are completely comparable to sputtered coatings. We measured hardness of 30 GPa and Young’s modulus of 380 GPa for the evaporated TiN layers deposited with moderate bias voltages. Further characterizations of the layer structure will be given in the talk.

Additionally, we will give an overview about other coatings which were deposited by high-rate electron beam evaporation in the near past in order to illustrate the possibilities of this coating technique in view of different surface functional requirements on 3D-parts.

**Keywords**
plasma-activated evaporation
high-rate deposition
hollow cathode
coating 3D-parts
Microstructural properties of Ti$_2$AlN coatings synthesized by multilayer deposition and subsequent annealing

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Ti$_2$AlN is a prominent ternary nitride and belongs to the class of nanolaminated M$_{n+1}$AX$_n$ phase materials which combine metallic and ceramic material properties. Due to the anisotropy in the lattice of M$_{n+1}$AX$_n$ phase materials, properties like conductivity, diffusion, fracture toughness, etc. are also anisotropic and are strongly influenced by the coatings texture. This, for possible application, a precise control of coating’s microstructure and texture is mandatory. In this work we report on the successful synthesis of polycrystalline Ti$_2$AlN thin films with a preferential (000l) orientation on Al$_2$O$_3$ and ferritic steel substrates [1]. Fabrication of the coatings included the deposition of multiple Ti-AlN double layers and a subsequent annealing step. Investigations with scanning electron microscopy (SEM), X-ray diffraction (XRD), electron back scatter diffraction (EBSD) and Raman spectroscopy reveal a successful transformation of the multilayer system into a polycrystalline and dense Ti$_2$AlN coating. EBSD measurements on these macroscopic grains point to a preferred orientation in the [000l] direction. In further experiments, the Ti-AlN double layer thicknesses were varied between 11 nm and 34 nm. The pole figure analysis of these samples reveal an increase in the full width half maximum (FWHM) of the (0006) peak with decreasing double layer thickness. Experimental results of the influence of the microstructure on the fracture tolerance of the coatings shall also be presented. [1] L. Gröner, L. Kirste, S. Oeser, A. Fromm, M. Wirth, F. Meyer, F. Burmeister, and C. Eberl, Surface and Coatings Technology, in press (2017)

Keywords
MAX phase
multilayer deposition
texture
EBSD
Modulating Low Energy Ion Plasma Fluxes for the Growth of Nanoporous Thin Films

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The growth of nanoporous layers by plasma-assisted deposition techniques is strongly mediated by the ion fluxes in the reactor. To analyze their influence we have deposited different nanostructured thin films by the magnetron sputtering technique at oblique angles, modulating the ion fluxes in the plasma by tuning the frequency of the electromagnetic signal from pure DC to 160 kHz DC pulsed mode. In the DC case, ions possess energies below 5 eV and do not induce noticeable changes in the film structure. However, when the signal is pulsed, ions with energies up to 40 eV impinge on the film, decreasing the porosity of the layers and tilting down the porous/nanocolumnar structures. As a result, we demonstrate that the overall porosity of the layers and the tilt angle of the columns can be tailored as two independent morphological quantities.

Keywords
Controled porosity
Low energy ions
Nanoporous thin films
Tilted nanocolumns
Glancing Angle Deposition (GLAD)
Production of unimodal size distribution nanoparticles by low pressure plasma, and illustration of their potential use in medicine

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Because of their interesting optical, electronics, magnetic, mechanical and structural properties, production of well-dispersed metallic and non-metallic nanoparticles with controlled size and shape is increasingly necessary to improve technological and medical applications. Among all methodologies used today to synthesize nanoparticles, one can cite vacuum technology to produce spherical non-agglomerated nanoparticles through a vapour phase approach by DC magnetron sputtering at high pressure. The idea was introduced for the first time by Takagi et al. in 1972 and was improved few years later by the use of inert gas condensation methodology based on magnetron sputtering which has the advantage of producing high-purity atomic vapour from a wide variety of solid materials or composites.

In this lecture, we will describe how this technique can be used to produce metallic and non-metallic nanoparticles such as Ag, TiO$_2$, Au, Y, C, Zn, ZnO, Fe and Co and polymer based nanoparticles. If time allows, results and an explanation about nucleation and growth processes will be also given for each cases.

Finally, we will focus on the Au case for which we will discuss the properties of nanoparticles produced by gaz aggregation technique. Medical application of Au NP will also be illustrated by a selected example from our group about the production of antibody-functionalized gold nanoparticles to selectively target cancer cells as well as probing their potential radiosensitizing effects under proton or X-ray irradiation. We will describe Au NP production, bioconjugation with monoclonal antibody, in vitro and in vivo cytotoxicity, and quantitative assessment of dose response relationship of several hundreds of bioconjugate-injected mice exposed to proton or X-ray beams.

Keywords
- nanoparticle
- gaz aggregation
- magnetron sputtering
- medical applications
Self-Affine Growth of Nylon-Sputtered Nanoparticles

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Rf magnetron sputtering of polymers is known to allow for the synthesis of plasma polymer nanoparticles with controllable size and chemical composition. Morphology of such nanoparticles can be very diverse ranging fascinatingly from smooth to orange-peel or to cauliflower texture. The particular morphology depends on the mechanisms of nucleation and growth. Here, nitrogen-containing plasma polymer particles were synthesized by rf magnetron sputtering of nylon in a gas aggregation cluster source with variable length of the aggregation zone. Spherical particles were produced with the mean size changing from 80 to 320 nm in dependence on the time the particles spent in the source. Markedly, the chemical composition and the particle number density remained constant. The morphogenesis of the particles was investigated by Atomic Force Microscopy with super-sharp probes. The roughness exponent of 0.78, the growth exponent of 0.34 and the dynamic exponent of 0.48 were derived from the advanced surface statistics. These critical exponents point at the self-affine mode of the particle growth and evidence that the particles evolve by the accretion of polymer-forming species from the gas phase and not by coagulation. Non-fractal morphology of the particles implies that the polymer-forming species attach with the probability of less than 100% and that the accretion is accompanied by the substantial redistribution of the incoming material over the particle surface as well as by the development of the inhomogeneously distributed inner stress.

Acknowledgement
This work was supported by the grant GAČR-17-12994S from the Grant Agency of the Czech Republic. P. P., D. N. and R. T. also appreciate the support from the student grant SVV 260444/2017 of Charles University.

Keywords
particles
plasma polymer
gas aggregation
super-sharp AFM
Pulsed Plasma Polymerization of Acrylic Acid for the Synthesis of Carboxyl-Functionalized Nanoparticles

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Polymer nanoparticles (NPs) have great importance in various fields of science and technology including biology and medicine where they can be used for targeted drug/gene delivery and for imaging purposes. Typically, macromolecular systems are designed to comprise specific functional groups that ensure the bioadhesion. In the last decades, considerable attention was drawn to plasma polymerization of acrylic acid for fabrication of coatings rich with carboxyl functional groups. The COOH groups are known to support adhesion and proliferation of different kinds of cells and can be used as immobilization agents to anchor biomolecules. Here, we show that plasma polymerization of acrylic acid (AA) can be performed in a manner as to produce COOH-functionalized nanoparticles (NPs) rather than thin films. For this purpose, we operated a gas aggregation cluster source (GAS) in a mixture of AA and Ar under the pressure of 100 Pa. An RF powered (13.56 MHz) electrode was used to ignite the plasma in a pulsed mode. Duty cycle (DC) and effective power ($P_{\text{eff}}$) were found to be crucial parameters that influence the size, flux and chemical composition of NPs. Under constant $P_{\text{eff}}$ of 40 W the NP size varied from 100 to 30 nm with decreasing DC. At high values of DC, only individual NPs were formed whereas coagulation of the NPs into larger agglomerates was observed at low DC. The phenomenon suggests that the accumulation of electric charge on the NPs during the on-time and its loss during the off-time are the concurring mechanisms that determine the resultant morphology. The concentration of COOH groups in the NPs was found to pass through minimum with varying DC from 100% to 32%. The maximal concentration of 12 at. % was reached at the lowest DC value.

Acknowledgement
This work was supported by the grant GAČR-17-12994S from the Grant Agency of the Czech Republic. P. P., D. N. and R. T. also appreciate the support from the student grant SVV 260444/2017 of Charles University.

Keywords
plasma polymer nanoparticles
functionalization
acrylic acid
Synthesis of Copper Oxide Nanoparticles by Reactive Magnetron Sputtering

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Gas aggregation cluster source (GAS) is an attractive plasma-based instrument for the preparation of nanoparticles (NPs) including those of metals and plasma polymers. Although the synthesis of metal oxide NPs was also demonstrated, the examples are really scarce. In this work, we used a magnetron-based GAS for the synthesis of copper oxide NPs which can be beneficial as catalytic, optically active and bactericidal agents. Reactive DC magnetron sputtering of Cu target in Ar/O₂ mixtures of different composition was investigated to achieve the stable production of the copper oxide NPs. It was found that 7 vol. % of O₂ is the optimal value in terms of the deposition rate. The post-oxidation SEM analysis showed the decrease of the NP mean size from 21 nm to 12 nm as compared to Cu NPs, and the HR-TEM analysis demonstrated that the NPs are crystalline. The formation of the oxide was confirmed by a 15 % increase of the oxygen content determined by XPS as well as by a significant shift of the Cu 2p XPS peak to higher binding energy with reference to metallic Cu NPs. The analysis also showed that the surface stoichiometry correspond to Cu (II) oxide. The UV-Vis measurements confirmed the formation of copper oxide by the loss of the plasmon resonance peak at 560 nm which was observed for metallic Cu NPs.

Acknowledgment:
The study was supported by the Charles University via the project GA UK No.1186217. D.N., P. P. and R.T. acknowledge the support from the student grant SVV 260 444/2018 of Charles University.

Keywords
copper oxide nanoparticles
reactive magnetron sputtering
gas aggregation cluster source
Tracking of cycling growth of hydrocarbon plasma polymer nanoparticles by in situ diagnostics

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Recent works have shown the potential applicability of gas aggregation cluster sources (GAS) for the synthesis of plasma polymer nanoparticles (NPs). However, deep understanding of the fundamentals of the NP formation is still lacking because the research has been focused mainly on ex-situ analysis of the NPs rather than on the processes taking place inside the cluster source. In this work, we simultaneously employed optical emission spectroscopy, mass spectrometry and digital camera to monitor in situ the phenomena occurring during the synthesis of hydrocarbon NPs by plasma polymerization of n-hexane. The voltage on the electrode and the deposition rate of the NPs were also real-time tracked. A 3-inch RF electrode was operated at a constant power of 50 W in a 4.6 % mixture of n-hexane with argon. Cycling instabilities in the deposition process were detected. The temporal measurement of both the voltage and the deposition rate revealed the period of oscillations to be about 80 s. These oscillations correlated with the instabilities observed in the mass spectra where analogous oscillations of the n-hexane molecular peak were detected. The temporal instabilities were further proved by optical emission spectra in which the intensity of the Ar spectral line was seen to oscillate with the same period. A phenomenological description was suggested to describe the cycling growth of the NPs and their ejection from the discharge zone.

Acknowledgments: The authors would like to acknowledge the contribution of the COST Action CA15107 (MultiComp) and support by the grant LTC17062 from the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords
nanoparticles
n-hexane
diagnostic
Enhancing the Palladium Nanoclusters deposition rate with the introduction of O2 in a Gas Aggregation Source (GAS)

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Palladium nanoclusters (NCs) are an outstanding catalyst for the electro-oxidation of small organic molecules. Magnetron Sputtering Gas Aggregation Source (MS-GAS) is known by producing NCs of different materials providing a continuous nanocluster beam but a challenge of GAS is to enhance its deposition rate. NC growth is controlled by thermodynamic and kinetic factors depending on experimental parameters as total pressure or target power. Interestingly, the addition of small amounts of a reactive gas (O₂ or N₂) increased the deposition rate of different metals. The aim of this work is to study the influence of O₂ addition on cluster size, crystal quality and the deposition rate during the growth of Pd NCs.

In the Pd-O₂ system, when the discharge voltage (V_d) raised, a transition zone (TZ) from a clean to a poisoned Pd target surface was detected and started at an oxygen flow rate as low as 0.030 sccm. Target poisoning affected NC size and deposition rate that reached a maximum value at the end of the TZ. While NC size varies between 3 to 6 nm, the deposition rate is enhanced almost four times. Moreover, above the TZ, it is possible to observe Janus Pd/PdO nanoclusters. Preliminary results show how the catalytic activity of Pd NC electrodes (towards glycerol oxidation) greatly depends on the O₂ addition in the Pd NC growth process.


Keywords
Gas Aggregation Source
Palladium Nanoclusters
Reactive Sputtering
Electrocatalysis
Molecular Dynamics simulations of plasma sputtered nanocatalyst growth

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On one hand, Pt based alloys are known to improve the activity and stability of PEMFC's catalysts [1,2]. On the other hand, magnetron sputtering deposition has already demonstrated its ability for the fabrication of efficient PEMFC electrodes with high Pt utilization rate [3]. In the present study, MD simulations on PtxMyNz (M, N, being less noble or common metals) deposition and growth are carried out for studying the preferred morphology and structure (size, geometry, atomic arrangements ...) of such clusters.

Recently, it has been shown that MD simulations allowed confirming and predicting the morphology and structure of Pt nanocatalysts [4,5] as well as of PtxPdyAuz nanomaterials [6], for which, a comparison is provided between sputtering and chemical methods.

Initial conditions of MD simulations are selected for matching experimental chemical and physical synthesis methods of nanoparticles. MD simulations of catalyst PtxPdyAuz, PtxNiyAuz, and PtxBi, supported on porous carbon mimicking fuel cell gas diffusion layers as well free nanocluster growth in conditions mimicking gas condensation nanocluster source are studied. Radial distribution functions and X-Ray Diffraction pattern are systematically computed for enabling direct comparison with experiments.

This work is partly funded by ANR project ECO-PLAN under grant ANR-16-CE29-0007 and by EC FCH-JU SMARTCat under grant GA325327.


Keywords
Molecular dynamics
Sputtering deposition
Nanoclusters
Catalyst
Effect of the nature of plates taped on the powered electrode on dust-particles generated in a CH4 radio-frequency discharge

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In a capacitively-coupled radio-frequency (RF) discharge (13.56 MHz) in CH₄, dust-particles are generated at low pressure (120 Pa). The gas is injected in the chamber with a flow rate of 5.6 sccm (9.45·10⁻³ Pa·m³·s⁻¹). The plasma is generated between two parallel plane aluminum electrodes: the upper one is powered (80 W) by the RF generator and the lower one is grounded. An impedancemeter follows the evolution of the plasma electrical parameters. In our conditions, the dissociation of CH₄ leads to the formation of dust-particles in the plasma bulk, and to the growth of a coating on the powered electrode. The dust-particles are trapped at the sheath boundary because of forces exerted on them, leading to the formation of dust-particle clouds parallel to the electrodes. When the dust-particles become too big and too heavy, they fall onto the grounded electrode, so they can be collected.

The purpose of this experimental study is to understand how the nature of the powered electrode can influence the plasma parameters and the dust-particles generation. First of all, the electrodes are cleaned with ethanol and sand paper. Then, thin plates of different materials are cleaned with ethanol and taped on the powered electrode with conductive tape. 60% of the powered electrode is covered with the plate. After this, the pressure is lowered and the chamber is filled with CH₄, and the plasma is turned on. After 15 minutes, the plasma is turned off. The dust-particles generated and the plates are collected in order to observe them by Scanning Electron Microscopy. The morphology of the coating formed on the powered electrode differs in function of the material of the plate. The diameter of the dust-particles and the electrical parameters of the discharge are also affected by the nature of the plate. Moreover, less dust-particles are generated when an insulator plate is taped on the powered electrode, compared to when a conductive plate is taped.

Keywords
Dusty Plasmas
Dust-particles
Methane
Radio-frequency
Nanoparticle cloud evolution in an acetylene dusty plasma

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The synthesis of nanoparticles for various technological applications requires a perfect control of their growth kinetics and dynamical behavior in the plasma. One important aspect that has to be taken into account for obtaining nanoparticles with desired size and density, is that nanoparticle growth is a cyclic phenomenon in typical low pressure reactive plasmas. This behavior can be easily observed by measuring plasma or discharge characteristics like the self-bias voltage, the plasma emission or the gas pressure. These successive generations can be also clearly evidenced using laser light scattering (LLS) to directly observe the evolution of the nanoparticle cloud. A laser sheet coupled with a high-resolution CCD camera reveals the details of this cyclic behavior and especially the role of the void in this process. Once the nanoparticles have reached a sufficiently big size, a void (central dust-free region) starts to appear in the middle of the cloud. Its size progressively increases up to a critical instant when the opening suddenly accelerates removing nearly all the nanoparticles from the plasma volume. This free-space can be a favorable place where plasma conditions are fulfilled for the growth of a new nanoparticle generation.

In this work, we will present LLS results performed in an acetylene/argon capacitively-coupled radio-frequency discharge and the effects of power, pressure and acetylene flux on the cyclic nanoparticle growth process. Changing discharge conditions plays a role on the nanoparticle growth cycle duration but also on the void evolution. The LLS results are correlated with the changes of the self-bias voltage showing that each cycle is composed of very clear phases. Especially, the final fast void opening corresponding to the nanoparticle expulsion from the discharge is well identified on these electrical measurements.

Keywords
Dusty plasmas
Nanoparticles
Acetylene
Void
In-situ monitoring of nanoparticle generation in plasma

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Nanoparticles (NPs) play an important role in the growing field of nanotechnology due to the unique properties associated with their small dimensions. Plasma based generation of NPs has been considered as an interesting approach for synthesis of NPs with tunable size distribution, morphology and chemical structure. Moreover, so-called gas aggregation sources (GAS), based on magnetron sputtering, have been utilized to obtain independent control of the size distribution and flux of the metallic NPs. However, the processes inside the GAS, leading to NP growth, are not fully understood yet due to the limited accessibility by most of the common analytical methods in vacuum and plasma environment.

In the work presented here, we report on the in-situ monitoring of the initial stages of metallic NP growth in a low temperature plasma by broadband transmission UV-Vis spectroscopy. We demonstrate that for several metals, due to strong particle plasmon resonance, NPs can be monitored by UV-Vis spectroscopy in-situ during their growth and transport in a GAS. Our results show that small NPs are already generated in the region close to the magnetron target surface and generally do not change their size much during transport through the gas aggregation volume. A strong broadening of the plasmon resonances, which results from a strong coupling between particles, in the vicinity of the magnetron indicates a high concentration of NPs in this region. In addition to the fundamental studies on pure silver NPs, we also show that utilization of a bimetallic sputtering target leads to generation of alloy NPs (e.g. AgAu, AgPt) with in operando tunable composition by simply changing the sputtering conditions. Moreover, optical emission spectroscopy (OES) in combination with in-situ UV-Vis allows for “online” monitoring and tuning of the chemical composition of such NPs.

Keywords
Nanoparticles
Plasma
In-situ
Gas aggregation
Plasmon resonance
Hydrogen Influence on the Synthesis of Tungsten Nanoparticles by Magnetron Sputtering Combined with Gas Aggregation.

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Tungsten nanoparticles with size in the range of 60-100 nm are produced using a cluster source based on magnetron sputtering combined with the gas aggregation technique. The metallic vapors obtained by sputtering are cooled down in the flow of the inert gas (argon); nucleation centers appear first, then the nanoparticles grow subsequently by accretion and coagulation and they are ejected from the cluster sources as a beam of particles. An undesired effect is the slowing down and cease of the deposition process in about 30 minutes, suggesting the dependence of the deposition rate on the presence of residual gases which are gradually consumed during the process. We show that by deliberately mixing the argon with small amounts of hydrogen the production of tungsten nanoparticles become continuous. Moreover, an oscillatory behavior of the main process parameters (target selfbias, pressure in the cluster source, intensity of the optical emission lines and the deposition rate) was noted. We present the correlation between the variation of these parameters, with the nanoparticles growth rate and morphology.

**Keywords**

nanoparticles
tungsten
gas aggregation source
Synthesis of particles from different metals by an atmospheric pressure plasma jet: a comparative study

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In the last decades, nano and micro metallic particles, have been investigated due to the unique properties when compared with their bulk metal counterparts. Mainly the large surface-to-volume ratio and the diversity of shapes and microstructures opened the door for a multitude of applications. As a result, various generation methods are nowadays developed and studied.

This contribution presents a versatile radio-frequency (RF) plasma jet source that operates in argon at atmospheric pressure, suitable for generation of metallic particles from bulk metals such as iron, copper, titanium, zinc or nickel. The metal source was represented by the RF powered electrode. More details on the plasma jet operation and the mechanism of production of copper particles one can find in Ref. [1, 2]. Optical and Scanning Electron Microscopy (SEM) analyses show that in selected conditions particles can be obtained, regardless of the used metal type. Energy Dispersive X-ray Spectroscopy (EDS) investigations reveal that metallic or oxide particles were synthesised. Depending on the applied RF power nano-particles with diameters between 20 and 50 nm or micro-particles with sizes of 1 to 3 μm were obtained. Moreover, the size, structure and shape of the particles is influenced by the metal type.

Acknowledgements: We acknowledge the support of the research financing Romanian authorities in the frame of IFA-CEA C5-07 project and the project Nucleu-2018 at INFLPR. V. Marascu acknowledges the financial support in the frame EUROfusion Consortium, project 1-EU12 WPEDU-RO.

References

Keywords
metallic particles
synthesis
RF plasma
atmospheric pressure plasma jet
Gold nanoparticles preparation by converging-type Atmospheric Pressure Plasma Jet

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A converging head embedded in the atmospheric pressure plasma jet was designed for the gold nanoparticle preparation via precursor solutions of HAuCl₄. Effect of DC powers and precursor solution concentrations were investigated to realize the parameters by converging-type atmospheric pressure plasma jet, as well as the plasma plume temperature evolution. Materials characterizations by transmission electron microscope (TEM), absorption spectrometer (UV/vis), and X-ray diffraction (XRD) were performed to analyze the surface morphology and particle size of gold nanoparticles. According to the measured plasma plume temperature, the internal temperature reached over 400℃, which can be feasibly made for the thermo-decomposition of HAuCl₄ solution under atmospheric pressure plasma. Analyzed results also show the precursor concentration of HAuCl₄ solution and applied plasma power evidently influenced the particle sizes and surface morphologies of gold nanoparticles. The optimal process in this study to prepare 20nm-Gold nanoparticles was performed at the conditions of 0.05mM HAuCl₄ precursor solution and plasma power of 300W. Meanwhile, the verification on the converging-type head in an APPJ process via HAuCl₄ precursor solution for the preparation of gold nanoparticles was feasibly achieved.

Keywords
Atmospheric Pressure Plasma Jet
Gold
Nanoparticle
Nanoparticles produced by magnetron sputtering and its application in catalysis chemistry

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Nanoparticles that are produced by a gas-condensation process in vacuum, have many advantages compared to those prepared via a conventional wet-chemistry route. Inherently these gas phase nanoparticles are very clean and pure, because there is no contamination from ligands, for example, which are often essential in other catalyst preparation methods, like precipitation or impregnation. As such, there is no need to carry out calcination processes afterwards to remove such organic materials, which could be a critical issue for some nanoparticle materials that are sensitive to high temperature.

We have developed technologies to deposit nanoparticles on powders directly in vacuum [1], and this made it possible to evaluate catalytic performance using conventional fixed-bed reactors.

However, one currently limiting factor of this technology is that the amount of nanoparticle materials produced is small. To address the issue, we carried out aerodynamic simulation to understand better how the gas dynamic influences the clusters’ formation and growth, and proposed new approach to improve the cluster throughput. By optimizing the gas dynamic inside the vacuum chamber, we were able to improve the cluster flux by 3 to 5 times. By adopting a different magnetron sputtering technology, we had another ~ 5 times flux improvement. Ultimately, we expect to improve the production rate by a factor of ~ 100. This will raise the possibility of mass-production of such high-purity and size-selected nanoparticles, which in turn will lead to many new and future commercially significant applications.


Keywords
nanoparticle
cluster
magnetron
sputtering
Characterization of various plasma reactors dedicated to nanoparticle functionalization

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The treatment of nanoparticles (NPs) has gained much interest during the last decade because it has been shown an essential step in the synthesis of high added value polymer nanocomposite. Indeed, to avoid NPs agglomeration and create a strong bonding interface with the host matrix, surface modification of NPs is required to improve their compatibility with the polymer and promote a good dispersion of the nanofillers.

Among the very various existing methods used to modify the NPs surface, the deposition of an organic coating by plasma polymerization shows numerous advantages such as high versatility and easy control regarding the incorporation of a chemical functionality, little use of chemicals and wastes to treat, simple apparatus, short process time and easy scale-up to mass production.

Nevertheless, the plasma treatment of NPs is a challenging task because an effective way to mix the powders during the treatment has to be found in order to obtain a homogeneous coating around isolated NPs. In this purpose, we compare in this work the efficiency of two different types of homemade low-pressure plasma reactors to coat NPs with plasma polymers: a capacitive magnetron rotating drum reactor and a so-called “gravitational” reactor, where the NPs fall through an inductively-coupled plasma discharge. More specifically, we place the accent on the deposition of amine-based plasma polymers on zinc oxide NPs.

Plasma diagnostic is performed by optical emission spectroscopy and mass spectrometry to better understand the dissociation of the precursor in the different reactor configurations and optimize thin film properties. Deposition rates, yields, functionalization degree and thin film quality and homogeneity around NPs are assessed by XPS and HR-TEM and compared to highlight strengths and limitations of each configuration regarding industrial issues.

Keywords
Nanoparticle
Plasma polymerization
Diagnostics
Surface functionalization
Adding advanced functional properties to nanoparticles via low-pressure plasma coating

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Nanoparticles (NPs) are now the object of intense study due to their perspective properties and numerous industrial applications. Some of these applications are facing with several limitations based on excessive reactivity or conversely low affinity to some matrixes. Nanoparticles coating can solve these problems creating a protective layer or changing the chemical composition of the surface, which can improve NPs incorporation and distribution in different matrixes.

In the present study the surface modification of nanoparticles of different nature (metals, metal oxides, ceramics etc.), size and morphology was performed via a low-pressure plasma polymerisation process. The composition and the morphology of created coating were characterized by physical methods (XPS, TEM, TGA). It was shown that the surface composition and the thickness of the coating are controlled by a variation of plasma treatment parameters.

The formation of an effective protective layer around nanoparticles that changes the material properties from hydrophilic to hydrophobic was demonstrated. We have also shown that the plasma treatment increase the NPs affinity towards various solvents resulting in improved NPs distribution in polymer matrices.

Keywords
nanoparticles
coating
functionalization
low pressure plasma
plasma polymerization
Metallic powder treatment by the magnetron sputtering technique: application to additive manufacturing

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Nowadays, the Laser Beam Melting (LBM) and binder-jetting 3D Printing (3DP) of metallic powders are promising for the fabrication of components used in several industrial sectors including the electronic, transport, aeronautics and aerospace areas. Nevertheless, the use of these techniques in additive manufacturing is hampered by the low laser absorption of the metallic powders and their proneness to oxidation, resulting in a poor sinterability.

In this context, in this work, the synthesis of a thin film (i.e. Ti, Cr, Ni-Cr) by the magnetron sputtering technique on Cu, Fe and Al powders is studied. The whole set of our data (i.e. XPS, SEM, XRF) indicate that the powder particles are homogenously covered resulting in the increase (i) in their laser absorption, (ii) their resistance toward oxidation and their (iii) wettability paving the way for their processability by the LBM and 3DP techniques.

Keywords
Additive Manufacturing
Metallic Powders
Magnetron Sputtering
Thin Film
3D Printing
Au-TiO₂ thin films exhibiting Localized Surface Plasmon Resonance effects and advantage of an Electron Nano-Tomography study

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Noble metal nanoparticles, NPs, especially those of gold and silver (Au, Ag), have received an intensive scientific attention due to their unique chemical and physical properties. In particular, interesting optical properties can be obtained when Au NPs are distributed into a dielectric media (e.g., TiO₂). These nanocomposite thin films, which can be prepared by reactive magnetron sputtering, followed by post-deposition thermal annealing, can manifest Localized Surface Plasmon Resonance behaviour (LSPR), which can be optimized for plasmonic sensing applications, namely those related with biosensing [1]. The LSPR effect is closely related to the size, distribution and shape of the nanoparticles, which may benefit much from a systematic 3D analysis at the nanoscale level. In this context, Electron Nano-Tomography (ENT) is a suitable approach [2] for such analysis, which was carried out for this study with a Cs-corrected Environmental TEM. ENT experiments consist in acquiring tilted series of projections of the nan-object, followed by aligning the projections to the rotation axis and reconstructing 3D sample from the aligned 2D projections [3]. ENT was performed in a Au-TiO₂ thin film, which was annealed at 400 and 600 °C to promote the microstructural changes that would allow the tailoring of its optical response in respect to the LSPR phenomena.

ENT studies confirmed the nanocomposite nature of the film, revealing the formation of nanoparticles of Au that increase in size with the increase of the annealing temperature. Moreover, the analysis showed also some particular features regarding the dielectric matrix (TiO₂), which shows some local crystallization. Finally, ENT results uncovered some particular features of the film related with the fact that NPs located near the outer surfaces of the film seem to grow significantly more than internal NPs due to the higher atomic mobility.


Keywords
Plasmonic films, nanoparticles
electron tomography, 3D characterization
Synthesis of Ag/YSZ nanocomposites thin films by reactive magnetron co-sputtering at high pressure for the electrochemical promotion of catalysis of ethylene into ethylene oxide

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The electrochemical promotion of catalysis is a well-known process [1] which enables to modify in operando performances of catalytic layer deposited onto electrolytic thick membrane. Indeed, by applying an electrical potential between a reference and a working electrode the migration of electronic membrane ions via Schottky defects is promoted what is modifies the oxygen reactivity at the catalyst surface. Institut Jean Lamour (IJL) has recently developed nanostructured electrochemical catalysts by magnetron sputtering in a multisource approach in which the catalytic film is a composite consisting of metal nanoparticles highly dispersed in an electrolyte matrix [2]. Au/YSZ nano-composite thin films deposited on β"-Al₂O₃ were found to be active in the partial oxidation of methanol with a high selectivity towards methyl formate. From this perspective, the first line of the EPOX project is the synthesis of dense working thin film electrodes made of Ag/YSZ using reactive co-sputtering for the electrochemical promotion of catalysis of ethylene into ethylene oxide. In order to obtain nano-dispersed silver within a ion conductive matrix, the elaboration conditions such as reactive partial pressure, working distance pressure product, pumping speed and electrical parameters have been tuned. The silver concentration within thin films was assessed by EDX in SEM. The fluorite type structure of YSZ and the cubic structure of Ag was determined by XRD. Thanks to HRTEM the presence of silver clusters has been highlighted as well. Last but not least, a botryoidal-like structure and the roughness of the films were respectively revealed and evaluated by SEM in high resolution top view and by AFM.


Keywords
Magnetron Sputtering
Ag/YSZ
Thin films
HRTEM
Catalysis
High-intensity pulsed ion beam (HIPIB) technology has been developed as a unique approach for surface modification of components, utilizing the significant thermal and dynamic effects under typical parameters with an energy density of several J/cm² at pulse duration of tens to hundreds ns order. Under the HIPIB irradiation, notable surface remelting and ablation, and thermal stresses and stress waves propagating inwards can improve the surface integrity of components with formation of non-equilibrium microstructure and new phases, and plastic deformation layer with high density defects, and associated high hardness and low friction etc., finally leading to a high performance of wear, oxidation, and/or fatigue resistance. In practice, it is still difficult to select HIPIB process parameters in advance for generating the desired surface integrity for high performance, even though the thermal and dynamic processes have been intensively explored by numerically calculating temperature and stress fields evolutions, i.e. material loading in the irradiated components. A transient heat transfer model incorporated with constitutive equation is constructed to elucidate the surface integrity formation mechanism with varying irradiation parameters/conditions including energy density, pulse duration, and pre-heating temperature etc., by which characteristic parameters of the material loading are proposed and discussed taking into account the transition from thermal energy to mechanical energy, to establish a characteristic correlation between the surface integrity and HIPIB process parameters for design and optimization of the processes.

Keywords
High-intensity pulsed ion beam
Material loading
Thermal energy
Mechanical energy
Residual stress
First stages of surface modification by low kinetic energy helium ions produced in a dedicated ICP-RF plasma source

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In the frame of nuclear fusion studies, it has been found that fiberform nanostructured tungsten (W), so-called “tungsten fuzz,” is formed on W surface by helium (He) plasma irradiation. This nano-structure has been observed to form at kinetic energy below the atomic displacement threshold, and exhibits a high porosity (90%), which could be of great interest for various applications (light absorption, catalysis etc.). Further investigations have evidenced the formation of such porous structures on molybdenum, nickel and iron surfaces. Even if largely studied, the first stages of the interaction between low energy He ions and metals still requires investigation in order to precisely control the features of the porous surface.

An ICP-RF plasma source has been developed at the GREMI to perform implantations at low ions fluxes, i.e. in a low electron density plasma. The interaction conditions have been precisely characterized using a Langmuir probe (plasma parameters), homemade retarding field analyzer (ion energy flux distribution), and energy flux diagnostic. Surface characterization by Nuclear Reaction Analysis technique with 3He isotope allowed to determine the He retention rates and Positron Annihilation Spectroscopy was used to investigate vacancy defect formation inside the W lattice due to helium accumulation.

Molecular Dynamics modeling of the implantation process has been carried out. In previous studies we have shown that comparison with experimental results give interesting insight into the mechanisms involved in the modification of W under He+ implantation: He atom interstitial diffusion, aggregation, formation of W vacancies etc. In the present work, He implantation depth and concentration profiles, bubble formation close to the surface and W rupture phenomenon have been investigated in function of the He ion kinetic energy and W lattice temperature.

Keywords
low pressure plasma/surface interaction
surface nanostructuration
ion implantation
molecular dynamics simulations
Plasma-assisted diffusion treatments are widely used in manufacturing for surface hardening of ferrous and non-ferrous materials. In particular, tribological properties of austenitic stainless steels (AAS) are improved by the formation of the so-called expanded austenite containing large amount of nitrogen or carbon. Depending on the conditions, it is commonly observed that the superficial content in nitrogen or carbon reaches a stationary value only for long times (some hours) during plasma assisted diffusion treatments. This phenomenon is difficult to observe during plasma assisted nitriding of ferritic steels due to the formation of iron nitrides with well defined composition. Low temperature nitriding of AAS offers the chance to reach a very wide range of superficial nitrogen content.

In this communication, we will present and compare the time evolution of the superficial content in interstitial elements for different plasma assisted diffusion treatments: nitriding, carburizing and nitrocarburizing. These treatments were performed on AISI 316L in a distributed electron cyclotron resonance plasma reactor. In such a system, the sample holder can be independently heated and biased and so sputtering due to ion bombardment of the surface is limited. The interstitial element contents are measured by Glow Discharge Optical Emission Spectroscopy.

For nitriding, the nitrogen superficial content exponentially increases to reach a stationary value at 9 h of treatment. This behaviour is modelled by using gain and loss terms source. Diffusion and recombination of nitrogen atoms on the surfaces are taken into account to describe the observed exponential law. Such non constant superficial nitrogen content has important consequences on the nitrogen distribution in the depth of the nitrided layer. For carburizing, carbides formation occurs very early in the process and the superficial carbon content can be considered as constant. For nitrocarburizing, the nitrogen superficial content also increases slowly with the treatment time, but the range of variation is much lower as compared to nitriding.

Finally, a discussion on the role of different surface mechanisms will be given in order to optimize this kind of process.

**Keywords**
nitriding
Artificial Neural Networks for the Prediction of Plasma Nitration Results

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Plasma nitriding is a state-of-the-art thermochemical treatment, which the processing industry uses for hardening of the surface layer of tools and components. In the past, the potential to generate optimal results was not fully exploited. For this purpose, a prediction tool which calculates appropriate nitriding parameters adapted for the required properties of the component or tool is to be developed. The aim is to perform optimized nitriding treatments taking into account for example the chemical composition, hardness and nitriding depth.

The prediction tool uses artificial neural networks (ANN). ANN usually consist of neurons which are connected and combined in an input layer, hidden layer and output layer. In order to train the network, the weight distribution of the connections, the number of hidden neurons and the neuron activation functions are varied. The aim of the ANN is to generate an output of different simulated hardness profiles depending on the chemical composition of the steel and the process parameters. In order to test the network, real-life trial results that are not incorporated into the training of the network will be used to confirm the results. This shows the accuracy of the prediction. The data base for the calculations and the training of the prediction tool are 42 variants of different nitriding processes. These are carried out using 12 different steels that differ fundamentally in their chemical composition. The composition and the process parameters have a decisive influence on the nitriding result. This generates varying hardness depth profiles in regards to the type of hardness gradient, surface hardness and the nitriding hardness depth. The data provided is used for initial training of the artificial neural network and evaluation of the predictions. Additionally, microstructural investigations enable for further analysis.

Keywords
plasma diffusion treatment
artificial neural network
Novel Atmospheric-Pressure Plasma Technology for Treatment of Fibrous Materials: Low-Cost, High-Speed Finishing of Nonwoven Fabrics and Low-Temperature Calcination of Inorganic Submicron Fibers

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The use of nonequilibrium atmospheric-pressure plasmas is emerging as an environmentally attractive alternative for the safe and economical surface treatment of fabrics. Since the growth rates of nonwovens production are extremely high, when compared with the conventional textiles industry, the novel plasma techniques for nonwovens surface hydrophilization are of particular interest, and there is an urgent need for the development of efficient, robust and cost-effective plasma treaters capable of in-line operation in ambient air at 100–1000 m/min nonwovens processing speeds. Standard "industrial corona" treaters generating highly nonuniform plasma at relatively low plasma power densities require minutes to activate nonwovens, which is too long processing time. A revolutionary plasma sources based on Diffuse Coplanar Surface Barrier Discharge (DCSBD) generating uniform diffuse plasma at atmospheric pressure make possible to reduce the processing times much below 1 sec. The results on high-speed, low-cost hydrophilization of PP nonwovens will be presented to indicate that the DCSBD technology is capable of meeting the basic in-line nonwovens production requirements. An important construction advantage of DCSBD-based devices is that the plasma is generated only in a small volume that roughly equals to the volume of the fabric treated, resulting in reduced power consumption. In the field of textile applications DCSBD plasma has been successfully tested for immobilization of nanoparticles containing the antimicrobial agent on PET nonwoven or improvement of PP nonwoven printing. DCSBD plasma also offers efficient, low-temperature and economic alternative to classical thermal calcination procedure for preparing inorganic submicron fibres (e.g. Al₂O₃, SiO₂, TiO₂). Exposure of organometallic fibres to plasma leads to removal of base polymer and formation of pure submicron fibres what was confirmed by surface diagnostic techniques.

Keywords
atmospheric pressure plasma
nonwovens
Investigation of surface pretreatment on cemented carbide cutting tools by plasma electrolytic polishing (PEP) for enhanced hard coating adhesion

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Machining tools such as milling, turning, or drilling tools play a key role in a wide range of industrial production sectors. In order to maximize a tool’s service life time, high-quality hard coatings on the tool surfaces are required. Prior to coating, the surface contamination created during the tool manufacturing process has to be thoroughly cleaned with a defined pretreatment method to ensure sufficient adhesion between hard coating layer and tool surface. The plasma electrolytic polishing (PEP) technology has received much attention owing to not only the significant improvement of surface properties in a short period of time, but also its ecological benefits. However, so far PEP treatment for carbide materials, a typical material for machining tools, is still a premature method as far as practical application is concerned. In this study, we report on the process optimization of PEP as a suitable pretreatment step on the surface of cemented carbide cutting tools. The PEP process was firstly conducted to clean the grease contamination smeared during cemented carbide tool manufacturing while minimizing tool surface compositional change and cutting edge deformation. The cemented carbide workpiece was immersed in a cathodic bath filled with an aqueous electrolyte solution and was anodically polarized (U = 90 ~ 300 V). Electrical conductivity and pH value of the electrolytic solution were controlled up to 200 S m⁻¹ and 11, respectively, by adding different types of salt. Furthermore, the workpieces were treated by varying the process parameters such as time, temperature, and workpiece position. Afterwards, a hard coating layer was deposited on the PEP treated surface by physical vapor deposition (PVD) and turning tests were performed to evaluate the coated tool’s service life time.

Keywords
plasma electrolytic polishing
pretreatment
hard coating
adhesion
Investigations on the antimicrobial effect and the surface modifications on cutting blades by atmospheric plasma jet treatment

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Manufacturers in food industries need to ensure high process hygiene, including effective as well as product-, material- and resource-friendly technologies for the decontamination of cutting blade surfaces. There still exist unsolved problems in the production of cold cuts, with regard to the avoidance of bacterial recontamination in the cutting process itself.

First experiments show the potential of atmospheric plasma jets as an alternative method for decontamination of cutting blades in food industry. For antimicrobial treatment, a variety of plasma devices are described in the literature regarding their type of ignition and the process gas used. The main reasons for the antimicrobial effect of such plasma jets are the reactive oxygen species (ROS) and nitrogen species (RNS) generated in the plasma.

Within this project* the antimicrobial effect of atmospheric plasma jets generated by different process gases (He, Ar, He/Ar mixture and O₂) on cutting blades, artificially contaminated with Listeria monocytogenes, Lactobacillus sakei or Serratia liquefaciens, were evaluated. ROS and RNS are detected on a microwave-driven atmospheric plasma jet by means of optical emission spectrometry (OES). In parallel, the cutting blade surface conditions after plasma treatment with respect to hardness and elasticity of the material are investigated.

The OES spectrum shows clearly that RNS and ROS intensities are changed with the variation of mixing ratios of He and Ar and the admixture of O₂. The impact of these findings on the bacterial inactivation will be further examined. Results will be presented and discussed.

*This research project was supported by the German Ministry of Economics and Technology (via AiF), the FEI (Research Association of the German Food Industry, Bonn). Project AiF 19256 BR.

**Keywords**
atmospheric plasma jet
antimicrobial effect
emission spectrometry
Surface modification of oxide-covered zinc and zinc alloys by means of DBD treatment

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Zinc and zinc alloy coatings are widely used nowadays due to their corrosion protection properties in the automotive and building industries [1]. Within this frame, it is of great interest to investigate the adhesion properties of such coatings. The native surface of zinc and its alloys is typically covered with the respective natural oxides and hydroxides, which have an affinity to most adhesives typically used. Surface modification by plasma can be implemented in order to modify the surface chemistry and the electrical properties to further enhanced adhesion [2,3].

In this work, the surface of oxide-covered zinc alloy ZnMgAl as well as reference zinc oxide films are modified by atmospheric-pressure dielectric barrier discharges in different gas atmospheres (Ar, Ar/O₂, Ar/H₂O). This leads to a variation in the surface chemistry and electronic properties of the oxides. The chemical surface modification is correlated to adhesion properties as determined by peel force tests. The plasma treatment is performed in a self-designed setup, which allows the in-situ characterisation of the surface with discrete polarised infrared reflection absorption spectroscopy (DPM-IRRAS) and Kelvin probe (KP) measurements. The plasma was characterized by optical emission spectroscopy (OES). Further chemical characterization of the surfaces is done ex-situ by X-ray photoelectron spectroscopy (XPS).

The financial support of the German Research Foundation (GR 1709/19-1) is gratefully acknowledged.


Keywords
DBD plasma
ZnMgAl
surface chemistry
Atmospheric pressure plasma treatment of polyurethane foams with oxygen containing feed mixtures

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Atmospheric pressure non-equilibrium plasmas attract growing interest in surface processing of materials, since the absence of vacuum equipments allows the reduction of processes and reactors costs, the employment of easy-to-handle apparatuses and the easier integration into continuous production lines. Dielectric barrier discharges (DBDs) are particularly suitable in this applicative field as for instance for the treatment of non-conductive materials (e.g., plastics, textiles, etc.) and of high specific area 3D porous substrates. Due to their operating conditions, DBDs allow the ignition of the discharge also inside small cavities and, therefore, assure the uniform treatment of the entire structure of porous substrates. This contribution focuses on the treatment of polyurethane (PU) foams by atmospheric pressure DBDs fed by He and O₂ mixtures, in order to functionalize the 3D foam porous structure with oxygen containing groups. Plasma treatments were carried out using a home-built atmospheric DBD reactor with parallel plate electrode configuration; commercial PU foams (pore density of 45 pores per inch, porosity of about 97%), were used as substrates. The surface chemical and morphological characterization of the PU foams was carried out with small spot X-ray Photoelectron Spectroscopy (XPS) and Field Emission Scanning Electron Microscopy. The treatments resulted in an efficient functionalization of the PU with oxygen containing chemical groups, including carboxylic moieties. The XPS characterization showed that uniform treatments were achieved, since appreciable composition differences were not detected also throughout the foam thickness. Treated PU foams were able to adsorb heavy metal ions from water. The adsorption capacity was evaluated for cadmium and lead by measuring, with Anodic Stripping Voltammetry, their concentration before and after the immersion of the foams in aqueous solution. The ageing of treated PU in water was studied with Nuclear Magnetic Resonance spectroscopy and High Resolution Mass Spectrometry. These investigations allowed us to obtain interesting details on the PU treatment with oxygen containing DBD and information on the chemical composition of the fragments released in water by the treated PU foam.

Keywords
DBDs, plasma treatment, PU, heavy metal adsorption
Surface Modification of Polytetrafluoroethylene by Atmospheric Pressure Plasma of Dielectric Barrier Discharge with Ar/Liquid Vapor Mixture Gas

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For variety of industrial application of Polytetrafluoroethylene (PTFE), it is required to improve the surface property of poor adhesion with other materials. Plasma surface treatments have been expected to modify the PTFE surface and some successful results have been reported. Atmospheric pressure plasma techniques have many advantages for treatment of polymer surface; no usage of vacuum system, simple configuration of apparatus, high density plasma for rapid treatment, small environmental impact, and so on. It is expected to rapidly prepare hydrophilic surface with improved adhesion on PTFE by atmospheric plasma irradiation.

We have been studying on surface modification of PTFE by atmospheric pressure plasma using mixture gas of Ar and some kinds of liquid vapor. A dielectric barrier discharge was operated in a simple configuration of parallel electrodes, i.e., in a small gap between a pair of glass plates with a pair of parallel electrodes stuck on both the outsides of the glass plates. A sample of PTFE sheet was placed on a lower glass plate with remaining small space for plasma production between the specimen and the upper glass plate. Ar gas was bubbled in liquid in a bottle for supplying the liquid vapor and the mixture gas was fed into the discharge gap. As the reactive vapor of liquid, ultrapure water, methanol, ethanol, 2-propanol and acetone were examined. After plasma treatment for 10 seconds, the static water contact angle was measured. In all the cases, the water contact angle was significantly decreased from the original surface. By using methanol or ethanol, hydrophilic surface of 20° to 30° contact angle was achieved while the original surface showed 109°. It has been confirmed that atmospheric pressure plasma treatment using our designed configuration with Ar/liquid vapor mixture gas can be useful for PTFE hydrophilization.

Keywords
Surface modification
Polytetrafluoroethylene
Atmospheric pressure plasma
Dielectric barrier discharge
PO2074

**Surface Modification by Atmospheric Pressure Plasma Jet for Texturing Monocrystalline Silicon Solar Cell**

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Types of atmospheric-pressure plasma technology, such as the thermal plasma torch, corona discharge, plasma arc, and plasma jet have been widely used in the field of surface treatment. In this study, atmospheric-pressure plasma jet (APPJ) was conducted to increase the surface roughness' structure of silicon wafers for the further texturing process with alkaline etching solution immersion. The surface characterizations and morphologies of APPJ-treated samples were observed by water contact angle (WCA) and field emission scanning electron (FE-SEM), respectively. The reflection behaviors were collected to analyze the samples' light absorption. The results show that the factors of scanning times, the distance of substrate to nozzle, and the plasma power highly affected the surface due to the levels of plasma ion bombardments on samples. Subsequently, the APPJ-treated samples were immersed in the alkaline etching solution to obtain a pyramid structure. Moreover, this study shows that the formation of pyramid structures was obtained with a lower reflectivity of 5%. Furthermore, this study proves that the combination of pre-treatment by APPJ on monocrystalline silicon and etching process is evidently proved to reduce the etching time and the quantity of etching solution, which can be viewed as the green chemistry for the solar cell industry.

**Keywords**

Atmospheric Pressure Plasma Jet  
Surface modification  
Alkaline etching solution  
Pyramid structure
Solder Wettability Improvement in Copper (Cu) Substrate using Direct Current Atmospheric Plasma

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Oxidation reaction has decreased the wettability of copper (Cu) substrate in soldering industries. The formation of native Cu oxide significantly reduced the solder-ability on Cu. Direct current atmospheric plasma (DC-AP) with the mixture of N₂/H₂ carrier gas can be carried out to reduce the surface oxide on Cu substrate and consequently improve its wettability. The plasma ion is producing an NH radicals and bombarding the oxide surface layer of Cu substrate. The wettability of SAC305 on Cu substrates with a dimension of 30 mm x 5 mm x 0.2 mm was tested by wetting balance following JIS Z 3198-4. The results show that the fast plasma scanning rates (30-60 mm/s) may well-cleaned the Cu surface and performed a good wetting. Furthermore, the mechanism of surface treatment and the effect of various gas sources will be discussed.

Keywords
oxidation
wettability
soldering
direct current atmospheric plasma
NH radicals
Surface Modification of Soda-Lime Glass by Low-Pressure Glow Plasma and Gliding Arc Plasma Treatments

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Surface preparation is the key step to better adhering multi substrates for electronics, photonics, architecture and packaging without facing with a poor performance. Soda-Lime Glass, being cheap and amorphous, is a very suitable substrate for preparing films. Since the process of printing on glass is so intolerable and because of the existing difficulties in activating its surface, we are trying to improve the procedure of dyeability and its adhesion properties by using plasma treatment on the surface of the glass samples. In this research, the surface of soda-lime glass was studied by the application of Low-Pressure Glow Plasma and Gliding Arc Plasma so that the key properties of glass such as water contact angle, roughness and dyeability could be tested.

In this study, Two basic parameters including Treatment Time and Power for both Low-Pressure Glow Plasma and Gliding Arc Plasma were taken into consideration. To study the improvement of the surface structure of soda-lime glass samples, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Fourier Transform Infrared spectroscopy (FTIR) and Water Contact Angle (WCA) were performed. The test of WCA shows that the angle of contact with the surface of the soda-lime glass, after plasma treatment, extremely decreased and the surface energy of the glass considerably increased in every test. Also, SEM and AFM show that plasma treatment has had remarkable impacts on the surface structure of the substrate in such a way that the increase in both the adhesion of the surface of the glass and its roughness is sensible. Tests of washing and rubbing show that in optimum case, the paint printed has acceptable stability. At last, the results obtained from both devices are compared to each other for industrial applications.

Keywords
Surface Modification
Atmospheric Plasma
Low-Pressure Plasma
Adhesion
Glass
Batch Microwave Plasma Cleaning for Robustification of Automotive Devices

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Considering the function requirements in the automotive industry, a more robust electronic system is required to ensure both safety and user satisfaction. The most common defect encountered in the IC packaging industry is interfacial delamination – caused either by material mismatch during thermal expansion or by surface contamination. The latter can be easily addressed with plasma cleaning techniques. This study attempts to explore the use of batch microwave (B-MW) plasma cleaning to address delamination on NiPdAu lead frames in the IC manufacturing industry.

Conventional plasma cleaning machines have a strip-type set-up which involves direct application of plasma onto lead frame strips. However, the direct flow of plasma has been observed to damage die and wire parts. The batch-type set-up is becoming increasingly popular due to its indirect application of plasma and higher throughput. Plasma cleaning mechanisms involve a combination of physical and chemical reactions; although, parameters can be adjusted to make either type more dominant. Physical reactions are typically more dominant in RF while chemical reactions are more dominant in MW.

Six factors were initially identified to directly affect the efficiency of B-MW plasma cleaning: power, cleaning time, flow type, gas mix, ratio of reactive-to-inert gas and staging time. Among these six factors, the flow type has the most profound effect on the cleaning efficiency – even affecting the role of the other five factors. Flow type is categorized into two: (1) pulsed and (2) constant flow. With the use of constant flow, the average contact angle is also reduced by 50% and uniformity improves.

Keywords
batch
microwave
IC packaging
automotive
electronics
Adaptations in diffusion treatments enable the tool life time enhancement of forging dies

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The economic viability of hot forging processes for the effective production of safety relevant parts with excellent mechanical properties depends on the occurring wear of the tools, which limits the service lifetime.

By modifying the surface zone layer it is possible to create a material resistance against thermal softening, which is provoking plastic deformation and pronounced abrasive wear. On the other hand, intensely nitrided surfaces often show an increased crack sensitivity and therefore the chipping of material is possible. New approaches in adapted processes will minimize the disadvantages and keep the high technological potential in reducing thermally caused damages.

State-of-the-art techniques are enabling localized treatments by applying pastes or other coverage in order to prevent certain sensitive areas from nitrogen diffusion. This leads to the new approach of structuring the surface with differently designed patterns generating a surface with ductile zones beneath nitrided ones. This influences the formation and propagation of cracks under thermal shock conditions.

To evaluate the advantages, an accurate system of testing rigs for the abstraction of the thermal shock conditions proves the technological potential of the development. This includes the constructed flexible testing unit with a heated punch and adjustable quenching conditions and serial forging tests. Special analytical methods characterize the crack sensitivity of the modified surface zone layers.

With an optimized crack behavior of the surface zone layer, the efficiency of the industrial production process is enhanced due to the stabilized and increased service lifetime of the tools.

Keywords
plasma diffusion treatment
patterning
wear reduction
hot forging
An investigation on pulsed microwave-driven plasma jet etching for borosilicate glass

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Reactive plasma jet etching is an alternative surface machining technique for the generation and correction of highly precise optical surfaces such as lenses and mirrors. For this technique a multi-component non-thermal chemically reactive plasma is employed. The active particles, which are created by pulsed microwave power, can react with the solid surface and form volatile compounds, and then the surface will be successfully etched. Etching processes have been tested so far mostly for quartz and silica-based glasses using fluorine-based chemistry (e.g. using CF$_4$ as precursor gas), as most of fluoride-silicon compounds are volatile. However, the borosilicate glass contains metal elements which produce non-volatile fluorides such that the dry etching of surfaces in the room temperature under the atmospheric pressure is a difficult task. On the other hand, the fabrication of a range of optical components requires the etching of borosilicate glass. It is expected that by the development of sufficient control on etching processes, novel fabrication processes in optical elements will be facilitated. Therefore, the development of a practical plasma etching process for borosilicate glasses is highly demanding in practice.

The applicability of reactive plasma etching for a difficult-to-etch borosilicate glass (e.g. N-BK7) requires expanding the choices of reactive etching gases and widening the temperature range under a vacuum condition. For this purpose, we develop a plasma jet that contains different reactive halogenated compounds as well as some non-halogenated etching gases such as oxygen which are admixed to inert plasma gases like argon and helium. Reactive atoms chemically react with the borosilicate glass exposed to the plasma and form volatile fluoride-silicon compounds and non-volatile metal fluorides. We perform experiments to optimize the relevant phenomena and process parameters in order to achieve etching of surface by removing non-volatile deposited fluoride residues. Subsequently, we establish a fundamental understanding of the chemical mechanisms and kinetics of etch product formation.

Keywords
plasma etching
metals
Remote plasma sources (RPS) operated by microwave power are widely used for different industrial etching applications, e.g. decapsulation of semiconductor chips for failure analysis, cleaning of plasma deposition chambers in semiconductor industry and production of micro components. The special feature of an RPS is limitation of the plasma to the plasma chamber inside the RPS. Being connected to the process chamber, only radicals produced in the plasma will migrate from the plasma chamber of the RPS into the process chamber and act on the surface of the substrate to be treated, thus avoiding any impact of bombardment by charged particles. Therefore, only chemical etching by radicals will occur in the process chamber. Fundamental understanding of the processes inside the plasma chamber of the RPS is necessary for improving process parameters, i.e. the etching rate in particular. Therefore, microwave coupling into and microwave distribution inside the plasma chamber were modeled by two different finite element method (FEM)-based simulation programs, namely COMSOL Multiphysics and CST MICROWAVE STUDIO. The simulation results obtained showed to be in very good agreement. Based on these results, a new RPS was developed and analyzed concerning different experimental parameters. Experimental characterization of the ignition process is fundamental for understanding the basics of the RPS and the most efficient way for microwave injection. Therefore measurements of the ignition time representing the time delay between microwave injection into the plasma chamber and final plasma ignition as well as of the time-dependent average light intensity and optical emission spectra providing information on the energetic state of the radicals and ions was performed. In addition, the kinetic behavior of the plasma during the ignition process was observed by a high speed camera system. The correlation of the respective simulated and experimental values and results will be presented in this paper. Finally, the improvements achieved with the newly developed RPS were evaluated by etching tests on standardized samples.

Keywords
Remote plasma source
Plasma Etching
Microwave Plasma
Optimization of novolak-based photoresists for ion beam planarization of aluminium mirrors

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Technical aluminium alloy materials as AL6061 or AL905 are widely used in fabrication of high performance mirror devices. The surface error topography after common manufacturing by single-point diamond turning meets the requirements for applications in the infrared spectral range. However, for short-wavelength applications in the visible and UV spectral range the demands on the optical surface quality increase immensely. To use the aluminum mirrors in the short-wavelength, i.e. visible and UV, spectral range, one technological solution is the coating of the Al optics with an amorphous nickel-phosphorous (NiP) layer and a metallization layer on top to realize ultra-smooth, highly reflective surfaces. The reduction of the surface roughness of aluminum optics without use of a NiP coating and accompanying the simplification of this process chain is preferable.

Ion beam planarization processes are a promising technology to transfer the ultra-smooth surface of a planarization layer into the underlying aluminum substrate. Novolak-based photoresists, which are commonly used in the semiconductor industry, were deposited on the single-point diamond turned aluminium mirrors by spin coating to compensate differences in height. By reactive ion beam processing, the ultra-smooth surface topography of the photoresist is transferred into the substrate. One important parameter which affects the transfer process significantly is the selectivity, the ratio of the etching rate of the underlying substrate to the etching rate of the planarization layer. An approximation of a selectivity of 1:1, that implies equal etch rates for planarization layer and aluminium substrate, is prerequisite for the transfer process. Thermal pre-treatment of the planarization layer and different operating gases affect the properties of the resist during the etch process and the selectivity significantly.

Keywords
Ion beam planarization
reactive ion beam etching
photoresist
mirror optics
Reducing the reflected light in optical systems represents one of the basic aims of photonics. Reflected light causes losses to the intensity of transmitted light and can generate ghost images and stray light. To reduce reflectivity, interference multilayers are typically used. The application of nanostructures with low refractive index represents an improved approach to realize antireflective (AR) properties. Nanostructured layers can be generated by plasma etching of organic materials. Only a few materials have been found yet which show the formation of a bumpy structure by etching without initial layer deposition. Especially, these “self-organized” nanostructures provide a well-controllable effective refractive index below 1.2 and a thin-film thickness higher than 100nm which is promising for broadband AR coatings. Aim of this work was to evaluate several biomaterials regarding their ability to form suitable nanostructured layers for AR. In a first part, materials directly provided by microorganisms were used. Optical characterization and etching experiments have been carried out on microbial polysaccharides (MPS) and on bacterial nanocellulose (BNC). Nanostructures with antireflection effect in the near-infrared region (NIR) could be achieved on MPS and BNC. In a second part of work, nucleobases like Uracil, Thymine and further biomolecules were investigated regarding their usability for thermal evaporation and structure formation. Uracil has been identified to form bump structures in a self-organized way. The development of the structure was studied by using Scanning Electron Microscopy and optical spectroscopy. A nanostructured Uracil layer has been applied as the last layer of an AR coating to demonstrate the improved antireflection function in comparison to commonly used inorganic AR coatings.

Keywords
nanostructures
etching
antireflection
biomaterials
Photoresists are used in industry for lithographic processes to produce surface structures in the sub-micrometer range. In the final step of the manufacturing process, the cured polymer layer acting as shaping die for the microstructures grown by electroplating has to be removed. Etching of the cured resist pattern poses an extreme challenge, as the microstructures must not be damaged. Dry plasma chemical etching by means of radicals generated in the plasma chamber of a remote plasma source (RPS) is a suitable means avoiding damage to the microstructures made of metals like nickel, copper or gold.

The aim of the study is to optimize the existing source with regard to its etching rate and gas temperature and to simplify its setup in order to save production costs. Using the FEM-based simulation software COMSOL Multiphysics a model of the RPS has been developed to investigate the microwave distribution and the microwave coupling into the plasma chamber for different RPS setups. If a plasma is ignited, the electron density and thus the permittivity and the conductivity increase, which changes the electric field distribution in the plasma chamber. For this purpose, the model has been extended in a first step by a collision-free Drude-Lorentz model. By using a high speed camera system during the ignition process the average light intensity can be plotted vs. the time and thus give information about the ignition process itself and the stability of the plasma.

The conclusion gained by the investigation of the RPS through the high speed camera will be presented as well as the FEM-based model of the RPS and results of the measured and simulated E-field distribution in the plasma source. The E-field distribution is experimental measured by heating up substrates and visualized by liquid-crystal sheets, thermal camera and thermal paper. Furthermore, the achieved etching rates and the spatial distribution of the etching rates will be presented.

**Keywords**

Simulation
Plasma Etching
Microwave Plasma
Plasma decapsulation of microchips with silver (Ag) bonding wires

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Future trends in semiconductor industry aim at 3-dimensional structures and further miniaturization of microchips for improved performance and higher energy efficiency. Amongst other challenges to be met, metals with improved electrical conductivity are indispensable for electrical bonding of the more and more complex microchip structures. Consequently, silver – providing the requested improved electrical conductivity – is increasingly replacing state-of-the-art metals used for electrical bonding.

Plasma decapsulation of microchips for failure analysis has to guarantee minimum damage of both the chip structures and the bonding wires. The Rapid Reactive Radicals Technology (R3T), introduced by the microwave driven Remote Plasma Source (RPS), provides the capability for fast plasma decapsulation of microchips with high selectivity and no attack on metals like gold (Au), aluminum (Al), copper (Cu) and alloys from copper and palladium (Pd) frequently used for conducting paths and bonding wires. The radicals generated by the RPS only produce chemical reactions at the surface of the substrates, leading to pure chemical etching at high rates with extremely low thermal load, thus keeping the effect on the microchip and on the bonding wires as low as possible.

Unlike the above-mentioned metals and alloys frequently used for bonding wires, silver can easily and severely damaged by radicals generated from oxygen and fluorine compounds. In order to be able to perform plasma decapsulation even of microchips with bonding wires made of silver, the R3T technology of Muegge enables damage free decapsulation introducing different process gases and varying process parameters by focusing on microwave power and chamber pressure. Different process conditions were applied in the tests. The results of this parameter variation that will be presented in this paper finally led to successful decapsulation of the microchip without damaging the silver bonding wires.

Keywords
Remote Plasma Source
Plasma Etching
Microwave Plasma
Plasma Decapsulation
Silver Bonding Wires
Plasma surface treatment of PLA polymers by PECVD in tissue engineering

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In tissue engineering, cell adhesion is an important feature for biomaterial which can be achieved with surface treatment. Complex structures and scaffolds can be easily processed in tissue engineering and may induce the desired functional group on their surface with plasma.

In this research poly lactic acid (PLA) was used as the raw material. To improve its surface characteristics, such as cell adhesion, plasma enhanced chemical vapor deposition (PECVD) was used in the radio frequency mode. The hydrophilicity and roughness of the PLA films were investigated after nitrogen plasma processing. Hydrophobic recovery of the surface was investigated in two different environments, room temperature and temperature between 0-8. Adipose tissue stem cells were cultured on the samples. After 3day SEM was done to illustrate cell adhesion.

Plasma diagnostic (optical emission spectroscopy) showed that N₂⁺ and N₂ species have an important role in nitrogen plasma treatment. For the hydrophobic recovery test, samples kept in low temperature maintain hydrophilic property after 30 days. Plasma surface treatment improves cell adhesion relating to high wettability and roughness.

Keywords
Radio frequency plasma
PECVD
Cell adhesion
Wettability
Roughness
Si based coated fabrics using plasma polymerization method for efficient oil-water separation

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In recent years, the increase of industrial effluents in particular the leakage of oil and the draining of industrial effluents in rivers, has created serious environmental hazards and huge economic lost. The use of hydrophobic and oleophilic fabrics has been considered as a way to clean up contaminants through the absorption and separation of pollutants from industrial effluents.

In this research, the low-pressure plasma polymerization method based on eco-friendly materials like Polydimethylsiloxane was used to fabricate hydrophobic and oleophilic cotton fabric. Also a low-pressure oxygen plasma pre-treatment was performed before plasma polymerization.

Contact angle test and absorption capacity test was used to represent hydrophobicity of coated fabric and to measure the absorbance ability of different oils. Also scanning electron microscopy (SEM) was used to observe morphological changes on the surface of cotton fibers and Infrared Fourier transform (FTIR-ATR) spectroscopy to detect the chemical bonds created on the surface of fibers. Water-oil separation efficiency and laundering test have been conducted to determine the separation rate and to represent durability of coated cotton, respectively.

The water contact angle of coated fabric was 142±3 and this high hydrophobicity behavior remained after 10 cycle laundering. Also SEM results showed that the surface of fibers was covered by a random distribution of several microscale structures or a hierarchical surface structure like the lotus leaf. Our Water-oil separation tests demonstrated that coated fabrics had a high separation efficiency of 85 to 95 percent after 15 cycles for most of the industrial oil. These results indicate that si based coated cotton fabrics has a high potential for application in water-oil separation and selective oil absorption and they are promising for the development an environmental friendly and recyclable separation of oil from water.

Keywords
Polydimethylsiloxane
plasma polymerization
hydrophobic-oleophilic fabrics
water-oil separation
Nanostructured W has been studied comprehensively through experiments due to the strong likelihood of W being included as a plasma facing material in future fusion reactors, most notably ITER and DEMO. The nanostructure, more often called fuzz, is produced when He ions of a sufficient energy irradiate a W surface and high pressure He bubbles are formed, with loop punching and W adatom processes being theorised to produce the tendril structure. The accepted values for the conditions required to produce W fuzz formation have been summarised and generally for surface temperatures of between 1000K to 2000K, a He ion energy of $\geq 20$eV and a fluence of He ions of at least $2.4 \times 10^{24}$ m$^{-2}$ W fuzz can be formed. Recently the importance of looking at lower flux devices has become more prevalent, particularly the use of magnetron sputtering devices to investigate He irradiation of W for fusion applications. The devices themselves allow sputtering of a known metal target due to confinement of plasma in front of the target, with energetic plasma ions bombarding the target surface and producing sputtered atoms which are deposited on a substrate. In this work this effect is used for insights in to deposition of metal atoms on to a W surface which will be transitioning to fuzz, and what the overall effect on the fuzz structure is in these deposition environments. Previous studies have focused on low fluence ranges in magnetrons ($\sim 10^{24}$ m$^{-2}$) but here we look at higher fluence ($\geq 10^{24}$ m$^{-2}$), deposition regimes. The ion energy is varied from the non-sputtering regime ($\leq 100$eV) to the sputtering regime of He on W ($\geq 100$eV). The surface structures produced from these two investigations will be analysed using SEM and FIB-SEM for thickness data, and EDX analysis for the chemical composition of the structures.

**Keywords**

Tungsten  
Helium  
Nanostructure  
Fuzz
High quality coatings with high deposition rate by PECVD with improved hollow cathode plasma

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A new type of Hollow Cathode device has been developed by AGC Plasma, the industrial vacuum equipment manufacturing segment of AGC. The scale-up of this device has been successfully performed for Plasma-Enhanced Chemical Vapor Deposition [PECVD] coatings on lab samples (a few cm²) up to jumbo-sized glass plates (3.2x6.0m²).

Many thin film coating applications require optical stacks including a thick layer. However, conventional vacuum deposition technologies like magnetron sputtering require too much processing time to be economically viable for such thickness. New coating process like PECVD (as done by Hollow Cathode) is now able to reach a very high deposition rate unlocking new possibilities.

This lab study is confirming both the performance of the new process and the coating quality. The main body of this paper is focused on SiO₂ deposition onto flat glass substrates at low temperature and under low pressure, which is compatible with inline production including PVD. The deposited films have been fully characterized including thickness, content, stress, and density.

Results have shown that carbon free silicon oxide coating can be obtained using typical precursor materials with well-tuned process parameters. OH fraction into the film deposited at low temperature needs to be reduced to maintain the desired density, especially after thermal treatment. SiO₂ deposition rate can be very high (at least 10 times higher than regular PVD). This process is not limited to SiO₂. Hollow Cathode PECVD can allow for coatings of a wide variety of other materials, like carbide, nitride or oxy-nitride if other precursors or reactive gases are injected.

Keywords
PECVD
Hollow Cathode
Coating
SiO₂
Si₃N₄
Modification of polymeric track membranes by exposure to various plasma configurations

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Intensive efforts have been devoted lately to the development of membrane processes including gas separation, water desalination, pervaporation, purification of biologically active compounds, etc. Nevertheless, the intrinsic properties of membranes, in particular those of polymeric materials, may be greatly improved by subsequent processing aiming the modification of composition and structure of the surface layer. In this work we present an overview of the results obtained upon processing of polymeric nuclear track membranes (TM) in various plasma configurations. Polymeric foils of polyethylene terephthalate (PET) and polypropylene (PP) have been irradiated by accelerated heavy ions (1-3 MeV/nucleon) and chemically treated in order to obtain TM with cylindrical nanochannels of 60 – 400 nm diameter. Various types of plasmas were considered for controlling the TM transport and/or filtration properties. The results showed that membranes exposure to non-depositing plasmas (like H₂, He, Ar, O₂, N₂, air, or halogens) conduct to surface etching, formation of conical-shaped pores and addition of functional groups on the membrane surface and inside its pores. On the other hand, exposure to depositing plasmas by means of PECVD or plasma polymerization processes with various precursors (C₂H₂, C₂H₂F₄), monomers (C₄H₄S, C₄H₅N) or organosilicon (HMDSO, HMDSN) vapors, or by physical vapor deposition processes starting from polymeric targets (PTFE, PP, UHDPE) in RF magnetron sputtering or electron beam deposition results in a wide variety of bi-layered membranes with transport properties controlled by the specificity of the deposited polymers in terms of chemical composition, morphology, and/or behavior in solution (e.g. swelling or wettability).

Acknowledgment. This work was performed in the frame of bilateral JINR-NILPRP collaboration (Protocols No 04-5-1076-2009/2016, 04-5-1131-2017/2021).

Keywords
polymeric track membranes
plasma processing & surface modification
transport properties
Cyclopropylamine, an isomer of widely known allylamine, is a promising candidate for deposition of amine-rich coatings thanks to the low toxicity, excellent stability of prepared coatings and relatively high content of amine groups. However, for further optimization and up-scaling of the process a deeper understanding is crucial. The presented work investigates some fundamental aspects of the deposition process by plasma diagnostics and discusses it within scope of the macroscopic kinetics. The gas phase processes are investigated by mass spectrometry and optical emission spectroscopy, whereas surface processes, mainly the ion bombardment, are studied by retarding field energy analyzer. This work provides insight into the correlation between the inner plasma parameters obtained from diagnostics and properties of the thin film characterized namely by X-ray photoelectron spectroscopy and infrared spectroscopy. Finally, the link between the external parameters and desired thin film properties can be established.

Keywords

cyclopropylamine
plasma polymerization
plasma diagnostics
amine-rich thin films
Comparative study of zirconium and titanium oxide thin films obtained from metalorganic precursors by LP-MW plasma process

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Comparative study of Zr and Ti oxide nanocoatings obtained by low P°PECVD is the subject of this work. Zr (IV) tert-butoxide (ZTB, ZrO4C16H36) and Ti (IV) isopropoxide (TTIP, TiO4C12H28) have been used as Metal organic precursors (MOP). Thin films were grown in a multi-dipolar ECR microwave (MW) plasma. O2 gas was used as an oxidant. Diagnostics such as OES, FTIR, XPS, SEM, AFM, XRR and ellipsometry porosimetry (EP) have been used to study the influence of 3 parameters on the plasma phase and the thin film characteristics: O2 gas proportion in precursor/O2 mixture, total gas pressure and addition of HMDSO to the gas mixture. First, O2 percentage was increased in the MOP/O2 mixture at constant total gas P° of 1 mTorr. Deposited ZrOCH and TiOCH thin films evolve from organic to almost inorganic. In O2-rich plasmas, the growth mode changes and columnar morphology appears. Nevertheless, in both zirconia-like and titania-like films, the density increases significantly compared to the films deposited at 100% MOP when a compact and uniform morphology has been observed. Next, total gas P° has been varied from 1 to 10 mTorr in a 5% MOP/95% O2 mixture. Thin film nanoporosity increases with total gas P° to reach 16% and 10% at 8 mTorr in ZTB and TTIP plasmas, respectively. In films deposited in ZTB/O2 plasma, remarkable changes in morphological properties are observed: from closely stacked columns obtained at 1-2 mTorr to the disappearance of columnar structuration at 8 mTorr. Last, HMDSO was added to the 5% MOP / 95% O2 mixture. Depending on the proportion of HMDSO, the morphology of the films can be uniform and compact with no observable structuration as well as columnar while chemical composition stays relatively stable. Thus, it has been demonstrated that these 3 parameters allow modifying and controlling the layers composition, morphology and properties over very wide ranges.

Keywords
low pressure PECVD
ZTB
TTIP
HMDSO
nanocoatings
Gradient Structures Enhancing Stability and Functionality of Plasma Polymer Films

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Functional plasma polymer films (PPFs), e.g. containing carboxyl or amino groups, typically reveal limited stability in aqueous media due to swelling and degradation. In particular, amine-functional PPFs were found to be prone to oxidation and hydrolysis reactions. To improve the stability of PPFs while maintaining a suitable amount of available functional groups, vertical chemical gradients in PPFs were thus explored based on a crosslinked structure that gradually becomes more functional towards the surface. Thus, migration and degradation processes can be effectively hindered. A comprehensive study involving plasma diagnostics (OES) and surface characterization methods (XPS, ToF-SIMS, AFM, contact angle, zeta potential) was performed to define a suitable vertical gradient structure on the nanoscale. The stability in water was compared for carboxyl- and amine-containing PPFs, with and without vertical gradient structure. Highest stability combined with functionality was achieved for 1-2 nm thick terminal layers of higher functional group density. Thereby, the initial number of functional, e.g. amino, groups can be preserved in aqueous environments, while a reference layer lost all –NH₂ groups after the first day of immersion in water. Chemical processes to support the stabilization of the functional surfaces are discussed. Finally, lateral gradients as well as combinations of N and O functional layers were investigated revealing important aspects with respect to protein adsorption.

Adjusting the thin film architecture of plasma polymer films thus provides an additional parameter to modulate surface properties of materials offering unique opportunities for biomaterials and chemical engineering.

Keywords
plasma polymer
chemical gradient
subsurface structure
protein adsorption
Nano crystalline diamond Microwave chemical vapor deposition growth on three dimension structured Si substrates at low temperature

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The unparalleled hardness, low friction and heat conductivity properties of diamond make it attractive for many applications. The use of diamond as a coating has increased with the development of high growth-rate protocols using Hot Filament Chemical Vapor Deposition (HF-CVD), which usually operates at high substrate temperatures around 600 to 900°C. Nano crystalline diamond (NCD) films grown at a temperature below 400 °C can open new applications on temperature sensitive substrates. One requirement for the applicative use of NCD is the ability of depositing on a structured substrate having high aspect ratio. This work presents a study on the three dimension (3D) conformity of NCD deposition at low temperature (350°C) and low pressure (30 Pa). Silicon wafers have been structured using a mask-less Deep Reactive Ion Etching (DRIE) process and seeded with nano-diamond particles. The NCD films were grown on these 3D patterned Si substrates with various trench geometries to provide means of determining the limiting geometries of this technique. The NCD deposition system employs a set of Hi-Wave microwave antenna each connected individually to a solid state microwave power generator. By measuring the step coverage with changing trench width, a threshold for conformal NCD growth can be determined. The NCD films at the bottom of the 100 µm deep trenches were continuous down to an aspect ratio of 1:7.

**Keywords**
Nano crystalline diamond
MEPS
3D Conformity
Surface modification of oil tube steel by plasma coating for corrosion resistance enhancement in CO2/brine

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More and more oil and gas reservoirs are used for commercial CO\textsubscript{2} enhanced oil recovery, resulting in associated CO\textsubscript{2} storage that occurs as part of the process. CO\textsubscript{2}/brine corrosion of oil tube steel that can occur anywhere along the wellbore is a challenging issue facing the oil and gas industry. To enhance their corrosion resistance in CO\textsubscript{2}/brine, J55 and N80 oil tube steels were coated with trimethylsilane plasma coatings (TMS-PCs) by plasma chemical vapor deposition (PCVD) method. Both atmosphere and vacuum direct current (DC) discharges were utilized for TMS-PCs deposition. X-ray photoelectron spectroscopy (XPS) was used to characterize the coating surface chemistry. It was found that TMS-PCs deposited by vacuum DC plasma coatings (VDCPC) had higher Si- and C-rich composition than atmospheric DC plasma coatings (ADCPC). The corrosion resistance of TMS-PC coupons was evaluated through weight loss method (WLM) and three dimension pitting corrosion quantitative evaluation method (3D-PCQEM), which was conducted in CO\textsubscript{2}/brine with the self-built corrosion resistant performance evaluation system (CRPES). The results demonstrated that the TMS-PCs can significantly decrease not only the uniform corrosion rate but also the pitting corrosion rate of N80 and J55 oil tube steels. TMS-PCs deposited by VDCPC showed less corrosion rate than that of ADCPC. The scanning electron microscopy (SEM) was used to characterize the coating surface morphology before and after WLM, and the results indicated less corrosion and pitting corrosion on coated coupons than uncoated controls. The energy dispersive spectrometer (EDS) was used to characterize the coating surface chemistry before and after WLM, which also indicated that the ferric content of coated coupons was higher than that of uncoated controls after WLM. The results obtained in this study indicate that plasma coatings may serve as a very promising barrier against the corrosion and pitting corrosion of oil tube steel in CO\textsubscript{2}/brine.

Keywords
Corrosion resistance
plasma coating
Trimethylsilane
CO2
FTIR and visible optical characterization of SiCN:H thin films deposited in Ar/TMS/N2 dual ECR and RF-PVD plasmas

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The particular optical and electronic properties of SiCN:H thin films make them useful for photovoltaic, optoelectronic and mechanical applications. Films properties depend strongly on their chemical composition and microstructure, and can be easily tuned through plasma process as well as gas mixture and composition. This work aims at modifying the physical properties of SiCN:H films by varying the Si content in the feed gases while keeping constant Ar, N2 and TMS (Tetra Methyl Silane). Films were grown on Si (100) floating or grounded substrates at a temperature of 400° C by dual ECR (2.45 GHz) and RF (13.56 MHz) PVD plasmas with silicon target, and variable RF biasing (Vbias). The plasma was characterized using optical emission spectroscopy (OES), and films were monitored in situ by visible reflectometry. They were analyzed ex-situ by SEM, FTIR, SIMS, and UV-Visible spectrometry. OES showed emission from Ar, Si, Hα lines and N2, CN, CH, NH rotational bands from the species in the plasma during the growth. Intensities of these excited states enhance with Vbias. IR optical index and film thickness were deduced using homemade software ASUVIR developed in MatLab from the measured transmittance with correcting its base-line. The film thickness thus found is in good agreement with SEM measurements. Moreover, this software allows a right estimation of film composition from FTIR spectra deconvolution. A sensible decrease of the CH2 line (2950 cm⁻¹) and increase of NH (3350 cm⁻¹) one with augmenting Vbias is obtained from FTIR spectra of thin films. For Vbias higher than 100 V it is possible to enrich the films with silicon. An increase of all density chemical bonds of SiC and decrease of SiN ones is observed when Vbias augments, indicating that the film composition varies from nitride to carbide-like films. However, the transparency of the films in the visible spectrum is decreased. This behavior could be corrected by hydrogen introduction in the feed gas. The SiCN:H obtained films appears very suitable for antireflective applications and Si-based PV. Moreover dual ECR –PVD plasma process appears very promising for high growth rate and homogeneous deposit on large scale substrates.

Keywords
Dual ECR-PVD plasmas
SiCN:H
FTIR
Effect of carbon presence in CrCN coatings on machining of aluminium alloys

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Precise and high quality machining of the surface is required for aluminium alloys used in the aerospace industry. The resulting surface treatment must not cause stress or defects that could cause the formation or spread of cracks in the surface. For this reason, two basic conditions have to be met: a) selection of a correct tool geometry allowing a smooth chip removal reducing local overheating of the tool and b) selection of a convenient chemical composition of the tool surface to prevent sticking of the machined material to the tool.

The effort to reduce costs and the ecological impact leads to the elimination of the use of cutting fluids and therefore high-speed dry machining is increasingly preferred. In this case, the tool surface must prevent possible chemical reactions or diffusion between the coating and the machined aluminium alloy at temperature peaks up to 650°C at the cutting edge of the tool. For the dry machining of aluminum alloys, ZrN and CrCN coatings are often used. In contrast, coatings containing only Cr and Al may be problematic because they can increase friction leading to welding with the machined material at elevated temperatures due to diffusion and the ability to create a mixed interface.

The aim of the work was to explain the influence of carbon in CrCN coating and to compare its behaviour with CrN coating and surface without any coating in direct contact with machined aluminium alloy under limit conditions, for example without cooling or at the maximum speed recommended for the given cutting tool.

Acknowledgement: Authors acknowledge support from the ESIF, EU Operational Programme Research, Development and Education, and from the Center of Advanced Aerospace Technology (CZ.02.1.01/0.0/0/0/16_019/0000826), Faculty of Mechanical Engineering, Czech Technical University in Prague.

Keywords
Aluminium alloys
Coating
CrCN
Dry machining
Mechanical properties of WN$_x$ films and their thermal stability

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The paper reports on the structure, microstructure, mechanical properties, oxidation resistance and thermal stability of the WN$_x$ films; here x=N/W is the stoichiometry of nitride films. The films were reactively sputtered from a W target of diameter of 100 mm on Si(100) substrates in a mixture of Ar+N$_2$ gases using an unbalanced magnetron powered by the AC pulsed power supply. The properties of sputtered WN$_x$ films were characterized by (i) X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) micro-indentation testing and (iv) ellipsometry. It was found that (1) the sputtered WN$_x$ films are polycrystalline nanocomposites composed of a mixture (i) low–T α-W and high–T β-W$_2$N the phases at 0 lower than x lower than 0.6 and (ii) high–T β-W$_2$N and low–T δ-WN phases at 0.6 lower than x lower or equal than 1.5 and (2) the as-deposited WN$_x$ films exhibit high values of the hardness H, ratio H/E*, elastic recovery $W_e$ increasing with increasing x up to 34 GPa, 0.13 and 88%, respectively; here $E^*=E/(1-\nu^2)$ is effective Young’s modulus and $\nu$ is Poison’s ratio and (3) thermal annealing of WN$_x$ at temperature of 500°C in air for 5.5 hours results in formation of WO$_3$ scale on the film surface with low values of H (4 to 5 GPa) and ratio H/E*=0.05.

Keywords
Magnetron Sputtering
Tungsten Nitride
Thin Films
Oxidation Resistance
Resistance to cracking
TRIBOLOGICAL PROPERTIES OF TUNGSTEN NITRIDE FILMS AT TEMPERATURES UP TO 500°C

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The paper reports on friction coefficient $\mu$ and wear rate $k$ of WN$_x$ films with a stoichiometry $x=N/W$ varying from 0 to 1.5 and measured at temperatures ranging from RT up to 500°C. The WN$_x$ films were reactively sputter deposited in an Ar + N$_2$ gas mixture onto Si(100) substrates using an unbalanced magnetron equipped with a W target (Ø 100 mm) and powered by the AC pulsed power supply operated in an unipolar mode at frequency 125 kHz with repetition frequency of pulses $f_r = 1$ kHz. The properties of WN$_x$ films were characterized by (i) X-ray diffraction (XRD), (ii) Scanning Electron Microscopy (SEM) and (iii) pin-on-disk tribometry. It was found that (1) WN$_x$ films are polycrystalline nanocomposites composed of a mixture of (i) low-T $\alpha$-W and high-T $\beta$-W$_2$N phases at $x\leq0.5$ and (ii) high-T $\beta$-W$_2$N and low-T $\delta$-WN phases at $0.5<x\leq1.5$, (2) the friction coefficient $\mu$ of WN$_x$ films increases with increasing $x$ from 0.26÷0.42 at RT to 0.75÷1.23 at 150°C and decreases to about 0.50 with temperature increasing above 150°C up to 400°C due to the growth of a WO$_y$ scale on the film surface, (3) the wear rate $k$ of WN$_x$ films increases from about $10^{-7}$ mm$^3$/Nm at 150°C up to about $2.5\times10^{-6}$ mm$^3$/Nm at 400°C, (4) the wear rate $k$ of the WN$_x$ film at given temperature is the lower, the lower is its stoichiometry $x$, (5) the wear rate $k$ of the WN$_x$ films with $x\leq0.27$ at $T=75^\circ$C is 10 up to 100 times higher than $k$ of WN$_x$ films with $x\geq0.64$, and (6) the WN$_x$ films with $0.2<x\leq1.5$ are completely removed from the substrate at $T=450^\circ$C due to the formation of the WO$_y$ scale on the film surface already at sliding distances of 350 to 600m.

Keywords
Tungsten nitride
Tribological
High temperature
Pulsed magnetron sputtering
Thin films
The microstructure of N-ion-implanted CrN coatings and the relation to the slip properties in plastic injection moulding

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In the plastic injection moulding industry it is well-known that by using N⁺-ion-implanted CrN coatings on the moulds, a significant process improvement is achieved (for certain plastic types) compared to both uncoated moulds and moulds coated with CrN without ion implantation. In certain cases, ion implantation is critical to make the moulding possible at all.

This study investigates the changes in the microstructure of N⁺-ion-implanted CrN coatings compared to an unimplanted CrN sample. The aim is to explain the impact of N⁺ on the improved demoulding properties. The ejection force in the moulding process is quantified for both types of coatings using industrially relevant test moulds and different plastic types.

The CrN coatings are deposited on Si wafer and on test moulds using a CemeCon CC800 unit. Ion implantation on a subset of samples is done in a Danfysik ion implanter. An RBS analysis shows that additional N⁺-ions are indeed present in the implanted coating and that the depth profile corresponds to the used energy and dose. Nanoindentation measurements reveal that implanted samples are harder than the CrN reference (21 GPa versus 18 GPa), which is similar to other observations in the literature.

Coatings are analysed with different experimental techniques (XRD, XPS and TEM) to obtain information about their microstructure including chemical composition and lattice structure. Measurements of the ejection force are done using the coated test moulds for several plastic types (PP, ABS, POM, TPU and PPA). These measurements show that lower values of the ejection force are obtained for CrN-coated moulds than for the uncoated CrN reference and that ion implantation further lowers the demoulding force in the case of PP, ABS and TPU. For POM, ion implantation does not lower the ejection force and for PPA, an increase in the force is observed.

Keywords
CrN coatings
Ion implantation
Plastic injection moulding
Ejection force
PO3016

**Correlation between process parameters and layer formation during plasma nitriding and boriding of nickel based alloys**

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In principle nickel based alloys are used for applications where the material is exposed to a high mechanical and thermal stress. Examples for these conditions are turbine blades and hot forming tools. Forming tools are additionally strained tribologically which leads to high wear because of the low hardness of nickel based alloys. In order to meet this challenging environment and ensure a long durability of tools, surface modifications are necessary. Hard coatings like DLC are not suitable for forming tools at high temperatures. Therefore plasma nitriding and boriding represent good alternatives for surface hardening Ni-based alloys.

Three different nickel based alloys were plasma nitrided and borinded with various parameters. The nitrided layers of the samples were 5 to 15 µm thick and reached hardnesses up to 1700 HV. Plasma boriding was carried out in a H₂-Ar-BCl₃ atmosphere for two hours. The Temperature was varied between 500 and 800 °C. The samples were characterized by cross-sections, EDX-analysis, hardness profiles, adhesion of compound layer and tribometer tests. The cross-sections show a compact boride layer of 20 to 60 µm thickness mainly consisting of a mixture of hard nickel and chromium borides. The measurements yield a hardness of approximately 3000 HV directly under the surface and a sufficient adhesion of the boride layer to the ground material. The tribometer testing revealed a low friction coefficient and great wear resistance.

Generally this investigation shows that nickel based alloys can be plasma nitrided and borided within a relativ wide array of process parameters. Plasma boriding has advantages over diffusion treatments using boron containing paste. Especially better controls of the surface properties through process parameters and less effort for per- and post-processing are considerable. Additionally, if a borided tool is in contact with air at high temperatures, boronoxyd can form at the surface which is known as a dry-film lubricant.

**Keywords**
Plasma boriding and nitriding
Diffusion treatment
Nickel based alloys
Nickel and chromium borides
Hard coatings on tools and carbon dioxide as volatile lubrication for dry metal forming

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Breaking new ground, but never losing sight of the goal, is essential in order to meet the increasing technical and statutory requirements. Low oil lubrication consumption in sheet metal forming plays an increasingly important role as the effects of lubricant application on the environment or health become more and more relevant. In addition, residual oil contaminations are a problem for subsequent processing steps such as painting.

In this paper, a promising combined approach for a dry process design and the fundamental feasibility of this new hybrid technology is given. First, a novel approach for temporary lubrication of deep-drawing processes with CO$_2$ as a volatile medium is used. This process allows for the introduction of an intermediate medium into the tribological system under high pressure by means of laser drilled micro-holes. After the metal forming process, no cost-intensive purification steps are needed since the volatile medium vaporizes without residue debris under ambient pressure. Second, dry metal forming can be supported by a hard coating system such as silicon nitride coating (Si$_3$N$_4$). By using both CO$_2$ lubrication and hard coatings, metal sheet forming with low coefficients of friction is possible. In this study, exchangeable drawing jaws with laser drilled micro-holes are provided with hard coatings and subjected to an exemplary strip drawing test. As analyzing methods, the surface energies of the plasma coating on the tool before and after the strip drawing tests are determined by means of contact angle measurements under liquid CO$_2$. The results from the strip tensile tests show a low coefficient of friction for a low surface pressure. The next step will be the implementation of this hybrid technology on a tool for deep drawing an U-Profile.

This work is carried out in close collaboration with IGVP, IFU, and IFSW, University of Stuttgart.

**Keywords**

dry forming

silicon nitride

friction coefficient

hard coating
Optimization of CrAlN PVD Coatings for Dry Machining by FEM Simulation

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The conventional development of a coating system for cutting inserts includes a variety of test series with elaborate experimental parameter studies. In particular, conventional investigations of the cutting behavior by trial and error cause a considerable consumption of time, resources and costs. Therefore, it is desirable to reduce the effort for the development significantly by using simulations of the cutting process to adapt the coating properties to the requirements of the specific cutting task.

Based on 2D FEM simulations using Deform 2D of the dry cutting process of 42CrMo4 steel by CrAlN-coated WC-Co cutting inserts, the deposition parameters were adjusted to improve the cutting behavior. CrAlN coatings with optimized as well as non-optimized properties were deposited onto WC cutting inserts. The coatings were deposited by reactive magnetron sputtering using an industrial PVD magnetron sputter unit CemeCon CC800/9. The coatings chemical composition was varied by variable target configuration using segmented targets of chromium and aluminum segments. The dry cutting performance of the coated inserts was experimentally tested with an orthogonal cutting process of 42CrMo4 steel without cooling and the results of the simulations were compared with the experiment. Furthermore, ball on disk wear tests were conducted by reciprocal dry sling tests by using a SRV 3 tribometer. The results of the wear tests were compared with the results of the cutting test.

It will be shown that the thermal conductivity of the coating, the hardness and the friction coefficient significantly influence the machining performance. The optimized coating exhibits a higher lifetime compared to the non-optimized coatings. The SRV wear test shows an opposite result compared to the results of the cutting test.

Keywords
CrAlN
PVD
Cutting Simulation
Cutting Test
SRV wear test
Development of PVD-CVD Hybrid Coatings for Thermoforming of Age Hardenable Aluminium Alloys

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Thermoforming of age-hardenable Aluminum alloys can avoid today’s major problems of conventional cold-forming processes, such as inadequate dimensional stability, in particular due to re-deformation from the forming tools geometry. One challenge for a successful application of thermoforming is to restrain the high adhesion affinity of Aluminum, especially at high temperatures.

To establish the thermoforming of age-hardenable Aluminum alloys, the Hessen State Ministry for Higher Education, Research and Arts funds the research cluster ALLEGRO (High Performance Components of Aluminum Alloys by Sustainable and Resource Efficient Technologies). Here, the surface treatment of the hot forming tools by PVD technologies is essential for a successful application of the thermoforming technology.

The use of conventional solid lubricants based on MoS2 or PTFE counteracts the problem of adhesion tendency in thermoforming of Aluminum, but causes problems in handling and cleaning of the components as well as ecological and health risks due to the misting of the substances. Therefore, surface treatments are necessary to avoid adhesion.

In the present study, a combined PVD and CVD hybrid process is developed. Due to their low adhesion tendency, the coatings should allow a complete elimination of lubricants and release agents.

The focus is on the development of CrAlN coatings, since they have better mechanical properties and higher oxidation stability compared to TiAlN at the typical hot working temperatures. In addition, the modulus of CrAlN-based layers is similar to that of the tool steel substrate, which in particular should prove beneficial under thermomechanical cycling. Also the effect of graded and multilayer coatings with DLC and Si-DLC, respectively, was examined.

The coatings were characterized concerning their microstructural, mechanical and chemical properties. Furthermore, ball on disk wear tests were conducted by reciprocal dry sling tests by using a SRV 3 high temperature tribometer up to 300°C.

**Keywords**
PVD
Thermoforming
DLC
CrAlN
Optimisation of multi-layer AlTiN coatings for improved wear resistance

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In order to improve the mechanical behavior of AlTiN coatings on cutting tools we varied aluminium content and layer architecture. Deposition was done in an industrial scale PVD unit using cathodic arc evaporation of Ti and AlTi with compositions ranging from 50 to 70 at. %. Monolithic and multi-layers were deposited on cemented carbide samples keeping the coating thickness between 3 to 4 micron. Basic mechanical properties like coating hardness and elastic modulus were determined by nano-indentation. Adhesion and toughness were characterised by indentation with a diamond tip. Film structure and chemistry was determined using EDX and XRD. Wear resistance of the coated substrates was analysed in cyclic impact tests with a polished carbide ball. The results are compared to realistic drilling tests with heat-treated steel 42CrMo4 (TRS=900 MPa) and turning tests in cast iron (mainly abrasive wear component). It was found that turning tests matched the impact tests better than drilling likely due to difference in loading (shear and torque forces in drilling). Nevertheless, we will demonstrate that a multi-layer design is better able to protect the substrate (tool) against abrasion and fatigue wear components than monolithic coatings.

Keywords
arc PVD
coating
wear
cutting tool
drilling
AlCrN coating has been used for various metal working tools including cutting tools and molds/dies for increasing wear resistance. Makino et al. reported, based on theoretical calculation called band-parameter method, AlCrN can maintain cubic phase at higher Al content (77.2 at%) than AlTiN (65.3 at%) [1]. Reiter reported property of AIP deposited AlCrN coating with different Al composition and reported that highest tool life in cutting test was obtained at 71 at% of Al, primarily due to high hardness, oxidation resistance and abrasion resistance which is related to presence of hexagonal phase [2]. In this study, AlCrN coatings with different Al compositions, particularity Al composition close to the maximum solubility, were synthesized by cathodic arc and mainly effect of substrate bias on coating property was investigated. AlCr targets with 65, 70, 75 and 80 at% of Al were used. Coatings were deposited by a laboratory type AIP equipment (Kobe Steel Ltd.) in under N₂ atmosphere at 4 Pa, I arc=150A. Substrate bias was varied from 20 to 175V. Oxidation behavior was investigated by annealing samples in air at 800, 900 and 1000 °C for 30min and surface O composition was measured by EDX. Coatings deposited using Al75Cr25 target, surface O concentrations were low at each annealing temperature for coating deposited at substrate bias between 70 to 150V compared to one at 40V. Contrary to this, O concentrations of coatings deposited using Al70Cr30 target were constant independent of substrate bias. XRD analysis confirmed that coatings deposited using Al70Cr30 target were all in cubic single phase, whereas coatings deposited using Al75Cr25 target, coatings deposited at low substrate bias were mixture of cubic and hexagonal phase and coatings deposited between 70 to 150V were cubic single phase. This substrate bias dependent difference in crystal structure can explain the different oxidation behavior.


Keywords
AIP
oxidation
AlCrN
cuttingtest
The purpose of this work is to increase the wear resistance of steel 321 by electrolyte-plasma saturation of the surface with nitrogen and carbon. As a working electrolyte, a solution of the following composition was used: 10% (by weight) of glycerol, 7% (by mass) of ammonium nitrate and 8% of ammonium chloride. The treatment temperature varied from 650 °C to 950 °C in 50 °C increments, with quenching from the heating temperature. EDX analysis data show that when the heating temperature is increased from 650 to 800 °C, an insignificant increase in nitrogen concentration is observed up to 0.2% at a depth of up to 15 μm. Further heating increases both the nitrogen content up to 2.32% and the depth of its penetration into steel (up to 35-40 μm). In the temperature range from 650 to 800 °C, the microhardness slightly increases from 242 HV$_{50}$ to 279 HV$_{50}$. A further increase in the heating temperature increases the surface microhardness to 455 HV$_{50}$. X-ray diffraction analysis showed that after the PENC, mixed oxides of the composition Fe$_2$O$_3$ (hematite) and Fe$_3$O$_4$ (magnetite) are formed on the surface of the samples. A further increase in temperature reduces the intensity of these peaks, which indicates a decrease in the proportion of these phases. The initial roughness of the samples was 1 ± 0.1 μm. After processing, the roughness values of the surface are reduced by approximately a factor of 2 and are 0.65 ± 0.1 μm at all heating temperatures, which indicates an intensive dissolution of the steel surface under PENC. The roughness dependence on the treatment temperature was not found. It was found that with dry friction by a counter-body made of alumina at a normal load of 5 N in a friction path of 100 m, the minimum value of mass wear of 3.0 mg is observed at a treatment temperature of 800-900 °C. When rubbing an untreated sample under the same conditions, the mass wear is 4.0 mg. The coefficient of friction increases non-uniformly from 0.65 to 0.68 with increasing treatment temperature from 650 to 950 °C.

**Keywords**
wear resistance
plasma treatment
austenitic steel
Comparative study of tribological behavior during running-in period of TiN hard coatings deposited by magnetron sputtering, cathodic arc and thermoionic arc ion plating

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In this paper we compared tribological behavior of TiN hard coatings deposited by magnetron sputtering, cathodic arc and thermoionic arc ion plating. The investigations were made for the running-in period of a sliding test. The microstructure, crystal structure, topography, adhesion and microhardness of TiN hard coatings were determined in scanning electron microscope by focused-ion-beam, an X-ray spectrometer, 3D-profilometry, scratch test and microindentation. We found a significant difference in the microstructural, morphological, and mechanical properties. The tribological characteristics of coated samples in sliding contact with an alumina ball were evaluated by ball-on-disc test equipment, where motion was reciprocal. The influences of post-polishing of the coating and the surrounding atmosphere were also investigated. Sliding tests have shown that different structure and topography of the three TiN coatings resulted in different friction and wear especially during the running-in period.

Keywords
PVD hard coating
tribology
cathodic arc
magnetron sputtering
thermionic arc ion plating
The tribological performance of MoC\(_{1-x}\) and a-C:H composites films by the plasma enhanced chemical vapor deposition under liquid lubrication system

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The cubic MoC\(_{1-x}\) and a-C:H composites which deposited by plasma enhanced chemical vapor deposition process using metal organic precursor as bis(tert-butylimido) bis(dimethylamido) molybdenum. Hydrogen as carrier gas and argon and nitrogen gases as reactive gas were used in deposition process, which in pulsed DC plasma at pressure of 5 Pa and temperature of 150 °C. This research focused to fine a feasibility for mechanical application on the automobile engine components through the investigation of tribological performance. Films were prepared on the nitrocarburized SCM435 steel which was material of automobile engine components. The films consisted composites of mixed cubic MoC\(_{1-x}\), amorphous carbon, and small amount of MoN. The films measured high hardness as 21 GPa and showed a good adhesion as over 30N (HF1). Crystallization of carbide and nitride was determined by the x-ray diffraction method. The tribological friction performance were surveyed by the ball-on-disk tribometer with MoDTC contained lubricants. Especially in case of 0W20 lubricant, friction coefficient showed under 0.05, whereas base materials as nitrocarburized SCM435 had shown 0.09. For presence of sulfur and wear by additives, the chemical bonding states were analyzed on as deposited films and to test films by the XPS. The responsibility of protective coatings for automobile components was evaluated by the motoring rig operation system (Lambda 3.3, 5W30 MoDTC) for tappets, which supported real-time operations in automobile engine. As a results, the frictional torque of coated tappets with cubic MoC\(_{1-x}\) and a-C:H composites reduced 20% compared with uncoated tappets at 2,000 RPM.

**Keywords**
molybdenum
carbide
PECVD
friction coefficient
XPS
The effect of hydrogen on the crystallization of MoC$_{1-x}$ at low temperatures by the plasma enhanced chemical vapor deposition using bis(tert-butylimido) bis(dimethylamido) molybdenum

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The complex composites of molybdenum carbide and amorphous diamond like carbon were deposited at temperatures ranging under 200 °C and pressure of 4 Pa by the plasma enhanced chemical vapor deposition using bis(tert-butylimido) bis(dimethylamido) molybdenum with hydrogen, and nitrogen. As well as argon was carrier gas to delivery of liquid metal organic precursors at temperature of 80 °C. For plasma generation in process, pulsed DC plasma used at negative voltage of -600 V with frequency of 150 kHz, and pulse reversal time as 1 μs. The chemical binding states of molybdenum contained complex composites were analyzed by the x-ray photoelectron spectroscopy and the Raman spectroscopy. The x-ray diffraction were obtained to determine the crystallography on the MoC$_{1-x}$ composite. In condition of only using argon carrier gas, films were strongly deposited by amorphous diamond like carbon with a high hardness as 23 GPa and consisted small amount of cubic structured α-MoC$_{1-x}$. However, introducing the hydrogen gas in deposition process, the α-MoC$_{1-x}$ composite was preferred growth, whereas composition ratios of amorphous diamond like carbon composite was reduced. To molybdenum carbide formation was recrystallization of molybdenum composites by the dissociation from molybdenum to nitrogen contained organic groups bonds in bis(tert-butylimido) bis(dimethylamido) molybdenum. The hydrogen as reactive gas play a role of catalyst for formation of molybdenum carbide at low temperatures. The α-MoC$_{1-x}$ phase rich films showed hardness as 20 GPa, well adhesion over 30 N (HF1) in plasma enhanced chemical vapor deposition process.

Keywords
bis(tert-butylimido)bis(dimethylamido)molybdenum
MoC
Hydrogen
low temperatures
XPS
The properties of Mo-Cu-N, Mo-Cu-X-N(X= Ti, Zr, Si) coatings synthesized by magnetron sputtering process with single alloying targets

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In this study, we tried to deposit Mo-Cu, Mo-Cu-X-N(X= Ti, Zr, Si) thin coatings showing high hardness and low friction at low and high temperatures to reduce energy consumption and wear problems in engine parts and tools. In general, this kind of nano-composite coating is made by various processes using multiple targets such as Mo, Cu and X(X= Ti, Zr, Si). However, it is difficult to control the exact composition, homogeneous deposition of large scale specimens during the deposition with multiple targets. We wanted to create the single Mo-Cu, Mo-Cu-X(X= Ti, Zr, Si) alloying targets with the composition showing the best friction coefficient and surface hardness. Single alloying targets with the composition showing the best properties were prepared by powder metallurgy methods, such as mechanical alloying and hot pressing. Mo-Cu, Mo-Cu-X(X= Ti, Zr, Si) targets were prepared subsequently. Also Mo-Cu-N, Mo-Cu-X-N(X= Ti, Zr, Si) coatings prepared using the single alloying targets and mechanical properties were analyzed.

Keywords
Mo-Cu
Mo-Cu, Mo-Cu-X-N(X= Ti, Zr, Si)
thin film
alloying targets
friction
Zr based coatings are used in various industrial fields due to their excellent mechanical properties and corrosion resistance compared to other hard coatings. In this study, a ZrCuSiN coating was deposited as a new Zr based coating material. The ZrCuSiN coatings were deposited by magnetron sputtering using a ZrCuSi single alloy target. The influence of the nitrogen gas flow rate in an argon-nitrogen gas mixture on the structure, mechanical and tribological properties of the ZrCuSiN coating were investigated. A single alloy target prepared by arc melting. A ZrCuSi layer (buffer layer) was deposited by non-reactive sputtering processes, under an Ar plasma discharge. Thereafter, ZrCuSiN coatings having various nitrogen contents were deposited by reactive magnetron sputtering. The structural and mechanical properties of the ZrCuSiN coatings were investigated by XRD, SEM, nano indentation and friction test.

Keywords
ZrCuSiN coatings
magnetron sputtering
single alloy target
friction test
Tribological properties of active Screen Plasma treated H13 tool steel, against aluminum and WC-Co.

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H13 (1.2344) tool steel is widely used in metal forming applications. Surface quality of the formed parts requires the tool to be free of defects, such as those due to surface scratches, and material adhesion. Moreover, if forming operations are to be reproducible, tool geometry should be kept into narrow tolerances, i.e. with minimum wear.

Active Screen Plasma (ASP) offers the potential to treat complex tool geometries with minimum edge effects or arcing risk, and the process temperature can be controlled independently of the bias applied to the treated part.

In this work, the authors have explored multiple ASP nitriding and oxi-nitriding treatments of the H13 steel. The tribological studies have comprised the assessment of both the wear rates and coefficients of friction. The performance of the nitrided surfaces has been evaluated both against softer material, prone to adhesive wear (aluminum), and harder material, prone to erosive wear (WC-Co).

Tribological results of the different surfaces have been related to the properties of the nitrided layers (thickness, hardness - HV, composition and phases – XRD), and to the plasma treatment processing parameters.

Results show that ASP treatments do in fact enhance the performance of H13 tool steel, in terms potentially relevant to metal forming applications.

Keywords
Active Screen Plasma
H13
tribology
nitriding
aluminum
Mechanical properties and cutting performance of multilayered AlTiN/TiBN hard coatings

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Transition metal nitrides, such as AlTiN, TiN and TiBN, have been used as protective hard coatings due to their excellent tribological properties. In this study, AlTiN/TiBN coatings were synthesized by cathodic-arc evaporation. AlTi and TiB alloy cathodes were used for the deposition of multilayered AlTiN/TiBN coatings. During the coating process of AlTiN/TiBN, different interlayers of AlTiN and TiBN were deposited to enhance mechanical properties and adhesion strength between the coatings and substrates. The multilayer thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. By controlling the cathode current and rotation speed, the deposited multilayered AlTiN/TiBN coatings possessed periodic AlTiN and TiBN layers. In this study, the microstructure of the as-deposited and high temperature annealed coatings was characterized by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) using Bragg-Brentano and glancing angle parallel beam geometries. The composition depth profile of the oxidized coatings was evaluated by secondary ion mass spectrometry (SIMS). Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindentation. Meanwhile, the multilayered AlTiN/TiBN, which forms stable and dense diffusion barriers at high temperature, is expected to possess good resistance to high temperature oxidation. The design of the multilayered AlTiN/TiBN coatings by using proper interlayers is anticipated to increase the adhesion, hardness, toughness and cutting performance of coatings. For the high speed cutting test of Ti-6Al-4V alloys, under proper cutting parameters, the multilayered AlTiN/TiBN with an interlayer of TiBN showed the lowest flank wear and the surface roughness of the machined Ti alloy.

Keywords
Hard coating
Mechanical properties
Cutting
Cathodic arc evaporation
Phase evolution and tribological properties of molybdenum- and tungsten carbide coatings

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Carbides have been in the focus of materials scientists for decades, due to their interesting mechanical properties and high temperature behaviour. Recently, they have also been investigated as reactive surfaces for tribological contacts to sustain tribo-chemical reactions to achieve self-lubrication. This lubricating effect in combination with excellent mechanical properties identifies tungsten carbide and molybdenum carbide as potential candidates for protective coatings with enhanced wear performance.

The wear protection and tribological capabilities of those coating materials, do not solely rely on the in-situ formation of solid lubricants such as MoS$_2$ and WS$_2$ but also require excellent mechanical properties. While hexagonal δ-WC benefits from high hardness and hence good abrasive wear protection, its thin films are very brittle and suffer from differences in thermal expansion coefficient compared to substrate materials, as well as carbon loss during the sputtering process. As a result non-reactively sputtered coatings have a tendency to form a sub stoichiometric cubic WC$_{1-x}$ phase with inferior properties. In comparison, molybdenum carbide coatings don’t demonstrate this tendency to sub stoichiometric structures and offer an easy access to tribo-reactive phases obtaining easy-sliding shear planes.

This work focuses on the phase evolution of non-reactively sputtered Mo and W based carbide coatings in relation to the carbon content and the influence of structural defects, such as carbon vacancies. The phase evolution was correlated to the obtained wear performance using x-ray diffraction, transmission electron microscopy and ball on disk tribotests.

Keywords

- tungsten carbide
- molybdenum carbide
- magnetron sputtering
- nonreactive
- wear performance
The role of applied bias on the properties of HiPIMS deposited nc-TiC/a-C:H coatings

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Nanocomposite coatings consisting of nanocrystallites embedded in an amorphous matrix such as nc-TiC/a-C:H can be tailored to exhibit an unusual combination of properties like high hardness and elastic modulus combined with low friction and wear. These coatings are usually deposited utilising direct current magnetron sputtering (DCMS) leading to low ionisation of the sputtered titanium and to lower Ar$^+$ ion bombardment impinging the growing coating. The ion bombardment of the substrates is routinely enhanced via increasing the energy of the bombarding ions due to the application of a negative bias onto the samples. The use of high power impulse magnetron sputtering (HiPIMS) usually leads to much higher ionisation of the sputtered titanium which can alter the deposition process and to more severe ion bombardment of the growing coating changing the properties of the deposited coatings. This contribution investigates the effect of the applied bias on the properties of nc-TiC/a-C:H coatings prepared by HiPIMS as the standard practice of “applying a bias for enhancement of coating properties” used for DCMS prepared coatings may not be easily applicable in HiPIMS. It will be shown that a simple “copy-paste” principle of methods useful for working with Ar$^+$ ion dominated DCMS plasmas may not necessarily lead to better coatings when metal dominated plasmas such as in HiPIMS are used. It will be shown that ion bombardment by heavy high energy film forming titanium ions may lead to microstructure changes leading to “weakening” of the coating structure that is highly detrimental for mechanical properties of the deposited coatings. Different bias levels will be discussed and levels of bias favourable for deposition of super-hard nc-TiC/a-C:H coatings using HiPIMS will be shown.

This research has been supported by project LO1411 (NPU I) funded by the Ministry of Education, Youth and Sports of the Czech Republic.

Keywords
nanocomposites
HiPIMS
magnetron sputtering
Effect of nitrogen doping on mechanical and tribological properties of SiCₓNᵧ thin films

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Amorphous SiC coatings are the promising solution for a variety of functional coatings intended for harsh environment due to their superior high chemical stability and temperature resistance. Despite the vast application potential of SiC, its structural applications are limited by its brittleness. The possible solution to overcome this drawback may be an introduction of nitrogen atoms into its structure. Besides, it allows tailoring of its electrical and optical properties.

The magnetron-sputtered a-SiCₓNᵧ coatings with various N content (0-40 at.%) deposited on silicon substrates were evaluated in this study at room temperature and after exposure to high temperatures of 700, 900 and 1100 °C in oxidizing air environment. Additional 900 °C annealing in vacuum was performed to distinguish influences of different thermally induced mechanisms (oxidation vs. short range ordering). Composition and structure was explored using variety analytical techniques (XRD, Raman and IR spectroscopy, SEM, GDOES). Mechanical properties evaluation was performed using nanoindentation, while tribological properties were assessed using scratch test method. Traditional techniques of scratch test evaluation (the depth change record and the microscopic observation) were expanded by the detection of acoustic emissions during scratch tests. The detection system of our own design allows simultaneous acoustic emission record at the high resolution, which significantly increased the reliability and accuracy of the scratch test evaluation.

Results show the beneficial effect of the nitrogen doping on the tribo-mechanical performance of resulting a-SiCₓNᵧ coatings. The improved fracture resistance of the SiCN films stems from the suppression of SiC clusters crystallization. Exposure to the elevated temperature led to the more pronounced oxidation of SiCN in comparison to the pure SiC sample. The formation of SiOₓ oxide film resulted to the better scratch test results.

Keywords
- silicon carbonitride
- nanoindentation
- scratch test
- high temperature coatings
- acoustic emission
Influence of Ti interlayer to adhesion and dynamic wear resistance of nc-TiC/a-C:H coatings prepared by DCMS and HiPIMS

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Nanocomposite coatings consisting of TiC crystallites embedded in hydrogenated amorphous carbon matrix (nc-TiC/a-C:H) exhibit unique combination of high hardness and low friction. The aim of the present work was to study adhesion and dynamical wear resistance of this coatings deposited on tungsten carbide substrates. The nc-TiC/a-C:H coatings were prepared using hybrid PVD-PECVD process of sputtering Ti target in argon/acetylene atmosphere. Two series of coatings with different content of carbon were prepared using both DCMS and HiPIMS. Chemical composition and microstructure of coatings were determined using XRD, XPS and EDX analyses. Nanoindentation test was used to determination of the hardness and elastic modulus. Coatings adhesion was determined using scratch tester with cone tip. To evaluate impact resistance of the coatings, an impact test with WC ball was used.

Adhesion of the DCMS prepared coatings exhibited local maximum at approx. 60 at. % of C, adhesion of the HiPIMS prepared coatings continually increased with increasing carbon content. The DCMS coatings under repeated dynamical impact load exhibited different behaviour than the HiPIMS coatings. Differences in the adhesion as well as in the impact wear resistance of the DCMS coatings and the HiPIMS coatings are discussed with respect to the coatings and adhesive interlayer microstructure and mechanical properties.

This research has been supported by Ministry of Education, Youth and Sports of the Czech Republic (projects LO1212, CZ.1.05/2.1.00/01.0017, LO1411 (NPU I) and Project 15-17875S) and by The Czech Academy of Sciences (project RVO:68081731).

Keywords
Dynamic impact test
scratch test
hard coatings
magnetron sputtering
adhesion
Nanoindentation Testing on Mo-B-C Micropillars Prepared by Focused Ion Beam Milling

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Mo-B-C thin films show a favorable combination of high stiffness, hardness and elastic modulus together with moderate ductility and are a promising candidate for the next-generation protective coatings. In this study we focused on micro-compression tests performed on well-defined micropillars with fixed aspect ratio of 2:1 (height x diameter), which were fabricated by a focused ion beam technique as a part of the scanning electron microscope LYRA 3 (Tescan). For the fabrication process, several Mo-B-C coatings with different microstructures were chosen in order to study the influence of the degree of crystallinity on the prevailing deformation mechanism. The micro-compression testing was performed on Hysitron Ti950 Triboindenter equipped with a flat punch indenter (10 µm in diameter). The nanoindentation test was controlled by load or displacement and from the geometry and load-displacement data the true stress and strain were calculated.

The post-mortem analysis on transmission electron microscopes (TEM) Philips CM12 STEM and JEOL JEM-2100F helped us to better understand the deformation mechanisms that lie behind the extraordinary plasticity and enhanced fracture resistance of these coatings. The lamellas for TEM were cut from the deformed micropillars and analyzed afterwards. The calculated critical stresses for Mo-B-C micropillars were compared with other ceramic materials typical for protective coatings in industrial applications.

The authors are acknowledging that this research has been done in cooperation with the Tescan company. This research has been supported by the Czech Science Foundation (Project GACR 15-17875S).

Keywords
Mo-B-C
nanoindentation
micropillars
SEM
TEM
Zwitterionic diamond-like carbon coatings with antifouling properties.

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The accumulation of unwanted material (“fouling”) on technical surfaces is a well-known problem in many sectors of industrial manufacturing with one very relevant example being milk processing. Here, fouling occurs due to accumulation of mineral and protein components from the milk, which is a great issue especially on heat transfer surfaces. A number of investigations applying surface coatings for fouling mitigation are known, with a moderate success so far. In a fairly new approach, zwitterionic surfaces, i.e., surfaces containing basic (e.g., amine) as well as acidic (e.g., carboxylic acid) functional groups, are utilized for the protection of surfaces against fouling. Normally such layers are fabricated via coupling of monomers containing acidic and/or basic functionalities which is not suited for food processing due to thermal, chemical and mechanical instability. In the present work a RF PECVD process was used to deposit zwitterionic DLC layers containing heteroatoms (e.g., O, N) which are present in the form of acidic and basic functional groups. As precursors we used (i) combinations of a hydrocarbon (\textit{CH}\textsubscript{4}, \textit{C}\textsubscript{2}H\textsubscript{2}) together with a heteroatom source (\textit{N}\textsubscript{2}, \textit{O}\textsubscript{2}, \textit{NH}\textsubscript{3}) and (ii) single precursors containing heteroatoms (e.g., pyrrolidine), respectively. Coatings were characterized by zeta-potential and surface-free-energy measurements. Also we used a tailor-made in situ ATR-FTIR setup to investigate functional groups attached to the surface. Fouling investigations, which were carried out in a laminar-flow channel using aqueous solutions containing whey protein and salts, showed promising results of the zwitterionic DLC with respect to fouling mitigation. To reveal possible mechanisms of the fouling process, an ATR-FTIR setup was used which allows in situ measurements in contact with aqueous solutions. Therewith it was shown that the fouling process is affected by the presence of charged groups on surfaces.

**Keywords**

Antifouling
Milk deposits
Zwitterionic DLC
in-situ ATR-FTIR
Prediction of DLC layer properties by plasma simulation

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Hydrogenated amorphous carbon films (a-C:H) as a kind of diamond-like carbon (DLC) coatings combine unique optical, electrical and mechanical properties, resulting in numerous applications in different kinds of industries. These plasma coatings are continuously of high interest for research and industry because of the possibility to adjust the layer properties in wide scope by varying the deposition conditions like pressure, temperature or power. DLC films are widely used in the automotive industry due to their unique tribological properties, especially as an enabler for modern fuel injection equipment. One important goal of a modern flexible industrial production especially for automotive mass production must be the control of properties regardless of the kind of plasma deposition system, e.g. chamber size or loading density. The combination of plasma simulation, coating experiments and plasma diagnostics enables the monitored deposition of hydrogenated amorphous carbon films.

The study will present a global model for acetylene and argon plasmas to support the process development for the deposition of a-C:H films. With this simulation it is possible to calculate all partial pressures of reaction products, relevant plasma parameters and particle fluxes. The functionality of the global model was validated with plasma diagnostics by measuring plasma parameters and comparing them with simulated results. The use of the presented global model allows it to reduce the influence of all adjustable machine parameters (e.g. bias voltage, gas flow, …) to only one main virtual parameter influencing the coating properties: the energy per deposited carbon atom. The influence of this parameter on relevant coating properties, e.g. indentation hardness or hydrogen content will be demonstrated. As a result, in the future it will be possible to adjust the required coating properties independently of machine parameters without a sophisticated design of experiments.

Keywords
DLC
simulation
diagnostic
plasma
a-C:H
**Wear character of diamond coatings in CFRP cutting**

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Diamond coatings are increasingly used as wear protection for cutting tools in the machining of composite materials like carbon fiber reinforced plastics (CFRP). Due to excellent mechanical and tribological properties of diamond the cutting of very high abrasive carbon fibers can be conducted with a reasonable tool life and high precision required e.g. in the aerospace industry.

Since the performance of diamond coated hard metal cutting tools depends on coating and substrate properties, tool geometry and cutting parameters a significant cutting test is essential for the investigation of wear character and understanding of its relationship with coating properties.

The development of cutting tests for milling and drilling in CFRP and investigation of coating wear properties will be presented and discussed.

**Keywords**
diamond coating
cutting test
CFRP
wear protection
cutting tool
Future combustion engines will require thermal stability up to 500 °C and increased wear resistance compared with present day solutions. Piston rings and cylinder walls also involve extreme contact pressures that increase even more the materials demand. Hard tetrahedral DLC coatings (ta-c coatings) have a high percentage of sp3 carbon bonds, very smooth surface and very low coefficient of friction, showing good performance in mixed and boundary lubricated systems, all features that fit to the new demands.

Production of ta-c demands highly ionized physical vapour deposition (PVD) deposition techniques, such as Cathodic Arc deposition. The sp3 bond content depends critically on the bombardment of ions with hyper-thermal energy during the deposition. The main drawback of arc deposition process is the ejection of “macro particles” from the target that degrade film mechanical properties. Filtering the plasma overcomes the problem but is an expensive solution that also strongly decreases the deposition rate.

Conventional d.c. magnetron sputtering (dcMS) can deposit DLC films with smooth surface, however, they present a low sp3 bond content (up to 45%) and consequently lower film density and lower hardness.

In this work, DLC films were prepared by DOMS using Ar and Ar/Ne gas in the same deposition system in order to evaluate the potential of DOMS for hard DLC synthesis. The films were evaluated with XRD, UV Raman spectroscopy, SEM and nano-indentation. Coefficient of friction was obtained using pin on disk apparatus.

**Keywords**
- DOMS
- DLC
- mechanical properties
Mechanical/plasma pre-treating of ceramic surfaces prior to multilayer micro/nanocrystalline CVD diamond coating

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Several surface pre-treating procedures were performed on silicon nitride ceramic substrates - sand blasting, CF4 plasma etching, diamond powder US seeding - and their effect on tribological properties was compared. Four-fold multilayer micro/nanocrystalline diamond coatings were produced using the hot filament CVD technique. For the surface characterization and wear evaluation, SEM/EDS microscopy and 3D optical profilometry techniques were employed. Different loads (40-200 N) were applied during reciprocating sphere-on-flat sliding tests using CVD diamond coated samples. Threshold loads of about 150 N with no delamination were achieved denoting a superior tribological performance and high adhesion levels.

Keywords
chemical vapour deposition
diamond multilayers
tribology pretreating
Substrate biasing effects on the mechanical and tribological properties of thick DLC coatings obtained by HiPIMS

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The mechanical and tribological properties of DLC coatings makes them suitable for a wide class of applications, making use of their high hardness, low friction coefficient and chemical inertness. Depending on the specific required properties different PVD or PECVD deposition techniques can be used for the synthesis of such coatings. In this contribution we will refer to both hydrogen free and hydrogenated DLC coatings obtained by using magnetron sputtering in a HiPIMS process. The target conditions were optimized to obtain a high current regime, without triggering a significant number of micro-arcing events. DLC films were deposited both on Si and 304L steel substrates, using a Ti based interlayer to improve the adhesion and mechanical stability of the coating. The main substrate parameter used for controlling the film properties is the bias voltage, both in terms of absolute values and type of biasing. In this respect, RF and synchronized pulsed bias were used and compared as alternatives for applying the negative voltage on the substrate. The micrometer thick DLC coatings obtained on steel substrates were characterized using standard tribological testing, in both dry air and lubricating oil environment. Scratch test performed in the 0 to 100 N force interval revealed good adhesion to the substrate, with critical loads exceeding 20-30 N for most of the samples. A comparison between deposition conditions is provided, aiming to link the process conditions with the mechanical performance of the coatings.

This work was supported by M-ERA Net project TANDEM through the Romanian Ministry of Research and Innovation, UEFISCDI, project No 56,57/2016, and National CORE Project 2018.

Keywords
magnetron sputtering
carbon sputtering
high power impulse magnetron sputtering (HiPIMS)
diamond like carbon (DLC)
mechanical properties
CVD synthesis of polycrystalline superhard diamond-cBN composite coatings

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We report about the CVD synthesis and characterization of superhard composite diamond-cBN coatings with superior chemical inertness over polycrystalline diamond and higher hardness than crystal cBN. The CVD synthesis of the coatings was carried out by hot filament CVD and in abnormal glow discharge plasma. The microstructure of the coatings could be controlled from microcrystalline to ultra-nanocrystalline. The thickness of the coatings in our experiments reached 50 mkm. The hardness of this composite reached values of 80 GPa. Microstructure and phase composition were investigated with SEM, TEM, X-ray diffraction and Raman spectroscopy. The process of coating oxidation in the air was investigated depending on phase composition in the temperature range 400-1000 °C. The results of high-temperature nanotribotests in the range 20-800 °C in air atmosphere are also presented.

Keywords
CVD coatings
diamond
cubic boron nitride
superhardness
chemical inertness
Improving the fatigue resistance of DLC coatings under highly loaded dynamic contact is an important step to increasing their performance in demanding applications. The nano-impact test is particularly effective at highlighting the limitations of thin hard carbon coatings deposited on hardened steel [1-2].

A novel micro-scale rapid impact test capability capable of producing repetitive impacts at significantly higher strain rate and energy than in the nano-impact test has been developed [3] enabling the study of coating fatigue with less sharp spherical indenters than in the nano-impact test.

This presentation describes results with the new micro-impact technique on a range of hard carbon coatings on hardened steel (multi-layered a-C, a-C:H, Si:a-C:H and WC/C). The role of mechanical properties on the fatigue resistance and the load-sensitivity of the impact failure mechanism is discussed.


Keywords
impact  
fatigue  
DLC  
micro-scale  
micro-tribology
Physical and electrochemical properties of Ni/Mo thin film deposited at different electroplating current density

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Abstract
In this work, electrodeposition technique has been used to codeposite molybdenum particles in nickel matrix as protective film against corrosion attacks, in addition the effect of electroplating current density on different properties of Ni/Mo thin films has studied. The numerous technique used to study the different properties of Ni/Mo thin films showed that, this films were observed to be fissured and porous in morphology. The main phases identified in different exposed films are MoNi$_4$, Ni$_3$Mo and Mo$_{1.24}$Ni$_{0.76}$. The effect of applied current density on electrochemical properties was studied. Inhibitory efficiency of gum arabic was controlled by the electroplating current density by testing the intensification of hydrogen reaction of this thin films using EIS technique. Moreover, this work gives a solution to the corrosion of crude oil desalter by electroplating Ni-Mo films and then injecting a small amount of gum arabic in the oil pipeline before dissalement, which gives long life to the reactor.

Keywords
Nickel
Arabic gum
Co-deposition
EIS
Molybdenum
The objective of this work is the characterisation of the composite deposits Ni-Cr on copper substrate. These deposits are obtained from bath of electro-deposition of sulphated nickel. Tests were carried out on nanocomposite coatings in order to characterize there structure, adherence quality and corrosion behavior in a solution of 3.5% NaCl. the techniques used are those of polarization and impedance. Morphology qnd structure are also followed by scanning electron microscopy, EDS microanalysis and X-ray diffraction. The results have revealed a good adherence, a high corrosion resistance of the composite deposits and a homogeneous morphology. They have, also, to determine the concentration of Cr added to the bath, which provided optimal protection against corrosion.

Keywords
calloings
corrosion
nanocomposite
electrodeposition
Ni-Cr
Influence of the electrodeposition current regime on the Corrosion Behavior of Zn and Zn-TiO2 Composite coatings

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This study report the influence of the current regime on the corrosion behavior of Zn \& Zn-TiO\textsubscript{2} composite coatings using both direct and pulse current electrodeposition techniques in acidic zinc sulphate solution. The electrodeposition process was carried out, in direct current at \( I = 57 \text{ mA/cm}^2 \), and in pulsed current at \((1, 10, 50) \text{ Hz}\) and a duty cycle \((25 \%, 50 \%, 75 \%)\) respectively, at a minimum current density of and high current density of \(57 \text{ mA/cm}^2\). Pure zinc coatings obtained under the same experimental conditions were used as a reference. Corrosion resistance properties of the coatings were studied using both of potentiodynamic polarisation techniques and weight loss measurements in 3.5 \% \text{NaCl} solution. The study revealed that both of potentiodynamic and weight loss measurement shows that good corrosion behavior of the coatings was obtained at low frequencies and low duty cycle. The addition of TiO\textsubscript{2} nanoparticles in the plating bath renders the Zinc deposit more resistant to generalized corrosion and leading to reduction in the current by half. Best results were obtained at \( f = 10 \text{ Hz}\) and a duty cycle \(= 25 \%\).

**Keywords**
electrodeposition
coating
composite
corrosion
current regime
DLC multilayers to improve fretting and corrosion resistance over nitrided martensitic stainless steel

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Martensitic stainless steels have different applications in industry where good corrosion and wear resistance are required. Moreover, in some applications, the fretting wear is one of the mechanisms responsible for the component degradation. DLC coatings can be used in order to improve the surface properties but sometimes a monolayer coating is not enough so several layers are necessary.

In this work, the fretting wear and corrosion behavior of DLC multilayers coatings were studied and compared to the monolayer coating. Both were deposited by PACVD (Plasma Assisted Chemical Vapour Deposition) on nitrided and non-nitrided martensitic stainless steels.

The coatings were characterized by Raman Spectroscopy, SEM, and OM. Fretting wear tests were carried out using different loads. Electrochemical tests were performed in NaCl solution. The adhesion was evaluated by scratch tests both with variable and constant load and also by Rockwell C Indentation.

The fretting wear resistance was better for multilayers than for monolayers, which in turn increased when the substrate was nitrided. The monolayer corrosion behavior was not as good as multilayers. Although both coatings presented defects, probably the presence of different layers makes it difficult for one of the defects that is in one layer to continue in the next one. In this way, the corrosive solution cannot reach the substrate and thus preventing the corrosion phenomenon from developing.

Monolayer adhesion was similar to that of multilayers when evaluated by both tests. Only the previous nitriding treatment improved the adhesion in both cases.

Keywords
multilayers
DLC coating
PACVD
corrosion
fretting
Influence of electrode distance on microstructure and corrosion resistance of Ni-Cr alloyed coating deposited by double glow plasma surface metallurgy

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In this paper, in order to improve the corrosion resistance of Q235 carbon steel, Ni-Cr alloyed coatings were deposited by double glow plasma surface metallurgy (DG-PSM) at different electrode distance. The results indicated that the Ni-Cr alloyed coatings with gradient distributed composition were dense and well bonded with substrate. The main phase of the coatings was Ni2.9Cr0.7Fe0.36. With the increasing of electrode distance, the thickness of Ni-Cr alloyed layer increased first and then decreased. The electrochemical studies showed that the Ni-Cr alloyed coating exhibited a more effective corrosion resistance against the 3.5% NaCl corrosive solution due to its compact microstructure and high potential phase. In the electrochemical impedance spectroscopy (EIS) examinations, the Ni-Cr alloyed coating deposited at 15 mm electrode distance represented the best corrosion resistance compared to the uncoated Q235 carbon steel and the coatings deposited at other electrode distances.

Keywords
double glow plasma surface metallurgy
Ni-Cr alloyed coating
electrode distance
corrosion resistance
electrochemical testing
PO3048

Corrosion protection of zirconium surface based on Zr-Fe-Si Heusler alloy fabricated by magnetron sputtering

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Zirconium is a very useful material for various technical applications especially in nuclear industry due to low neutron capture cross-section or as a getter for storage of hydrogen. Unfortunately the Zr alloys changed by oxygen/hydrogen diffusion are less dense and are mechanically weaker than the original material. The processes of Zr alloys oxidation and hydrogenation lead to limitation criteria in justifying fuel rod life time. To develop new protective coatings of claddings we performed three different studies: Firstly we systematically studied the Zr H interaction which is the crucial step for theory, data interpretation and technology on the surface sensitive techniques on the Zr(0001) single crystal. Secondly we studied initial stages of Fe and Si atoms interactions with Zr (0001) surface. Ultrathin Fe-Si films were evaporated on the Zr(0001) surface. The formation of the stable corrosion resistance. Fe\textsubscript{2}ZrSi or FeZrSi Heusler alloys was formed, which addresses the problem with hydrogen. Finally by means of DC magnetron sputtering the multicomponent gradient films Fe-Si-Zr from Zr, Fe and Si targets were fabricated on polycrystalline disc Zr (99\%) with diameter 12 mm. The depositions were carried out in UHV conditions in pure argon atmosphere at substrate temperature varied from 20-700 °C. The properties of all films were studied by surface techniques such as STM, AFM and by NanoESCA instrument, which is a based on a PEEM (Photoelectron Emission Microscope) and PES (Photoelectron Spectroscopy). The structural properties were characterized by XRD and SEM equipped by EDX and EDSB techniques. Electrochemical Impedance Spectroscopy was employed to analyse the corrosion characterization of Zr with protective Heusler-like films. The effect of Fe-Si-Zr films composition and structure on surface chemistry, morphology and corrosion behaviour of Zr was examined and evaluated.

Keywords
magnetron sputtering
corrosion protection
zirconium
Heusler alloys
thin film
Deposition and characterization of Cr-Al-C thin films for accidents tolerant zircaloy claddings

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\( M_{n+1}AX_n \) phases (MAX-phases), ternary compounds where M denotes an early transition metal, A is an element of group A and X is either nitrogen or carbon with \( n=1, 2, 3 \), are interesting materials which present several potential applications, for example as protective coating in corrosive environments. These materials exhibit a high corrosion resistance, a thermal-shock resistance as well as a good thermal and electrical conductivity. With the aim of protecting zirconium-based alloys as accident-tolerant fuel (ATF) cladding, low deposition temperatures are needed in order to preserve the clad properties. High power impulse magnetron sputtering (HiPIMS) presents several advantages in comparison to other conventional magnetron sputtering techniques since it improves film density and adherence to the substrate. In this context, HiPIMS facilitates the crystalline films deposition at low deposition temperature due to increased ionization rate and atom mobility released by the sputtered target. Our study aimed at developing robust MAX-phase coatings on zirconium alloys, to protect these alloys against hydrothermal corrosion and high temperature steam oxidation.

In the present work, Cr-Al-C thin films were synthesized by HiPIMS from a \( \text{Cr}_2\text{AlC} \) compound target. The effects of different process parameters, such as the duty cycle and the substrate polarization, on plasma and on the coating development were studied. Amorphous films were formed at room temperature, and crystallized to form MAX-phases after the annealing to 550°C in air. The thermal stability of the structure, microstructure, and mechanical properties of the films were investigated in air and steam at temperatures from 700°C up to 1100°C. This study focuses on the potential of HiPIMS technology for enhancement of structural and mechanical properties of Cr-Al-C coating.

Keywords

MAX Phase
HiPIMS
Protective coating
Properties
Oxidation resistance of CrN/SiNx and ZrN/SiNx multilayered films deposited by magnetron sputtering technique

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Transition metal (TM) nitride films, e.g. CrN or ZrN, are widely used as hard and wear-resistant coatings in cutting tool or manufacturing industries. However, they rapidly oxidize at temperature as low as 600°C. One promising approach of both improvement of mechanical properties and resistance to high-temperature oxidation is the formation of multilayered film structures. Multilayers consisting of alternate stacking of TM nitride and SiNₓ layers are characterized by very low intermixing that promotes their thermal stability and oxidation resistance.

We report here on CrN/SiNₓ and ZrN/SiNₓ multilayered films deposited on Si by a reactive magnetron sputtering under Ar+N₂ plasma discharges. Multilayers with various thickness ratio of elementary layers were synthesized by sequential sputtering from elemental Cr (or Zr) and Si₃N₄ targets. According to TEM and XRD analysis, the multilayered films consist of nanocrystalline (002)-oriented CrN (or ZrN) and amorphous SiNₓ layers. Reducing the CrN (or ZrN) layer thickness fraction with respect to bilayer thickness leads to decrease in crystallite size and increase in the lattice parameter of CrN (or ZrN) phase due to higher compressive stress.

The oxidation resistance under air was studied using in situ XRD, in the temperature range from 400 to 950°C, as well as by WDS and SEM methods after air annealing procedure. While the reference CrN and ZrN film start to oxidize at T_{ox}=700°C and 550°C, respectively, a much higher oxidation resistance, till T_{ox}=950°C, is found for multilayered films with CrN (or ZrN) to SiNₓ thickness ratio of 2 nm/5 nm and 3 nm/5 nm. We also find that CrN/SiNₓ films are overall more resistant to high temperature oxidation than ZrN/SiNₓ films. The influence of the interface density and chemical composition on the formation of Cr₂O₃ (or ZrO₂) oxide phases is discussed.

Keywords
Multilayer
Hard coatings
Ti$_2$AlN is a prominent member of the MAX phase materials, which are known to combine metallic and ceramic properties. Especially aluminum containing MAX phases are known to be oxidation resistant due to the formation of dense oxide scales which protect the underlying Ti$_2$AlN and the substrate from further oxidation [1]. The purpose of this study is to investigate the adhesion of the oxide scale and the influence of the oxidation process on the mechanical and tribological properties of MAX-phase coatings. Ferritic stainless steel samples were coated with Ti$_2$AlN using a multilayer physical vapor deposition of Ti and AlN layers and a subsequent annealing for 1h at 700°C [2]. After a characterization of the initial coatings microstructure, the samples were oxidized in a muffle furnace in ambient air for 5, 10, 20, and 100 h. The thermally grown oxides were identified as mainly α-Al$_2$O$_3$ with a minor fraction of TiO$_2$. The formation kinetics of the α-Al$_2$O$_3$ scales were investigated by XPS depth profiles. Similar to other MAX phase materials, a cubic oxide growth behavior was found. Further investigations on the mechanical properties of the oxidized samples were performed with scanning scratch tests, nanoindentation and tribological tests. In scratch tests, no spallation of the α-Al$_2$O$_3$ scales could be observed, which indicates a good adhesion to the underlying Ti$_2$AlN film. Nanoindentation experiments were performed to compare changes in hardness and elastic modulus of the oxidized film. Tribological tests at elevated temperatures were performed to investigate the coating’s suitability for possible applications in aggressive Environments. [1] D. J. Tallman, B. Anasori, and M. W. Barsoum, Mat. Res. Lett. 1, 115–125 (2013); [2] L. Gröner, L. Kirste, S. Oeser, A. Fromm, M. Wirth, F. Meyer, F. Burmeister, and C. Eberl, Surf. and Coat. Techn., in press (2017)

**Keywords**
MAX phase
Oxidation
Nanoindentation
Tribology
On the reactive-element effect of Y in the oxidation of CrAlYN films

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CrAlYN coatings were deposited by magnetron sputtering on M2 steels for improvement of the oxidation resistance and hardness properties. Two different average aluminium concentrations were selected (16 and 25 at.%) and variable yttrium content (1.2 to 5.7 at.%). The coated steel samples were submitted to thermal annealing in air during 2 hours to investigate the oxidation resistance, thermal stability and diffusion processes. The best performance is obtained for the CrAlYN coating with ~16 at.% of Al and intermediate values of Y (3.4 at.%) where the initial cubic phase (fcc-CrAlN) was preserved under a thin mixed (Cr,Al)₂O₃ oxide layer. The CrAlYN coatings with higher aluminium contents showed lower thermal stability decomposing into h-AlN and Cr phases accompanied by metallic elements diffused from the steel substrates. The role of Y in the oxidation mechanism was investigated using XRD, GDOES and analytical TEM techniques. The result of the oxidation processes is highly influenced by the concentration of yttrium present in the film. CrAlYN coating (1.2 at.% Y) was not able to prevent the iron diffusion along the coating reaching the surface where gets oxidized. Higher Y amount (independently of the aluminium content) avoided the iron diffusion but favoured extremely the penetration of oxygen inwards leading to partial or full oxidation. HAAD-STEM images and EDX elemental map obtained from the oxidized films demonstrated the segregation of yttrium at the column boundaries (film) and grain boundaries and interface (scale). These experimental evidences confirm the role of yttrium affecting the ion transport processes retarding the oxide scale growth.

Keywords
Reactive element
oxidation resistance
CrAlYN
magnetron sputtering
high temperature
Optimized design of cathodic arc evaporated nitride multilayer coatings regarding their high-temperature oxidation resistance and mechanical behaviour

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Nitride multilayer coatings have been widely studied to protect steel substrates in structural components of steam power generation plants. According to the literature[1], recent works of the authors showed that the oxidation behaviour of CrN coatings in a 100% steam atmosphere at 650ºC is excellent compared to TiN. However, the larger hardness and Young modulus of the latter, and the multilayer effect in both, the mechanical and the oxidation response, is a relevant issue under investigation. The design of the experimental setup to obtain meaningful information of the mechanical behaviour of the multilayer coatings poses a crucial challenge, due to the wide range of involved parameters in the overall response. The use of nanoindentation tests seems to be the most appropriate technique to this aim, although the ratio between the individual film thickness and the indentation depth becomes crucial to understand and devise optimal coatings for applications involving mechanical stresses. The present study combines a deep investigation of the oxidation response of these systems in the simulated working conditions of steam power generation plants, and the mechanical analysis of these multilayers in order to propose the optimal coating architecture for this industrial application.


Keywords
Multilayers
Corrosion
Nitrides
Nanomechanical analyses
Coating architecture
This work focuses on the effect of Y, Ho, Mo, Zr and Ta addition into hard and thermally stable Hf-B-Si-C-N films in order to improve their optical transparency or electrical conductivity. The combination of the sufficiently high hardness, high thermal stability in air and optical transparency or electrical conductivity opens up a new scope of applications involving high-temperature protection of electronic and optical elements or capacitive pressure and tip clearance sensors for severe oxidation environments.

Hf-B-Si-X-C-N films were deposited onto Si(100), SiC and glass substrates using pulsed magnetron co-sputtering of a single B₄C-Hf-Si-X target in Ar + N₂ gas mixtures. A planar unbalanced magnetron was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with a fixed voltage pulse length of 50 µs. The total pressure was 0.5 Pa and the substrate temperature was adjusted to 450°C during the deposition on the substrates at a floating potential.

All Hf-B-Si-X-C-N films possessed a sufficiently high hardness (close to 20 GPa), low compressive stress, high elastic recovery and high oxidation resistance in air at elevated temperatures (above 1000°C). Addition of Y and Ho into the Hf-B-Si-C-N films prepared at the 25% N₂ fraction in the gas mixture resulted in enhancement of the optical transparency. Addition of Mo and Ta into the Hf-B-Si-C-N films prepared at the 15% N₂ fraction in the gas mixture led to an increase in the electrical conductivity.

Keywords
Hf-B-Si-X-C-N films
pulsed magnetron sputtering
electrical conductivity
optical transparency
oxidation resistance
CO2-based test for the detection of defects in oxygen barrier layers

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Barrier layers’ performances for food packaging and encapsulation of electronic devices are severely limited by the presence of punctual micro- and sub-micro-metrical defects. In order to determine their density in layers obtained by means of Plasma Enhanced Chemical Vapor Deposition, their origin and overall effect on oxygen transmission rate, a new non-destructive test has been developed and optimized.

Thin films acting as oxygen barrier layers have been deposited on thin PET foils by means of an Electron Cyclotron Resonance (ECR) low-pressure, microwave-sustained plasma, with HMDSN/O\textsubscript{2} gaseous feeds. The coated sample in the sealed testing cell is interposed between a pure CO\textsubscript{2} atmosphere and a saturated limewater solution: CO\textsubscript{2} permeates preferentially through the pinholes in the barrier layers, causing the precipitation of calcium carbonate crystals on top of the defects. Real-time analysis is performed by means of an optical microscope on top of the cell’s transparent lid. The position of the crystals and the underlying defects can be later retrieved for further investigations at a scanning electron microscope by means of markers placed on the sample itself.

Average defect densities for different substrates and for a wide range of thicknesses and chemical compositions of silica-like barrier layers have been calculated and compared to their respective oxygen transmission rate and barrier improvement factor. The time required for crystals to appear on top of defects (i.e. the time required for CO\textsubscript{2} to permeate through the whole length of the defect) has also been calculated and correlated to the rise time of the oxygen and CO\textsubscript{2} permeation curves.

Repeated oxygen permeation analysis, after the formation of crystals on the samples surface, show remarkably reduced transmission rates, thus confirming the growth of crystals directly on top of pinholes and hinting at their formation mechanisms, as well as delimiting the applicability of a purely defect-based permeation.

Keywords
Barrier layers 
Pinholes 
Microwave plasma 
ECR
PO3056

Moisture Barrier Property and Mechanical Flexibility of Residual Stress Controlled SiOx Thin films Deposited by Pilot R2R-PECVD

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The technique of plasma enhanced chemical vapor deposition (PECVD) is increasingly being used in barrier film development on flexible substrates. Barrier films deposited on flexible substrates are essential for flexible device based on QD or OLED, OPV modules. PECVD technique brings a number of advantages including low temperature process, less damage to the flexible substrate and the possibility of high deposition rates.

In this study, a large area (over 500 mm width) of SiOx thin film was uniformly deposited on PET substrate using R2R-PECVD and SiH₄-NH₃ gas were used as precursors. We observed the residual stress change of the SiOx thin films with varying deposition process parameters and investigated the relationship between moisture barrier performance and mechanical flexibility according to the residual stress change.

In detail, the characteristics of residual stress, refractive index, radius of curvature, and water vapor transmission rate (WVTR) were investigated according to process power and reactive gas flow ratio. Under optimal process conditions, the moisture barrier performance of SiOx thin film on PET was reached down to $1.4 \times 10^{-3} \text{g/m}^2 \cdot \text{day}$ at 40% and 90% relative humidity condition. In terms of mechanical flexibility, two-point bending tester results showed excellent radius of curvature of less than 2 mm in compressive mode. In addition, the fatigue test was carried out to confirm the reliability of the SiOx thin film. As a result, WVTR value can be kept below $4 \times 10^{-3} \text{g/m}^2 \cdot \text{day}$ even after 10,000 cyclic bending test in the compressive mode.

Keywords
SiOx
R2R-PECVD
WVTR
Residual Stress
PO3057

Chemical compositions and its moisture barrier performances of the silicon nitride films by R2R PECVD process

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Silicon nitride films deposited by PECVD have attracted attention in the fields of semiconductors, solar cell as well a gas barriers for flexible display due to their inherent physical properties. The PECVD silicon nitride films can be represented by a non-stoichiometric chemical formula, SiNₓ: Hᵧ, with atomic ratios depending considerably on the deposition process. [1-2].

In this study, we have analyzed the role of the chemical compositions of hydrogenated silicon nitride films (SiNₓ: Hᵧ) on the moisture barrier properties of the SiNₓ: Hᵧ / PET structure. The films for moisture barrier were deposited onto PET (Polyethylene Terephthalate) by roll to roll plasma enhanced chemical vapor deposition using a 2.46 GHz microwave power source and a SiH₄/NH₃ gas mixture. Bonding concentrations of Si-Si, Si-H and N-H were obtained by FT-IR spectroscopy and moisture barrier properties were examined by differential pressure method. Refractive indices and elemental compositions also measured by spectroscopic ellipsometry and AES (Auger electron spectroscopy). It is shown that there is a strong correlation between the deposition conditions, the chemical compositions, optical properties and moisture barrier properties of the silicon nitride film.

REFERENCES:

Keywords
SiNx
PECVD
Barrier
FTIR
AlxMn1-x coatings elaborated by PVD as alternative to cadmium for steel corrosion protection

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Cadmium coatings are still widely used in the aeronautic field for the corrosion protection of aircraft parts made from high strength steel. However, Cd is an inherently toxic heavy metal being restricted under REACh regulation. Only aircraft and military industries are exempt from obeying the banning legislation.

In this study, thin coatings of Al\textsubscript{70}Mn\textsubscript{30} at.% and Al\textsubscript{60}Mn\textsubscript{40} at. % alloys have been deposited by magnetron sputtering as an alternative to cadmium for steel corrosion protection. Their microstructures, morphologies and hardnesses have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nanoindentation. The corrosion resistance of the coatings has been tested by potentiodynamic polarization and immersion in 3.5 wt.% NaCl solution and by salt spray test (SSP). The corrosion properties were dependent on the coatings microstructures which were influenced by the process parameters. Higher corrosion resistance was reported for Al\textsubscript{70}Mn\textsubscript{30} at.%, up to 216 h in a salt spray cabinet without red rust apparition for 1 µm thick coating deposited at 150 °C.

Keywords

corrosion
durability
steel
PVD
AlxMn1-x coatings
**Characterization of thermochromic VO$_2$ films obtained by the oxidation of sputter-deposited thin films in a semi-industrial machine**

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VO$_2$ is a widely studied thermochromic material, which exhibits a metal-insulator transition approximately at 68°C, accompanied by a crystallographic transition from a low temperature monoclinic phase to a high temperature tetragonal rutile structure. Optical and electrical properties also change drastically with phase transition of VO$_2$ and make this material convenient for several applications, such as near-infrared modulation in smart windows, thermal solar collectors, ultrafast electronic devices and so many others. Nevertheless, elaboration of VO$_2$ films with good thermochromic properties still remains a challenge because is mandatory to avoid other intermediate phases belonging to the vanadium-oxygen system [1]. In this work thin films were reactively sputter-deposited on Al substrates by using an in-line semi-industrial machine. The films of 150 nm thickness followed an annealing process performed at different times and three different temperatures in the range of 450°C-550°C. X-ray diffraction, Raman spectrometry and Secondary ion mass spectrometry were performed for structural characterizations and qualitative elemental depth profiles of the oxidized films. The thermally-induced properties of the oxidized films were analyzed in term of their optical properties by infrared camera. The wide range of time and temperatures during the annealing process together with the characterization techniques used, allow us to find the accurate parameters to synthesize thermochromic VO$_2$ films. [1] X. Xu, X. He, G. Wang, X. Yuan, X. Liu, H. Huang, S. Yao, H. Xing, X. Chen, J. Chu, Applied Surface Science 257 (2011) 8824-8827.

**Keywords**
Vanadium dioxide
Vanadium nitride
Sputtering
Thermochromic
Doping of VO$_2$ selective coatings for solar thermal collectors

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The reversible semiconductor-to-metal transition in VO$_2$ at 68 °C makes this material suitable for various technological applications. Apart from studies for use as coating for smart windows or sensing devices, doped VO$_2$ layers were investigated as functional (thermochromic) coating material for solar thermal collectors [1] [2]. For solar absorbers, in order to ensure optimal collector efficiency, the absorption of solar irradiation has to be maximised while the thermal emissivity has to be minimised in the visible and mid-infrared wavenumber region. Today state of the art commercially available absorbers with non-thermochromic and selective coating materials fulfil these requirements. However, avoiding extensively high stagnation temperatures in modern solar thermal collectors results in a raising interest in absorber coatings that may change their optical behaviour with temperature.

We co-sputter various doping metals [Me] and vanadium in a magnetron system constructed by DREEBIT GmbH to identify doping effects on VO$_2$ with respect to the optical behaviour and the temperature of the semiconductor-to-metal transition. We perform a subsequent annealing in air to form crystalline phases in this V$_{1-x}$[Me]$_x$O$_2$/SiO$_2$-layers. We vary the content of the doping metal and the temperature-time-profile of the subsequent annealing process. Samples are analysed by XRD-measurements for phase identification, stoichiometry is determined by EDX-measurements and morphology by SEM-pictures. As optical properties are essential for such films we perform optical analysis using reflection, transmission and ellipsometry spectra in die visible and mid-infrared wavenumber region.

We show recent results on morphology, optical behaviour and changes in transition temperature of these layers.


Keywords
vanadium dioxide
doping
thermochromic
cosputtering
Optimization, design and preparation of metal–dielectric multilayer coatings for optical elements

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Large variety of optical elements are base on multilayer coatings. Often, they are consisting of low and high refractive index layers such as metal oxides or metal fluorides. Formation of these multilayer (>20 layers) coatings could be very complicated; it requires high precision and process control. Additionally, optical properties of every single layer may be influenced by the preparation conditions [1]. Recently, it was reported that optical elements could be made with the use of ultrathin metal and metal oxide/fluoride layers.

In current research, as an example of optical component we selected non-polarizing beam splitter (nPBS). For nPBS formation ultrathin metal and niobium oxide layers were deposited by magnetron sputtering. Firstly, it was optimized preparation of each layer. Niobium oxide films were prepared with the high deposition rate by the use of reactive magnetron sputtering with a feed-back optical emission monitoring [2]. Secondly, in-situ growth of metal layer was investigated. Conditions for ultrathin continuous metal film formation were found. Thirdly, a new cube broad-angle nPBS device was designed, prepared and characterized.


Keywords
multilayer coating
ultrathin film
optical properties
magnetron sputtering
in-situ monitoring
In this contribution, we describe the structural modifications that occur in M/CuO\textsubscript{x} (M=Ag, Au) nanocomposite thin films after annealing at different temperatures. Films are deposited by reactive magnetron sputtering of a Cu target doped with different amounts of Au and/or Ag pellets. The characteristics of the films are evaluated by X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS).

It is observed that ‘as deposited’ thin films are homogeneous in depth, and relatively amorphous. In contrast, the formation of CuO and precipitation of noble metals is observed by XRD after annealing. The net gain of oxygen atoms in the film can be precisely measured by RBS, while the quantity of the other elements remains constant. In addition, the concentration of Ag and/or Au near the film surface is dramatically reduced. Further, it is verified that the in-depth homogeneity of the films is broken, leading to ‘layered’ structures different for Ag- and Au- containing films. Interestingly, films doped with both Au and Ag resembles those containing Au. All these results are described in detail and interpreted considering the diffusional behavior of the different elements of the films. The correlation with the observed optical behavior is also discussed.

Keywords
plasmonic
annealing
CuO
Ag
Au
Optoelectronic properties of TiO$_2$ thin films elaborated by pneumatic spray

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Abstract
Titanium oxide is a widely used material in several electronic and optical application domains. The purpose of this study is to produce uniform TiO$_2$ thin films using Titanium (III) Chloride (TiCl$_3$) as an inorganic precursor and Titanium (IV) isopropoxide Ti(OCH(CH$_3$)$_2$)$_4$ (TTIP) as an organometallic precursor by a home-made spray pyrolysis system. The concentration of the solutions was varied during TiO$_2$ thin films elaboration to optimize its electrical, morphological and optical properties for photovoltaic and catalytic applications purposes. The TiO$_2$ thin films were characterized by several techniques such as SEM, EDS, DRX, UV-Visible transmission and four-probe point measurements. The relation between the properties to the elaborated TiO$_2$ thin films structures will be discussed in detail in this work.

Keywords
thin film
TiO2
pneumatic spray
molarity
properties
Enhanced photocatalytic activity of metallic oxide nanostructures synthesized by a plasma afterglow-assisted oxidation process.

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Metallic oxide nanostructures are promising materials in photocatalysis applications, for example in water treatment and disinfection or for hydrogen production by water splitting. Growing metallic oxide nanostructures can be achieved by simple thermal oxidation of raw metallic materials. The use of direct plasma treatments increases the growth rate of nanostructures by several orders of magnitude whereas remote plasma treatments improve the control of the design of nanostructures by moving the temperature window where nanostructures are formed by about 100 K downward. This shift enables the development of higher stress levels and offers the possibility to create dense areas of nanostructures [1]. For a given nanostructure, it is even possible to design them by driving growth instabilities using mixtures of metals [2]. We can thus expect to control the growth of ultrathin nanowires where quantum confinement is possible. For instance, the synthesis of ultrathin, single-crystalline zinc oxide nanowires was achieved by treating in a flowing microwave plasma oxidation process zinc films coated beforehand by a sputtered thin buffer layer of copper [3]. An average diameter of 5 nm correlated with a mean length of 750 nm can be reached with a fairly high surface number density for very short treatments, typically less than 1 minute. An enhancement of photocatalytic activity and photocurrent intensity under visible and UV light is observed for ultrathin nanowires, attributed to high separation efficiency of photoinduced electron-hole pairs.

References

Keywords
Photocatalysis
Plasma afterglow
ZnO nanostructures
Structural phase-dependent resistivity of Nb-doped titanium dioxide (TiO$_2$:Nb) thin films

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Recently, Niobium doped titanium oxide (Nb-doped TiO$_2$) emerged as a potential indium-free transparent conducting oxide material due to its low resistivity and high visible transparency, with source materials being inexpensive and nontoxic. In the present work we studied the correlation between Nb-doped TiO$_2$ thin films’ conductivity and their crystalline structure. In particular we demonstrated that a fine control on the amount of anatase phase with respect to rutile one is critical for achieving low resistivity values. The films with various levels of Nb in corporation were grown by RF sputtering at 200 °C and then annealed at 400 °C. The resistivity values of the films doped with oxygen vacancies and Nb+5 decreased from 3.8×10$^{-1}$ to 4.1×10$^{-3}$ Ω cm when the weight percent of rutile in anatase-rutile phase mixture decreases from 52.8% to 32%. Furthermore, the lowest resistivity value of 2.37×10$^{-3}$ Ω cm was obtained for the doped TiO$_2$ films having single phase anatase structure. The physical processes responsible for the diverse electrical properties are discussed and are associated with the growth conditions, in particular the growth temperature.

Keywords
Transparent conductive oxides
RF sputtering
structure
Correlation of the optical, electrical and morphological properties of ITO layer
grown by DC pulsed magnetron sputtering with process parameters.

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There is a strong demand for deposition on ITO layers as transparent electrodes for
many optoelectronics devices. Magnetron sputtering is the most widely used
fabrication methods for these layers. Despite these layers are already manufactured
at industrial scale, to obtain stable film properties for large area with exceptionally low
resistivity and high transmittance in the visible range it is still a challenge. This is due
to the strong dependence of the ITO films properties on sputtering process
parameters. There are many partial studies regarding the influence of some sputtering
parameters on the properties of ITO films. However a deep study encompassing the
main sputtering process parameters and correlating these parameters with the optical,
electrical and morphological properties is still missing for industrial size magnetron
sputtering equipment. In this work we deeply analysis the influence of the process
pressure, oxygen flow, substrate temperature and thermal annealing treatment on the
optical, electrical and morphological properties to further understand the nature of the
conducting properties of ITO layers. The main objective is to design an industrial
deposition process stable for large coating areas.

An industrial magnetron sputtering deposition equipment has been used to deposit
140 nm ITO films on microscope slides. An ITO ceramic target (In$_2$O$_3$/SnO$_2$ 90/10
wt%) of 550´125 mm size with an unbalanced magnetron evaporator was used. The
power source was dual output pulsed-DC (5 to 350 kHz) from AEI Pinnacle Plus + 5/5
kW.

Keywords
Transparent Conductor Materials
Magnetron Sputtering
Optical Properties
Electrical Properties
Morphological Properties
TCO planar sputtering targets manufactured by spark plasma sintering (SPS) technology: Advantages on target microstructure and coating properties

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TCO (both ITO and AZO) planar sputtering targets synthesized by conventional methods (slip-casting and hot pressing) are prone to nodule formation during sputtering process, which induces arcing and lack of reproducibility, sputtering rate decrease and deterioration of ITO and AZO deposited film properties. In this study, spark plasma sintering (SPS) technology was applied for the fabrication of ITO and AZO sputtering targets using high purity complex ITO and AZO powders. SPS technique allows the fabrication of high density targets, avoids the grain growth during sintering and maintains the nanostructure of raw powders at fast production rates. The manufacturing of both small and large size (up to 250 mm in diameter) ceramic targets was carried out to demonstrate the scalability of this synthesis process. During this work, the influence of SPS technology on target microstructure and TCO coating properties was analysed. For that purpose, comparison between commercial targets and SPS manufactured targets was performed. Both ITO and AZO thin films were grown using different targets and optical and electrical properties were compared. Each target microstructure was investigated before and after sputtering process to evaluate nodule and defect formation. Results and conclusions are presented in this work.

Keywords
TCO
Spark Plasma Sintering (SPS)
Microstructure
Optical properties
Electrical properties
New approaches for improving isolation strength of magnetron sputtered dielectric films

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For sensor technology there is a demand for isolation films with a high breakdown voltage on large areas and temperature resistance as well as high bonding strength on different substrates. Physical vapor deposition (PVD), especially magnetron sputtering, already allows to deposit films fulfilling the requirements of a variety of applications. One limit of further increase of breakdown voltage however is the defect growth, which is inevitable associated with magnetron sputtering. Small particles or point defects during the film growth act as starting point of cone-shaped defect growing throughout the film. The experiments presented in this paper show new approaches to prevent or stop defect growing in $\text{Al}_2\text{O}_3$ films deposited by reactive pulse magnetron sputtering.

One approach of the improvement was to add in between the sputtered film a thin intermediate layer using atomic layer deposition, pulsed laser deposition or a PVD layer with enhanced ion bombardment. To enhance the ion bombardment during the sputtering process rf-bias was applied to the substrate. It was found, that especially an $\text{Al}_2\text{O}_3$ interlayer deposited by ALD improved electrical strength and specific resistance most.

Another approach was the study of co-sputtered $\text{AlSiO}_x$ nano-composite films. This material combines the higher temperature resistance and the higher isolation strength of $\text{SiO}_2$ with the advantageous mechanical properties especially stress and coefficient of thermal expansion of $\text{Al}_2\text{O}_3$. $\text{AlSiO}_x$ achieves a high isolation strength also on rough metal surfaces and was coated with a high deposition rate of 2 nm/s.

With both approaches an isolation film on a rough steel substrate with an electrical strength of 2000 V and a specific resistance higher $1\times10^{15} \, \Omega\cdot\text{cm}$ was achieved. One example of the application of the film is a pressure sensor. This film fulfills the breakdown voltage of 2000 V required for explosion prevention in hydrogen technologies.

Keywords
- pulsed magnetron sputtering
- aluminium silicon oxide
- electrical isolation
- breakdown voltage
Study of sputter deposited silicon dioxide films for temperature compensation of frequency filters

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Temperature compensated surface acoustic wave (TC-SAW) frequency filters have opened a new field of applications in mobile communication. As standard SAW filters show a temperature-dependent frequency drift of -20 ppm/K up to -40 ppm/K, many high-frequency applications as well as communication in narrow RF bands would not be possible. The application of silicon dioxide (SiO\textsubscript{2}) for temperature compensation allows the reduction of the filter frequency drift of a TC-SAW filter down to 0 ppm/K \textsuperscript{[1]}. However, the filter performance strongly depends on the quality of the deposited SiO\textsubscript{2} as it contributes to the acoustic wave propagation.

In this study, high-quality SiO\textsubscript{2} thin films deposited by the magnetron sputtering system scia Magna are presented. The influence of the RF substrate bias on the SiO\textsubscript{2} properties is investigated. It is shown, that the RF bias significantly influences the SiO\textsubscript{2} properties such as refractive index, stress and film density.

The applicability of the deposited SiO\textsubscript{2} films for TC-SAW filters is proven by SEM cross-section on TC-SAW filter structures. As the acoustic wave propagation and, thus, the device performance is influenced by any scattering site, the SiO\textsubscript{2} film has to be dense without any seams or voids. It is shown, that the introduction of the RF bias changes the film growth on the IDT finger structure from a void-dominated film to a uniform, void- and seamless coating well suitable for TC-SAW. Finally, the SiO\textsubscript{2} was deposited on a TC-SAW filter, which shows the expected reduction of temperature-drift.

\textsuperscript{[1]} Wang et al., “A Zero TCF Band 13 SAW Duplexer”, IEEE International Ultrasonics Symposium Proceedings (2015), DOI: 10.1109/ULTSYM.2015.0092

\textbf{Keywords}
reactive magnetron sputtering
acoustic wave filter
temperature compensation
silicon dioxide
substrate bias
**3D kinetic Monte-Carlo modeling of random metallic network: optical and electrical characterizations**

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Conductive transparent devices have numerous applications today, such as transparent electrodes (like front-side electrodes of solar cells), thin-film heaters… Many recent technologies related to this research field can provide those characteristics: transparent conducting oxides, metallic nanowires or carbon nano-tubes for example.

Our work focuses on the numerical modeling of random metallic networks obtained by atomistic deposition of silver or aluminum on a substrate (glass, TCO…). An optical and electrical characterization of such structures is done to optimize its transparency in the direction normal to the substrate and its electrical conductivity in the lateral and/or the normal direction. The modeling of the network is done thanks to the Nascam software, which is based on a 3D kinetic Monte-Carlo method. Then the reflectance and the transmittance are computed by using the effective medium theory based on the Maxwell-Garnett and Bruggeman models. The effective electrical conductivity of the network is also estimated by solving the Maxwell-Faraday equation by finite-element analysis. The investigated parameters are the average thickness of the metallic network, the substrate coverage, the energy of deposited atoms and the influence of the roughness/nanostructuration of the substrate surface.

We show that the deposition of high-energy metallic atoms on a flat substrate is needed to obtain a significant electrical conductivity of the network without increasing too much the average thickness, and then the reflectance. Indeed, a low-energy atomic deposition can induce the formation of islands not connected electrically. However, the structuration of the substrate allows to decrease the energy of deposited atoms while avoiding the apparition of such islands.

**Keywords**
kinetic Monte-Carlo modeling
metallic network
transparent conductive thin-film
Development of a Process Chain for Structuring and Coating of AlN Ceramic for Ion-Traps

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An integrated laser-processing and coating process for the fabrication of AlN sintered ceramics ion-traps to be used as the centre-piece of novel optical clocks was developed. AlN was used for its ideal properties with respect to the subsequent laser-cutting and structuring process.
A polished AlN tile (thickness approx. 0.4 mm) was patterned using a UV-laser and a 4-axis high precision robotics. To prevent contamination a protective coating was applied. After thorough cleaning the tile was coated with up to 5 µm of gold and a thin Titanium adhesive layer. To further enhance adhesion by means of stress release the tile was annealed in a vacuum furnace. Hereafter conducting paths were structured by evaporating the gold coating using the laser-robotics again.
Under the influence of the UV-laser the surface of the semiconducting AlN ceramic transforms into a conducting Al layer with a thickness of up to several micrometers. The Al layer is removed using buffered phosphoric acid.
After cleaning and testing for shorts surface-mounted devices can be soldered by standard means.

Keywords
Laser-processing
gold coating
ion-traps
optical clocks
structuring
Multiple plasma source synchronization for improved process optimization: a Ti-Cr-based anticorrosion coating case study

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As the magnetron sputtering deposition of functional coatings is a common production step used for variety of high-tech and daily-use products, a lot of manufacturers invested much effort into the optimization of this technological step. The optimization itself, is commonly focused on process metrics such as its velocity measured by throughput or effectively judged by the amount of faulty products from one process batch. Plasma power supply is one of the key components required for magnetron sputtering deposition and in many cases a system used for coating deposition uses multiple magnetron sources, thus, more than single power supply. Furthermore, the optimization and development of sputtering processes is often based on application of different plasma generation technology i.e. DC, AC or RF. Thus, it is crucial to develop new algorithms allowing mutual communication of all power supplies used on one system, independently from their working principle or application. This contribution focuses on a novel approach to power supply operation in sputtering systems equipped with multiple plasma sources. As a model magnetron sputtering system a batch-type coater, with at least four single- or dual-target magnetrons and a negatively biased substrate holder, has been chosen to study the efficiency of synchronized power supply operation. First the concept of configurable exchange of synchronization signal between different generators in the event of arc detection on one of them will be introduced. As next, the results of Ti-Cr-based anticorrosion coating deposition by mixed Bipolar and HIPIMS sputtering will serve to discuss the influence of power supply synchronization on the quality of deposited films. The discussion will be concluded with an analysis of the full system solution approach, where magnetron and bias power supplies are synchronized together for further reduction of faulty products due to arcing.

Keywords
magnetron sputtering
plasma source synchronization
Bipolar
HIPIMS
Preparation of good adhered cobalt oxide films on stainless steel support by combination of reactive magnetron sputtering and electrochemical deposition

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Thin films of Co₃O₄ were deposited on stainless steel sieves by combination of reactive magnetron sputtering and electrochemical deposition. The films deposited by reactive RF magnetron sputtering or by reactive high-power impulse magnetron sputtering (HiPIMS) served both as interlayers for subsequent electrochemical deposition of cobalt oxide or as interlayer and layer on the top of the multilayer system (“sandwich”). Formation of Co₃O₄ after reactive magnetron sputtering as well as after heating of the electrochemically deposited product was confirmed by XRD. The surface structure was observed by SEM. The thin films deposited by the magnetron sputtering showed very good adhesion to the stainless steel surface. Coating of the stainless steel sieves with thin Co₃O₄ sputtering interlayers considerably improved also the adhesion of Co₃O₄ crystals deposited by electrochemical way; a major improvement of their adhesion was observed especially when HiPIMS interlayer was applied. The combined magnetron sputtering and electrochemical deposition of Co₃O₄ can be used for preparation of supported catalysts; therefore, the prepared materials were tested as catalysts in the total oxidation of ethanol.

Keywords
HiPIMS
sputtering
thin films
plasma deposition
catalysts
Low-temperature deposition of thermochromic VO$_2$ films on glass and kapton using reactive deep oscillation magnetron sputtering

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A modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, with a pulsed O$_2$ flow control and to-substrate O$_2$ injection into a high-density plasma in front of the sputtered vanadium target was used for low-temperature (330 °C) deposition of thermochromic VO$_2$ films onto conventional soda-lime glass (1 mm thick) and flexible kapton polyimide foil (25 µm thick) substrates without any substrate bias voltage and without any interlayer.

The depositions were performed using a strongly unbalanced magnetron with a planar vanadium target of 100 mm diameter in argon-oxygen gas mixtures at the argon pressure of 0.5 Pa. Voltage macropulses, composed of 10 voltage micropulses (pulse-on time of 20 µs and pulse-off time of 30 µs), with a total length of 500 µs and repetition frequency of 640 Hz were used for all depositions with a maximum target power density of up to 735 Wcm$^{-2}$ during pulses at a deposition-averaged target power density close to 20 Wcm$^{-2}$.

A high modulation of the transmittance at 2500 nm (even between 77% and 17% for VO$_2$ films on the kapton substrate) was achieved for the VO$_2$ films on the glass and kapton substrates at the transition temperatures of 57-64 °C.

This low-temperature magnetron sputter technique is of key importance for compatible fabrication of thermochromic VO$_2$-based multilayer coatings for smart windows and smart radiator devices (spacecrafts) applications requiring enhanced luminous transmittance and solar transmittance modulation at a decreased transition temperature.

Keywords
Reactive DOMS
Thermochromic VO2 films
Low-temperature deposition
Microwave plasma assisted chemical vapor deposition of silica

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Silica coatings are part in many optical and electrical applications. Especially, in electrical applications, e. g. as insulator the thin films have to be deposited defect-free. One solution for depositing silica is reactive sputtering, but this process needs usually active process control and leads to low deposition rates compared to CVD. Therefore, CVD-processes are favored in industrial applications. Especially microwave excitation offers a tool for cost efficient production.

In this presentation, we will focus on microwave processes using a parabolic microwave source for deposition of SiO\textsubscript{2}-films. The working pressure was varied, as well as the source power and amount of HMDSO/TMS-gas. The plasma is characterized by optical emission spectroscopy. The deposited films are characterized with respect to their electrical (i. e. insulation) and optical properties.

Furthermore, the characterization is complemented by SEM investigations of the topography and morphology of the films with top view and fracture cross section.

**Keywords**

CVD
microwave
silica
insulator
Dynamic Measurements of Secondary Electron Emission Coefficient during PIII Processing

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Plasma based deposition processes are commonly used in industry to guarantee high quality coatings with versatile properties. Modern technologies including magnetron sputtering and HiPIMS crucially depend on the plasma and electrode parameters. For example, secondary electron emission due to impinging ions is an essential intermediate step in these PVD processes. At the same time, secondary electrons are an ubiquitous nuisance in plasma immersion ion implantation (PIII) since they increase the primary current for the pulse generator by nearly one order of magnitude for voltages higher than 10 kV. Nevertheless, it is still feasible to measure secondary electron yields for arbitrary materials in the energy range between 0.5 and 5.0 keV. Using a passive thermal probe, the emission of secondary electrons can be detected with reasonable time resolution, which allows detailed in-situ measurements of the surface state (i.e. metallic, oxidised or nitrided) and its time evolution during either sputtering of surface layers or growth of compounds by ion implantation. Thus, a dedicated investigation of the relative secondary electron emission of materials is possible. In this presentation, the time evolution of the secondary electron emission is presented as a function of ion energy using argon ions for selected metals including Al, Mg, Ag and Ti to elucidate the nature of the native oxide layer. Using ion implantation with very short pulses and surface neutralisation by electrons between these pulses, even non-conductive materials can be investigated. For a proof of principle, the secondary electron emission of polymers is investigated to establish whether prolonged storage in air leads to differences in the secondary electron yield.

Keywords
secondary electron emission
passive thermal probe
Cylindrical magnetron with multiple dynamic areas of toroidal plasma

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The new cylindrical magnetron with a dynamic oscillatory magnetic field, as developed at the Institute of Precision Mechanics, is of innovative design, which is not currently being used on the domestic market. In the course of an analysis of publication databases on the Internet, and contacts with research-production centres associated with the domain of the presented innovation, it was revealed that there are only two research centres (in the US and the UK) which deal with this type of design and magnetron. The proposed design of a magnetron-type plasma source and the method of coating vacuum deposition by magnetron is applied to large closed and open spaces, e.g. in pipes of heat exchanges, inner surfaces of combustion engine cylinders, gun barrels, application of coatings on plastic and fabric foil products. Until now, inner surfaces of metal pipes operated under corrosion and impact loads have been modified by coatings, e.g. Cr\(^+6\) coatings obtained by Cr galvanisation which poses a great environmental burden. A crucial utility and innovative factor of the presented magnetron is the development of functional coating application on long pipe inner surfaces, which are from 45 mm to 200 mm in diameter and from 100 to 1500 mm in length. The application of a magnetron and plasma environment for the synthesis of coating materials results in obtaining advanced metallic coating materials, nitric/carbide/oxide metals included in the groups IVB to VIIB of the periodic table (e.g. CrN, NbN, ZrN and ReN, etc.). Therefore, it has become possible to conduct research on new aerological material systems featuring better functional properties.

**Keywords**
MS PVD
Cylindrical Magnetron
Toroidal Plasma
OES
TiN TiCN CrN
Controlled the Stress in Titanium Nitride Thin Films by Reducing the Amount of Doubly-Ionized Metal Ion in HiPIMS discharges

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Controlling the properties, such as hardness and stress, is a crucial task for successful applications of transition metal nitride thin films on various substrates. High-flux low-energy ion bombardment in reactive discharges is commonly used as an approach for tailoring the film properties. In high-power impulse magnetron sputtering (HiPIMS), wherein the high plasma density results in a high degree of ionization of the sputtered material, the ion bombardment by the deposition species themselves plays an important role in the film growth. The energy of the bombarding ions, to which hardness (H) and stress (σ) values depend strongly, are determined mainly by a substrate potential (U_b), where singly ionized ions accelerate up to a maximum energy of q·U_b, where q is the elementary charge. Doubly ionized ions can accelerate to twice the energy (2q·U_b) and this need to be taken into account when using HiPIMS and sputtering situations where the first ionization potential of the sputtering gas (i.e. Ar) is higher compared to the second ionization potential of the target material (e.g. Ti, Hf, V, Zr and Nb). In the present work, TiN was deposited by reactive HiPIMS in Ar/N2 environment without substrate heating or bias, and the effects of Ti2+ ions on the resulting films properties was investigated. In order to control the contribution of Ti2+ ions incident at the substrate plane, the power per pulse (P_pulse) was varied from 5 to 25 kW, while maintaining an average power of 1.5 kW. In situ energy-resolved mass spectrometry analyses of the ion flux reveal that by increasing the Ppulse, the doubly-to-singly charged metal ions ratio (Ti2+/Ti+) increases from 0.2 to 0.5. This effect was then correlated to the crystal orientation, film stress (σ), microstructure and hardness (H). It was found that increasing Ppulse strongly affect the microstructural development of the deposited films, resulting in a clear improvement of the H values, but with a steep price of a high-level of compressive stress. A good compromise of σ = -0.9 GPa and H = 22.7 GPa was achieved when using Ppulse = 8.3 kW corresponding to Ti2+ /Ti+ value of 0.3.

Keywords
Reactive HiPIMS
TiN
stress
Investigation of a pressure gradient Ar plasma sputtering for metal thin film deposition

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Ar plasma sputtering is a well-established thin film deposition technique since Ar gas in process is chemically stable and the mass is heavy enough to sputter metallic atoms from the target. The conventional working pressure is around a Pa or less because of sustaining magnetron plasma and of the decrease collisions between sputtered metallic species and Ar atoms from the target to substrates. However, the low pressure condition is not always good for the sputtering process because such a low pressure is difficult to sustain a stable plasma. In this study, we have investigated a pressure gradient Ar plasma sputtering system for metal thin film deposition. We set an orifice plate between the sputter cathode and the substrate. Ar gas was introduced from the cathode region and evacuated from the substrate region. The ratio of the pressure in the cathode region and that in the substrate region is successfully increased from 1.3 to 2.8 by controlling pumping speed. Using the pressure gradient sputtering, we achieved higher deposition rate which was more than double. The higher pressure in the cathode region maintains the magnetron sputtering and the lower pressure in the substrate region reduces the collision between sputtered atoms and Ar atoms leading to increase the deposition rate. The results shows adding the simple orifice is a promising to increase the deposition rate.

On-site, we will discuss the mechanism of the pressure gradient sputtering deposition

Keywords
Deposition rate
plasma sputtering
pressure gradient
Titanium deposition on polymer substrate by high-power pulsed sputtering
Penning discharge in Ar/N2 mixture gas ambient

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High power pulsed sputtering (HPPS) is the method of obtaining metallic plasma by applying negative high voltage pulses with peak power higher enough than the electric power used by DC sputtering to a cathode. We cause HPPS-discharge using a Penning discharge type target cathode. HPPS Penning discharge is featured that the plasma is generated at a space consisting of a pair of cathodes as sputtering target (W24×H20×t5) in parallel each other. Distance between targets is 10 mm. The magnetic field is provided by setting a set of permanent magnets (O14×17, NdFeB) behind the targets. Energetic argon ions accelerated by a voltage difference between the cathode and the plasma are bombarded to the sputter target, and emit the metallic target atoms and secondary electrons. Secondary electrons are confined between the two targets by magnetic field and electrical potential wall, ionize the target atoms, and improve the metallic plasma density. Therefore the metallic plasma flows out to the deposition area. When thin film is deposited on the substrate in this plasma, a substrate is not heated so much because the sputtering targets which become high temperature are perpendicularly to the substrate. We generated titanium plasma under argon/nitrogen mixture gases, and tried deposition of the titanium thin film on a polymer substrate. The voltage pulse-train (amplitude of -800 V and pulse duration of 50 µs) was applied to the titanium sputter target at the repetition rate of 500 Hz under the argon gas of 10 sccm, nitrogen gas of 0.26 sccm, and the gas pressure of 0.5 Pa. The titanium thin films were deposited on the glass, polypropylene (PP) and polypropylene (PS) substrates located at 30 mm from the plasma source. The XRD pattern of any substrate showed that deposited thin film was titanium nitride. The color of thin film on a glass was clear gold. On the other hand, it was dull gold on PS and was dark gold on PP.

Keywords
Pulsed sputtering
Penning discharge
titanium plasma
Reactive deposition
Polymer
Reactive HiPIMS deposition of MgO thin films using peak current regulation and its in-vitro corrosion performance for medical applications

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Magnesium and its alloys as a biodegradable material have great potential to be developed due to its excellent biocompatibility and similar mechanical properties to natural bone. However, poor corrosion resistance has to be improved for medical applications. In this study, MgO films were deposited by reactive high-power impulse magnetron sputtering (HiPIMS), using peak current regulation mode to realize the high-rate deposition stabilized at transition mode in reactive process. The plasma state was also characterized using voltage/current measurements and in-situ optical emission spectroscopy (OES). The chemical composition, surface morphology and phase composition of the films were analyzed by electron dispersion X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. As results, stoichiometric composition and good crystallinity of MgO (2,2,0) films were successfully deposited with high deposition rate of approximately 27 nm/min, under the reactive condition of O\textsubscript{2} and Ar gas mixtures at the working pressure of 1 Pa under 24 A peak current regulation. Further investigation on the in-vitro corrosion behaviors of MgO films were conducted by immersion test in Hanks’ balanced salt solution (HBSS) and electrochemical measurements. Improvement in corrosion resistivity by the HiPIMS deposited MgO film were successfully demonstrated.

Keywords
HiPIMS
MgO
Reactive sputtering
Peak current regulation
In-vitro corrosion
Effect of ion-to-neutral ratio on thickness distribution of Ti and Al films on inner wall of small hole deposited by HiPIMS

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In the previous report, the authors have demonstrated the availability and advantages of high-power impulse magnetron sputtering (HiPIMS) in the control of the direction and energy of the ion flux incident to the inner walls of sub-millimeter scale tubular components. For the deposition of Titanium Aluminum nitride ( (Ti, Al)N ) films, the chemical composition was varied in the deeper position of the inner wall. In order to clarify the transportation behavior of the sputtered species into the small hole structure and to deposit the film with uniform chemical composition in any depth of inner wall of small hole, the present study focused on the effect of ion-to-neutral ratio in the HiPIMS plasma on the thickness distribution at the inner wall surface. Control of ion-to-neutral ratio of Ti and Al was achieved by changing pulse peak current density under constant input power of 220W and pulse width of 100 μs. The pulse repetition frequencies were varied from 80 to 500 Hz to achieve the different peak current density of 0.5, 1 and 2 A/cm². After the confirmation of the different ion-to-neutral ratio by the optical emission spectroscopy for different peak current density, depositions of Ti and Al into the small hole structure with a width of 2mm were performed. Surface morphology and cross-sectional microstructure of the films on the inner wall were observed using scanning electron microscopy (SEM). Fabrication of the film cross-sectioning was performed by focused ion beam (FIB). As results, Ti film was deposited at maximum 5 mm of depth on inner wall under the condition with the highest ion-to-neutral ratio. On the contrary, Al was deposited at maximum up to 10mm of depth in the lowest ion-to-neutral ratio. The role of ionization of sputtered species and its effect on the particle trajectory into the small-hole structure are discussed by comparing the thickness distribution of Ti and Al film.

Keywords
HiPIMS
small hole
inner wall
peak current density
ion-to-neutral ratio
HYDROGEN-FREE DLC COATINGS DEPOSITED BY HiP GIMS

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DLC-type carbon coatings produced by PA PVD methods were entered to the scientific circuit almost 50 years ago. In the production of hydrogen-free coatings by the PA PVD methods, the most effective synthesis environment is the high-energy plasma where dominates an ionization of carbon vapors via electron collisions. Such plasma is most efficiently generated by arc methods. However, these methods generally require a complex instrumentation that eliminates the emission of micro- and macro particles of the carbon target used as carbon vapor source. The use of high power magnetron sputtering (HiPIMS) seems to be a promising and competitive technique for producing carbon coatings due to the expected plasma properties necessary for the creation of $sp^3$ orbitals. Recently, more and more publications have started to appear in this area. In our research, we applied the HiPIMS technique too but contrary to the known solutions, at now the plasmoids generation was fully controlled by the working gas pressure pulses in the range of its critical values (Gas Injection Magnetron Sputtering, GIMS). The graphite target mounted in the unbalanced 50 WMK magnetron was the only source of the carbon vapors. The argon injected by the fast impulse valve to the inter-electrode space in the form of discrete gas pulses (pressure changes range of $10^{-3}$-10$^{-1}$ Pa in the gas pulse) was the sputtering gas and it played the role of the only discharge ignitron in the system. Carbon coatings were deposited on the unheated monocrystalline silicon wafers. The HiP GIMS (High Power GIMS) deposition process consisted of a sequence of 1000 plasma impulses generated at frequency of 0.5 Hz with the use of capacitor of 25-50 mF charged to the voltage of 1-2 kV as a source of the electric energy. As a result, for the best case of the plasmoids with the energy of about of 16 J, the 70% of the $sp^3$ hybridized carbon bonds were detected (Raman) in the phase composition of the carbon coatings.

Keywords
DLC coatings
HiPMS
GIMS
Comparative microstructure, chemical composition, optical and tribo-mechanical properties of CrAlN coatings deposited by HiPMS and DC magnetron sputtering

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Chromium aluminium nitride films by magnetron sputtering develop an excellent high temperature protection behaviour and tribo-mechanical properties. In this work, different coatings based on Cr(Al)N are deposited by D.C. reactive magnetron sputtering and HiPIMS reactive magnetron sputtering on silicon and steel substrates. The optical properties like emissivity are measured at room temperature by mean of FTIR spectrometer with values of $\varepsilon$ higher of 85\%. The microstructure and chemical composition of the coatings are studied by mean of scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) looking for differences induced by the high ionization plasma in the case of the HiPIMS. In order to increase the knowledge about the consequences of this chemical and microstructural differences, mechanical and tribological properties of coatings prepared by both techniques (DC and HiPIMS) are measured and compared.

Keywords
CrAlN
HiPIMS
Emissivity
Tribology
EELS
PO4015

Synthesis of highly adhesive and hard amorphous carbon films on Silicon and PTFE substrates by dual magnetron sputtering for sensing applications

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Hard amorphous carbon deposited on silicon and polymer substrates can be easily used for electrochemical sensing applications. Owing to the difference in the film stress between substrate and depositing film with high hardness, a weak film/substrate adhesion shortens the working device lifetime. In this work, the energetically deposited carbon films on silicon substrates or PTFE substrates exhibit improved adhesion to HF1 level based on the generation of thick film/substrate interface of about 8 nm due to subplantation of deposits by energetic bombardment, and on the film stress values limited to 3.5 GPa. Apart from excellent adhesion, the films demonstrate good homogeneity, excellent electrical conductivity and superior electrochemical performance when doped with Cr (2%) by dual magnetron sputtering. Moreover, this approach opens up new avenues to the fabrication of thin amorphous carbon film electrodes by lithography.

Keywords
undoped and metal-doped amorphous carbon
HiPIMS
hardness
electrochemical sensing
adhesion
New approach for arcing mitigation methods

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Over last year an interest in High Power Impulse Magnetron Sputtering (HIPIMS) technique have increased significantly. Until now anti-wear and protective coatings prepared by HIPIMS won an established position and are used commercially. Newest market trends show the HIPIMS technology will soon became a standard production tool for oxide coatings, both conductive and non-conductive. In order to keep pace with market development HIPIMS power supplies also require further evolution to meet high productivity, stability and reproducibility demands of the industry. To fulfill these rigorous requirements HIPIMS power supplies must offer versatile arc management, unique control of voltage and current peak shape and the average power delivery control – sophisticated features previously unavailable in any other HIPIMS power supply units.

This contribution is focused on two aspects of HIPIMS technology: (i) arc detection and suppression methods (ii) stabilization of reactive sputtering processes performed with HIPIMS.

The first part will be opened with the description of basic methods for detection of discharge shift from glow to arc type. Two supplementary detection methods based on current and voltage threshold monitoring will be discussed with respect to the suppression time and associated arc energy. It will be shown that application of regulated quasi-rectangular HIPIMS voltage and current pulse shape does not lead to increased probability of arc formation.

Next, based on the results of HIPIMS sputtering using planar Ti and Al targets in mixed Ar with oxygen or nitride atmosphere, it will be shown that combined peak current value and average power control algorithm can be used for stabilization of reactive sputtering processes. The influence of various average power control algorithms on the pulse shape and deposition rate will be discussed.

Keywords
HIPIMS
Reactive HIPIMS
Arcing
Process stabilization
Titanium-based compound materials, such as TiN, TiO$_2$, TiO$_x$N$_y$, show excellent mechanical, tribological, optical and photocatalytic properties, making them very useful as thin films in a wide range of applications. These films are usually prepared by plasma-based methods including reactive High Power Impulse Magnetron Sputtering (HiPIMS). HiPIMS plasmas exhibit a high ionization fraction of the sputtered material as well as high kinetic ion energies. In the case of Ti, the ionization fraction typically exceeds 60% but has been shown to reach above 90%. The high degree of ionization in HiPIMS allows for control of the energy and direction of the film-forming species, which results in higher film density, higher hardness, lower electrical resistivity, lower surface roughness, etc. Reactive HiPIMS has also other advantages over conventional techniques, such as eliminated/reduced hysteresis and stable high-rate deposition in the transition mode, which are key ingredients for increased productivity. However, the energetic ions are also responsible of promoting high-energy phase selective growth, e.g., rutile instead of anatase in TiO$_2$, and considerable intrinsic compressive stress, leading to film delamination, e.g., in TiN coated tools. Moreover, the deposition rate for Ti-based compounds are often lower in HiPIMS compared to competing techniques. In this contribution, we address these issues by identifying suitable operating conditions (pulse parameters, substrate biasing, and working pressure) to minimize, or eliminate, the undesirable effects. This includes new routes to depositing phase pure anatase TiO$_2$ films with improved crystal quality at high deposition rates using ion bombardment of weak to moderate intensity. In addition, new results on intrinsic stress tailoring will be presented when using advanced HiPIMS substrate biasing techniques during growth of TiN.

**Keywords**
- HiPIMS
- thin film
- process optimization
- titanium dioxide
- titanium nitride
Fast Impedance Matching using Semiconductor Switches

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Impedance matching is a crucial problem in rf plasma process control. Today’s matchboxes are using adjustable capacitors. They have low losses and allow fine adjustments, limited by the mechanical system and the control system accuracy. Drawbacks are moving parts with lack of reliability and limited lifetime as well as slow operation, limiting process options, particularly for fast and pulsed processes.

We present a new matchbox design without moving parts using new types of semiconductor switches which can operate at 13.56 MHz at high voltages and high currents. A specialized circuit layout allows a wide matchable impedance range. Due to the fully semiconductor design without moving parts, very fast tuning operation can be achieved which allows high speed process control.

Data of test bench impedance measurements are shown as well as examples of several plasma processes using the new matching technology. A comparison between the old matchbox and the new one is made, differences are shown. Strategies for tuning are discussed.

**Keywords**
impedance
matching
matchbox
switch
W-B-C hard yet ductile coatings prepared by High Power Impulse Magnetron Sputtering

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As the demands for the quality and speed of machining increase, the application of protective coatings on the used cutting tools becomes ever more important. Nowadays used ceramic protective coatings exhibit high hardness and toughness, however, they suffer from inherent brittleness. This can lead to a premature failure of the coating and of the cutting tool as a whole due to rapid crack propagation. Therefore, a new generation of coatings combining hardness and moderate ductility is sought for. Such a coating was recently in the form of an inherently nanolaminated X₂BC, where X is a metallic element. Mid-frequency pulsed DC magnetron sputtering was used in our previous study as a means to enhance the ion bombardment of the growing coating for preparation of W-B-C coatings whilst avoiding the complexity and the cost of HiPIMS. The W-B-C system was chosen as the calculated mechanical properties of W₂BC even surpassed those of the only experimentally reported in the literature - Mo₂BC. The deposition temperature of ~ 500 °C was used. The W-B-C coatings had a nearly amorphous or a nanocomposite structure with sparse grains with the size of < 5 nm. Columnar growth was typical for all coatings. The resulting hardness was in the range of 22 – 26 GPa. This contribution summarizes the properties of the W-B-C coatings when HiPIMS was used for the deposition. The changes in the microstructure as compared to the pulsed DC case are described. These are also correlated with differences in the mechanical properties.

Keywords
Magnetron sputtering
Hard coatings
Nanostructure
HiPIMS
Options to Tailor Thin Film Properties by Ion Beam Sputter Deposition

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There is an increasing demand for thin films with optimized properties. This requires the use and control of adequate deposition techniques. Ion beam sputter deposition (IBSD) is capable to fulfil the technological demand, because it offers the unique opportunity to tailor the properties of the film-forming particles and, hence, thin film properties. This is related to the fact that the generation and acceleration of the primary particles (ion source), the generation of the film-forming particles (target) and film growth (substrate) are spatially separated. Thus, by changing ion beam parameters (ion species, ion energy) and geometrical parameters (ion incidence angle), the angular and the energy distribution of the sputtered target particles and backscattered primary particles are modified.

Systematic investigations of the correlation of process parameters, the properties of the sputtered and backscattered particles, and thin film properties were performed. Exemplary, three materials were used: Ge (semiconductor), Ag (metal) and TiO₂ (dielectric). Though the materials are very different, the fundamental systematics were found to be the same. It could be shown that (i) the most important parameters are the scattering geometry and the primary ion species, or more precisely the mass of the primary particles in relation to the mass of the target particles, (ii) ion energy and ion incidence angle have only a small or negligible impact, (iii) backscattered primary particles have a higher impact on thin film properties than the sputtered target particles.

The results are illustrated by selected examples of the IBSD process of Ag and TiO₂. The influence of the process parameters on the energy distribution of the film-forming particle and on the thin film properties, such as, structural properties, composition, surface roughness, mass density, electrical or optical properties are shown.

Keywords
Ion beam sputter deposition
Film properties
Particle properties
Silver (Ag)
Titanium dioxide (TiO₂)
Modern applications of micro- and nano-electronic devices require complex multilayered structures of various crystalline (semi-)conducting, piezoelectric or isolating materials. In certain occasions, it has turned out useful to create these layers not by means of deposition but rather by composing the layer stack from pre-manufactured wafers of the required materials. Well known since years are silicon on insulator (SOI) wafers, while new compound wafers like lithium niobate (LN) or lithium tantalate (LT) on silicon are recently upcoming new combinations. Both find increasing interest for the manufacturing of micro electro-mechanical systems (MEMS) devices. The LN/LT-compound wafer re-gained industrial interest in the field of telecommunication filtering because of the steady growing demand for bandwidth utilization of mobile communication devices. The layered wafer structure gives high Q factors, due to its intrinsic better confinement of the acoustic wave, challenging the aluminum nitride (AlN) film bulk acoustic resonator (FBAR) filters. In addition, the underlying SiO$_2$ layer can control the temperature coefficient of frequency (TCF). In all cases, the layer thickness influences directly the resonance frequency of the device, and the layer uniformity results in higher yield, higher quality, and reduced manufacturing costs. Either smart cutting or bonding, subsequent grinding and final chemical mechanical polishing (CMP) sets the thickness of the final top "device" layer. However, oftentimes the specification for the layer thickness homogeneity becomes stricter than those methods can deliver. In these cases, ion beam trimming of the top layer drastically improves both, the thickness uniformity (and thus subsequent device yield) as well as the desired target thickness accuracy. By means of the applied trimming technique, the functional layer thickness can be adjusted down to $< +/−2$ nm off the target value for all the investigated materials. The standard deviation of the thickness topology error decreased significantly with typical improvement factors of 20 to 50, depending on the incoming quality, respectively.

**Keywords**

ion beam trimming
MEMS
LT / LN / SOI
Modern short-wavelength imaging systems in the visible and UV spectral range are based upon complex figured mirror devices with a spherical, aspherical or free-form surface shape. Recently it has been shown, that the application of reactively-driven ion beam tools allows the direct surface figure error correction of mirror optics made from aluminium technical alloy materials AL6061 or AL905 [1,2]. With this innovative technology it is now possible to correct the figure error of the mirror surfaces up to 1 micron in height while preserving the surface roughness.

Non-toxic gases as oxygen and nitrogen are used for ion beam processing. The erosion process rests upon pure physical sputtering enabling a high degree of process control. For reasons of device shape flexibility a deterministic machining approach with a small-sized tool function is examined: First, a dwell-time algorithm is applied to transfer the figure error profile into a motion map. Following this simulated motion profile the ion beam is then moved deterministically along the device surface. This approach allows the figure error correction of huge and diversely shaped mirror devices.

As an example the figure error correction of a deep concave parabolic mirror with an aspect ratio of central depth to open aperture of \(\approx 0.6\) is focused. The contribution comprises technological aspects as the generation of a focused millimeter sized ion beam, the evaluation of different machining geometries within the particular ion beam erosion model scheme, and several trial process applications of reactive ion beam machining at aluminum sample devices.

[2] Bauer, J., Ulitschka, M., Frost, F., Arnold, T.; EOS Optical Technologies: Figure error correction of aluminium mirrors by deterministic reactive ion-beam machining; Munich / Germany, 26.-29.06.2017

Keywords
ion beam figuring
reactive ion beam etching
metals
mirrors
optics
High precise local film thickness and surface correction using an ion beam tool

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The increasing requirements for microelectronics, MEMS and acoustics need very precise films with a low deviation of the film thickness across the substrate surface. Therefore a modulation of the deposited films is necessary as existing deposition methods do not meet these requirements.

This precise modulation has very high demands to the system. Meyer Burger (Germany) GmbH has more than 15 years experience in building and developing such tools. Using this tool a local, spatial resolved modification of the surface is possible to achieve homogeneities over a substrate in a sub-nanometer range. The main components to achieve such a local variation are the substrate handling including clamping, the controlled movement of the substrate and the ion beam source together with the analyzation components. The surface of each substrate can be processed individual to achieve the best result for every single layer. Even substrate to substrate modulations in the film thickness from the deposition tool can be corrected. All this has highest demands to the repeatability, uptime and precision. The repeatability is not only needed for the etch rate stability it is also needed for the accuracy of the movement system. To meet this requirements the necessary components e.g. ion beam source and substrate holder (mechanic and electrostatic chuck are available) have to be improved and analyzed continuously.

The details of the tool and further possibilities of the usage are presented in this poster.

\textbf{Keywords}
ion beam trimming surface correction
High precise local film thickness correction

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The increasing requirements for microelectronics, MEMS and acoustics need very precise films with a low deviation of the film thickness across the substrate surface. Therefore a modulation of the deposited films is necessary as existing deposition methods do not meet these requirements. The state of development of scanning ion beam tools allows a correction of such films. Due to a continuous improvement of these tools better and highly resolved processes are possible. It is possible to modify all typical semiconductor and oxide materials e.g. Si, SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, AlN as well as metals e.g. Au, Cu, Mo or W. Typical film thicknesses vary less than 1 nm from the target thickness after correcting a wafer. The error distribution is usually much below 1 nm (typical is a range of 0.1 nm to 0.2 nm for one sigma). In order to get such results some requirements have to be fulfilled. This are stability of the ion beam source regarding etch rate and beam size, precision of the movement of the axis system and a precise calculation of the local dwell time. Based on the local target removal an internal software calculates the dwell time at each point of the wafer. Therefore the local target removal should be known in advance in detail. This calculation is done for every single wafer which allows a compensation of slight variations during the previous deposition. Besides such a smoothing of the film thickness across the wafer also each wished topology can be trimmed. This is selectable by changing the local target removal in the desired way.

The details of this process and some process results are presented in this poster.

Keywords
ion beam process
etching
local
high precise
Ordering of Nitrogen-Supersaturated Interstitial Solid Solution in Fe-Cr-Ni Austenitic Alloys and Steel Modified by Plasma-Based Low-Energy Ion Implantation

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The formation of a metastable and nitrogen-supersaturated f.c.c. interstitial solid solution layer on Fe-Cr-Ni austenitic stainless steel at a moderate temperature around 400°C is not completely understood. In this work, seven designed Fe-Cr-Ni austenitic alloys containing of 0-17.66 wt.% chromium and the commercial AISI 304L austenitic stainless steel are modified by the plasma-based low-energy nitrogen ion implantation at 380°C for 4 h. A duplex layer structure is confirmed on all the nitrided Fe-Cr-Ni austenitic alloys and AISI 304L austenitic stainless steel by optical and magnetic force microscopy, X-ray diffraction and transmission electron microscopy, although a single layer was usually observed on the austenitic alloy and steel composed of a high Cr content above 12.00 wt.% by metallography, X-ray diffraction and electron probe micro-analysis, respectively. The outer sublayer is characterized as a nitrogen-supersaturated γ′-Fe4N-like ordered phase (γ′N), and the inner sublayer is as nitrogen-supersaturated disordered f.c.c. phase (γN). All the γN phases on the Cr-varied Fe-Cr-Ni austenitic alloys are isostructural with the stable γ′-Fe4N phase, moreover the γN phases are isostructural with a nitrogen-saturated f.c.c. solid solution (γ*N) on the Cr-free austenitic alloy. A cell model, considering atomic interaction between nitrogen atom and octahedral interstice consisting of six varied Cr, Fe and Ni atoms, is established to understand the mergence of duplex layer when Cr content above 12.00 wt.% in alloys, which based on the addition of Fe4N-like long-rang ordered Fe-N interaction in the γN phase together with the short-rang ordered Cr-N interaction as in the γN phase. The ordering of the nitrogen-supersaturated f.c.c. interstitial solid solution from the γN to γ′N phase carry out over a critical concentration dependent on the Cr-N interaction and Fe4N-like Fe-N interaction in the nitrided Fe-Cr-Ni austenitic steel and alloy.

Keywords
Plasma-based low-energy ion implantation
Austenitic alloy
High nitrogen f.c.c. phase
Isostructurality
Cell model
Oxidation behavior of Zr–1Nb in air at 400°C after Titanium Plasma Immersion Ion Implantation

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Zirconium alloys have been widely used in nuclear reactors due to low thermal neutron capture cross-section, excellent corrosion resistance and acceptable mechanical properties. Nowadays several methods apply for improving hydrogen and corrosion resistance such as addition of stabilizing additives (yttrium), deposition of thin solid films, micro-arc oxidation and modification of the surface by electron beam. Despite the multiplicity of the methods hydrogen embrittlement is still a pressing issue. Previous results have shown the positive influence of plasma immersion titanium implantation on the hydrogenation behavior of Zr–1Nb and Zr–2.5 Nb. After Ti implantation hydrogen preferably accumulates in the modified surface layer comprising the implanted Ti. Furthermore, the hydrogen concentration is considerably less inside the zirconium modified sample than in the as-received samples.

The integration of elements into the zirconium lattice can influence the valence of the surface and change corrosion and oxidation rates of the alloys. So it is very important not to decrease the zirconium oxidation resistance due to Ti implantation. Therefore, the purpose of this research is to study of the influence of Ti implantation on surface morphology, oxidation rate and phase structure of the Zr–1Nb alloy after oxidation on air at 400°C for 5, 24, 72 and 240 h. The results show that the oxidation kinetics after Ti modification of the zirconium alloy changed. Although the weight gain of the implanted sample remains approximately the same, it can be considered that Ti implantation stabilizes the oxide layer and has beneficial influence on the oxidation protection of Zr-1Nb.

Keywords
Zr–1Nb
titanium ion implantation
oxidation
plasma immersion ion implantation (PIII)
DSC
Electrodeposited hard chromium (EHC) coatings have been widely used for improving wear characteristics of engineering tools and components. In the electrodeposition process, in general solutions containing hexavalent chromium have been used, which is classified as a carcinogenic compound. The environmental concern on the use of this coating stimulated the research activities for alternatives of hard chromium. In addition, the crack pattern of the hard chrome surfaces can represent a problem for wear and corrosion resistance.

Plasma nitriding or nitrocarburizing plus oxidizing is a promising duplex process, which can replace EHC in low and medium alloy steels. In this work, AISI 1045 was nitrocarburized, AISI 4140 was nitrided, both in a DC Plasma industrial equipment, and they were oxidized as post treatment in the same chamber. Surface layers were characterized by XRD, Raman, optical and electronic microscopy. Both groups of oxidized samples were tested in wear and corrosion experiments, comparing them with the base material and the nitrided/nitrocarburized steel without oxidizing. Pin on disk, abrasion, scratch test, salt spray fog and electrochemical measurements were carried out.

The results showed nitrided AISI 4140 is a better substrate for the oxide layer than nitrocarburized AISI 1045, regarding wear resistance. In the scratch tests, the oxide layer delaminated for lower loads in nitrocarburized samples than in nitrided ones. For both substrates, the oxide layer as post treatment was good for atmospheric corrosion resistance tested in salt spray fog. In accelerated corrosion tests, on the other hand, more than the oxide layer, the integrity of the nitrided/nitrocarburized compound layers and the surface finishing were determinant.

**Keywords**
plasma nitriding  
nitrocarburizing  
oxidizing  
duplex processes
INVESTIGATION OF MECHANICAL, STRUCTURAL AND CORROSION RESISTANCE PROPERTIES OF LOW CARBON STEEL AFTER PLASMA CARBURIZING AND CARBONITRIDING PROCESS

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The use of surface treatments by plasma technology has increased substantially in the recent years for applications where wear and corrosion resistance properties are required. Among the different plasma surface hardening techniques, plasma carburizing has yielded good results for low carbon steels. Plasma carburizing is considered to be of more advantage over the conventional carburizing process mainly due to the reduced time and gas consumption during the treatment and also for its environmentally friendly nature. Moreover, with the use of plasma carburizing processes it is possible to achieve better dimensional control even for complex geometry components. Another variant process of plasma carburizing called plasma carbonitriding has also been recently developed where along with carbon, nitrogen is allowed to diffuse simultaneously into the steel.

In this paper an attempt is made to optimize both plasma carburizing and carbonitriding to enhance both surface hardness and corrosion resistance properties of low carbon steel (AISI 1020) treated at different temperatures. Plasma carburizing process was carried out using 98% hydrogen and 2% acetylene gas mixture whereas plasma carbonitriding was carried out using 80% hydrogen, 18% nitrogen and 2% acetylene gas mixture. The surface hardness of these plasma nitrocarburized stainless steel specimens increased by a factor of two compared to the untreated specimens. Moreover, there was only a marginal improvement in the corrosion resistance after these treatments. The advantages of having high surface hardness along with good corrosion resistance after these processes were explored. This paper also discusses the distortion studies of actual gears after plasma carburizing and carbonitriding processes.

Keywords
plasma carburizing
carbonitriding
distortion
corrosion
hardness
Improvement of Hardness and Toughness by Combined Heat Treatment of High Temperature Plasma Nitriding and Austempering

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The steel used for machine components is heat treated (e.g. carburizing and nitriding) in order to improve wear resistance and fatigue strength. However, they have some disadvantage. In carburizing, deformation is occurred and it exhausts greenhouse gas. In nitriding, the treating time is long. Nitrogen infiltrating and quenching, which is named “N-quench” has many good properties. In this treatment, specimen is quenched after the nitrogen is infiltrated about 1000K or more in Fe-N austenite phase, so the distortion is lower than carburizing, and the treating time is shorter than nitriding. However, N-quench uses NH₃, which is not safety for human. Novel heat treatment process high temperature plasma nitriding, which is called “plasma N-quench”, that applies plasma to activate the nitrogen for infiltrating instead of the NH₃ and austempering which is an isothermal heat treatment, when applied to steels, that produces a structure that is harder and tougher than comparable structures produced with quenching treatments are combined for improvement of hardness and toughness. The hardenability of low carbon steel is low because it is not included the alloy elements, therefore it is difficult to improve hardness and toughness by austempering treatment. If the nitrogen content of steel is increasing, the hardenability is increased. In this study, plasma N-quench process is used for increasing the nitrogen concentration and hardenability and austempering is used for increasing the toughness. In fact, combined heat treatment was applied to JIS-S45C steel to realize improvement in hardness and toughness. The toughness value of combined heat treated specimen was 4 times that of the quenched and tempered specimen, and a hardness of 10% higher than that of the same toughness value specimen which was treated only with the austempering was obtained.

Keywords
Plasma Nitriding
Austempering
Low Carbon Steel
Cromatipic; A sophisticated way of Metallizing plastics with in-line technology for high quality and productivity.

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Plastics are natural choice for various decorative application due to its low weight and non-corrosion behaviour. In automotive industry, plastics are metallized to provide premium look with bright or matt finish. Automated lacquering and metallization by Sputtered PVD on plastic can provide a high quality coating to satisfy various industrial standards. To achieve a bright color; Chrome plating has been the only solution for decorative coatings on plastics. This method, however, faces increasing environmental restrictions and is mainly applicable to ABS or ABS-PC substrates. In the recent past several processes have been developed involving lacquer and PVD coatings, sometimes with a lacquered top coat, sometimes without. In this talk an overview for an In-line metallization process will be given. This process aims to fulfil several automotive standards with high productivity and reduced cost of ownership. In modern era, fully automatic in-line technology is in demand to reach high productivity. In-line lacquering and PVD coating technology is a market requirement to reach better yields. During this presentation, we will explain about metallization by PVD integrated with lacquering in a production line.

The Author will explain about the importance of dealing appropriately with mutual influences between lacquering and PVD process. This will result in high a quality product and fulfil various industrial standards. To achieve different surface finish such as bright and matt, within production environment will be explained as well.

**Keywords**
Decorative
Non-corrosion
Plastics
lacquering
metallization
**Plasma deposition of textiles for obtaining electromagnetic shielding and fire-retardant properties**

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The stringent regulations regarding the electromagnetic exposure and fire safety have gained particular importance in the recent years. In this context, the obtaining of smart textiles in accordance to these regulations, by eco-friendly plasma-based techniques, is of tremendous interest. The present contribution reports on the synthesis and characterization of metal-organosilicon composites or layered materials by using hybrid PVD/PECVD techniques. The deposition of metal and silicon-based materials was conducted in a stainless-steel vacuum chamber provided with a magnetron sputtering source and a PECVD plasma source. The sources were mounted perpendicular one to each other, and respectively at 45 degrees in respect to the substrate. The textile substrate of natural or synthetic composition is sequentially exposed to plasma generated by magnetron sputtering of a metallic target (Cu, Ag) and to the plasma generated by PECVD source in an Ar/HMDSO mixture. According to the experimental parameters used for each plasma source, layered or mixed structures of metal-polymer coatings are obtained on the fabrics surface. The topographical and morphological characteristics of the as-synthesized textile materials were investigated by means of Scanning Electron Microscopy (SEM) techniques. The chemical composition of the obtained materials was evaluated through Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) investigations. The fire-retardant properties and electromagnetic shielding effectiveness of the smart textiles were investigated utilizing the standard procedures SR EN ISO 6941/2004, and ASTM D4935 standards, respectively.

Acknowledgements. This work has been performed in the frame of TexEMFiRe project in MANUNET III-2017.

**Keywords**

smart textiles  
combined PVD/PECVD  
electromagnetic shielding  
fire retardant
Bilayer coatings obtained by a combination of electro-spark deposition, magnetron sputtering and pulsed arc evaporation

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Deposition of multilayer and functionally graded coatings can improve erosion, corrosion, abrasion and fatigue strength of machine parts and structural materials. Herein two-layer coatings were deposited using a combination of different methods: electro-spark deposition (ESD), pulsed arc evaporation (PAE), and magnetron sputtering (MS). Using this approach, it is possible to combine the main advantages of each method when depositing coatings in a single technological cycle. The surface treatment was performed in a mixture of various gases at a pressure from atmospheric to 0.01 Pa. ESD in a reaction medium at a reduced pressure, optimal for gas discharge, is characterized by high process efficiency. The gradual decrease in pressure to 0.1 Pa, which is a characteristic of PVD processes, and the gradual increase in the distance between the electrode and the surface, provides a transition to the process of PAE or MS. Two-layer coatings have several advantages over their single-layer counterparts: ESD layer provides exceptionally high adhesion and a sufficiently high coating thickness (up to 100 μm), whereas the upper, more thinner layer (up to 10 μm), deposited by PAE or MS, ensures high mechanical and tribological properties. Two examples are considered. (1) Bilayer coatings in which the bottom Ti-C-Ni-Fe layer obtained by ESD using TiCNi electrode and adjacent to steel substrate has a relatively high thickness and toughness, whereas the top Ti-C-Ni-Al layer fabricated by MS of TiCNiAl target has enhanced tribological properties and high corrosion resistance. The chemical, mechanical, and tribological characteristics of such bilayer coatings are compared with their single-layer Ti-C-Ni-Fe and Ti-C-Ni-Al counterparts. (2) Two-layer WC/C coatings in which the sublayer, consisting of TiC, WC\textsubscript{1-x}, α- and β-Ti phases, was formed by ESD and the top layer, consisting of W\textsubscript{2}C and WC\textsubscript{1-x} phases, was fabricated by PAE either in argon or in nitrogen atmosphere.

Keywords
Electro-spark deposition
Magnetron sputtering
Pulsed arc evaporation
Tribological coatings
One-dimensional nanoelectrodes fabricated by plasma-assisted techniques

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The control of the material structure at the nanoscale has received a significant attention of researchers during the last decades to tailor and enhance their properties. A perfect example of the relevance of nanostructuration can be found for one-dimensional (1D) materials such as nanowires or nanotubes that present longitudinal sizes orders of magnitude larger than the cross-sectional.\textsuperscript{1} The strong structural anisotropy of 1D-materials together to their nanometer size provide them with new and exciting properties that have opened a wide range of applications such as optics, sensing or electronics. Particularly important are the electronic applications, since this 1D structuration requires the implementation of rationally designed conductive electrodes that reduce electronic losses through the pathway along the mayor axis of the nanostructure.\textsuperscript{2}

This work presents an evolved methodology\textsuperscript{3} for the synthesis of supported conducting nanotubes (NTs). Concretely, we show the formation of Indium Tin Oxide and Copper NTs deposited by magnetron sputtering on organic nanowires acting as easily removable 1D template.\textsuperscript{3} Combining experiments and Monte Carlo modelling, we control the thickness, porosity and microstructure of the walls and NTs density and length, paving the way towards the development of 1D nanoelectrodes under design. We show the optical and electrical properties of the NTs making a special effort in the elucidation of individual conductivity by assembling single-wire nanodevices and measuring them in a 4-probe platform installed in a SEM.


Keywords
One-Dimensional nanomaterials
Development of Ion Source for Novel Applications

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The use of Linear Ion Sources has been in the increase over the past 20 years. The present paper is an attempt to bring this type of sources to new research and industrial fields. The main application is still dominated by ion cleaning pre-treatment of substrates prior to coating deposition in order to enhance the coating adhesion. This is now a common application for high end market products of some display coating applications. An area of great interest has been the use of this sources in Plasma Enhanced Atomic Layer Deposition (PEALD). Following similar concept a combination of Ion Source and new processes have been developed in order to offer a research tool able to create new materials and surface condition. The ability to reproduce and upscale processes from the small R&D tool to large industrial level has made this type of source an interesting proposition. The present paper will present some new applications of the linear ion source in several fields and technologies of interest.

Keywords
ion source
PEALD
surface conditioning
Plasma Hardening of Sol-Gel Coatings

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Sol-gel deposition is a common way to apply functional nm- and µm-coatings onto a broad range of materials. By adapting the chemical composition of the precursor solution, the resulting surface properties can be tuned, like wettability, easy to clean behaviour, gas permeability, corrosion protection or scratch resistance.

State-of-the-art technologies for hardening of sol-gel layers are either heat treatment or UV-irradiation. In case of thermal annealing the applied temperature and dwell time are dependent on the sol type and the substrate material. For a TEOS sol common post-treatment conditions are e.g. 2h storage at temperatures above 100°C or more.

An alternative possibility for sol-gel layer hardening is the application of atmospheric pressure plasmas. The plasma mixture of reactive species, radiation from UV until infrared and thermal energy leads to the hardening of sol-gel coatings after short times, like seconds.

Two different plasma sources were tested successfully for this application, a plasma jet and a surface dielectric barrier discharge. In dependence of the used plasma source and the treatment parameters sol-gel coated temperature-sensitive materials can be treated as well as coated glasses and metals.

The effect of sol-gel hardening was verified by FTIR-spectroscopy. Changes in chemical bondings (network formation) and their relative absorption intensities are indicating the hardening effects. Thus, a comparison between different hardening technologies is also possible.

Besides the thin film analytic, optical emission spectroscopy (OES) was carried out to evaluate the plasma composition.

OES- and FTIR-results help to optimize the plasma hardening of sol-gel coatings. These plasma techniques are especially suited for areal (preferably flat), linear or local treatments.

Keywords
Atmospheric pressure plasma
Sol-Gel coatings
Hardening of coatings
FTIR & OES
Advanced Fibers by Plasma-Deposited Multilayers

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Metallised fibres have been a key topic over the last decade in the field of smart textiles. PVD technologies such as magnetron sputtering enable the metallization of fibres at the nanoscale combining electrical conductivity with textile properties – the base for new innovations in textiles. First applications for silver and gold coated fibres included antistatic, low friction and medical products such as embroidered body electrodes for measuring electrocardiogram besides haute couture fashion applications.

Current developments involve hybrid processes like deposition of multilayer coatings on metallised fibres providing additional functionality such as protection/passivation, electrical insulation or adhesion promotion.

Different multilayer coatings on fibres deposited with Physical Vapour Deposition (PVD) and Plasma Enhanced Chemical Vapour Deposition (PECVD) were studied. Ti sputtering (PVD) enables deposition of ultrathin titanium oxides as passivating topcoat. The Ti/Ag interface was investigated for their stability in aqueous environments showing a distinct reduction in Ag release from the Ag-coated fibre surface by maintaining the electrical properties. Semiconductive Ge-based coatings were developed on fibers demonstrating a well-defined temperature sensing effect by a colour change.

PECVD processes yielding a-C:H:O plasma polymer coatings were recently a good candidate to improve the wettability of surfaces. On fibres, the functional plasma polymer film acts to improve adhesion both on uncoated and metallised fibre surfaces for composite materials. Overjacketing of electrical conductive fibres with polymers can be used for data transfer or in general as an electric line. Finally, plasma polymers were also investigated as barrier layers to modulate drug release.

Since all processes are continuous (reel-to-reel), plasma technology provides a versatile tool to fabricate fibres with advanced properties.

Keywords
Plasma processes on fibers
diffusion barrier
silver release
temperature sensing
Synthesis of PbO2 nanosheets by discharges in liquid nitrogen

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A simple method to synthesize hexagonal sheets of lead, which belong to the class of two-dimensional materials, is presented. These objects can be collected on a substrate located under two lead electrodes between which nanosecond-pulsed spark discharges in liquid nitrogen are ignited. The hexagonal sheets are single crystals produced by gas phase condensation. Once nitrogen is fully evaporated, they are oxidized in the air and turned into a new phase of PbO₂. The oxidation process induces stress that may pleat the uppermost sheets or open cracks in the centre of the structure. The thickness of individual objects varies typically from 4 to 20 nm. If the number of discharges exceeds about 2000, two types of PbO₂ sticks start being observed: bundles made of nanosticks (5 μm in length and 50 nm of diameter) and isolated stick (20 μm in length and 500 nm in diameter) in addition to sheets. These new nanostructures are mainly due to the way lead electrodes are eroded by the discharge. At the beginning, the anisotropic erosion driven by the orientation of crystallographic planes of lead crystals produces octahedra and nanosticks, these latter growing longer and longer on electrode surfaces as discharges proceed. After about 2000 discharges, nanosticks are long enough to be easily broken, likely by mechanical stress, and fall onto the underlying substrate.

Keywords
Liquid nitrogen  
spark discharge  
PbO2  
nanosheet  
2D materials
In-situ statistics of microdischarges by image processing as a means of process control during plasma electrolytic oxidation (PEO)

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Plasma electrolytic oxidation is a plasma enhanced process for the passivation of lightweight metals (Al, Mg and Ti alloys). Microdischarges formed in the electrolyte-ceramic and gas-ceramic interface change the composition of the produced ceramic. A large amount of physical and chemical processes are involved on many time and length scales.

A unique characteristic of this process is the stochastic production and self-extinguishing of microdischarges. The collective behaviour of microdischarges changes over the course of treatment time. A thicker coating results in larger microdischarges and reduced number density. Arcing may occur after prolonged treatment time and diminishes coating quality. During unipolar pulsing, the duty cycle can be used to initiate a so-called ‘soft mode’, which is characterized by a large number density of discharges with low individual energy.

The authors present a measurement method for in-situ microdischarge characteristics like number density and discharge intensity. A CCD-Camera records the microdischarge emission during treatment time. Image processing analyzes microdischarge statistics between two consecutive exposures. Microdischarge information is then used as feedback signal for process control. The duty cycle is controlled to maintain stable microdischarge properties over treatment time. To correlate the change of process parameters to coating properties, analysis of defect statistics (cavities and cracks) is performed by SEM measurements and image processing.

The support by the Collaborative Research Centre (CRC) 1316 “Transient atmospheric plasmas – from plasmas to liquids to solids” is greatfully acknowledged.

Keywords
PEO
diagnostics
process control
microdischarges
liquids
Influence of a liquid surface on the reaction chemistry of a cold atmospheric pressure plasma jet

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Cold atmospheric pressure plasma (CAPP) sources are of interest for applications in the field of plasma medicine and plasma agriculture. The biological response is based on different aspects of the complex plasma system, e.g. excited and charged species, (V)UV radiation, radicals and energy influx [1]. To understand the influence of the different contributions one has to tailor the discharge operating in controlled regime and to find ways controlling the production of different chemical compounds. In particular, the interaction of the plasma with liquid media is of special interest.

In this study a cold atmospheric plasma jet kINPen Sci (neoplas, Germany) [2] was operated above a distilled water reservoir with a shielding gas device producing an annular flow of a defined gas surrounding the effluent of the plasma jet [3]. Nitrogen (N₂) to oxygen (O₂) mixtures were used for different atmospheres surrounding the effluent of argon.

Reactive O₂ and N₂ species (RONS) in the far field downstream region of the jet were measured. Introducing a liquid surface into the system leads to an increase of nitric oxide and resulting RONS by a factor of 2-3. It follows that water from natural humidity of biological tissues cannot be neglected.


Keywords
plasma-liquid interaction
atmospheric pressure plasma
plasma chemistry
Plasma in liquid for nanocellulose modification

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Submerged plasmas in liquid have a high applicative potential in decomposition of chemical compounds for waste water decontamination, inactivation of microorganisms, for nanomaterials synthesis, but also for nanomaterials functionalization. Specific chemical reactions may take place at the interface of plasma with liquid media due to presence of electric field, UV radiation, charged particles, excited species, ozone, hydroxyl and peroxide radicals. Bubbling can speed up these reactions.

In the present study we use a submerged plasma jet source, which was previously used for functionalization of graphene dispersion [1], with the aim of modification of nanocellulose suspensions. We used a suspension of 2% nanocellulose in distilled water. The modification of nanocellulose was done by injection in the main Ar discharge of various gases (O₂, N₂ and NH₃), at different ratios, RF power and treatment time. Besides the expected pH decrease of suspension after treatment we studied the chemical surface modification of nanocellulose. The XPS results showed that oxygen and nitrogen containing functional groups were inserted on cellulose in different amounts after plasma in liquid treatment. The treated nanocellulose was used for fabrication of nanocomposites with biopolymer matrices.

Acknowledgments:
This work has been financed by the Romanian National Authority for Scientific Research and Innovation in the frame of the project PN-III-P2-2.1-PED-2016-0287, within PNCDI III and Nucleus programme 2018.

References:

Keywords
nanocellulose
nanocomposite
nitrogen incorporation
plasma functionalization
plasma in liquid
Investigation of DC-Arcjets for the Ignition of Coal Powder

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The growing trend of renewable sources of energy force coal-fired power section to increase the flexibility of the plants. The utilization of oil or gas as the conventional method for start up face several issues with more frequent shut down and start up. The application of arcjets is an interesting alternative for direct start up with coal. In this work dc-arcjets were investigated for their ability to ignite different types of coal under cold start-up conditions. The plasma of the arcjets was first characterized by optical emission spectroscopy and high-speed camera measurements to determine the gas temperature and dynamic behaviour of the plasma jet. Subsequently, a small lab-scale experiment with a corresponding burner geometry and a special coal particle injection was set up to study the basic interactions of the plasma with small amounts of coal particles of different types.

In the next step, the arcjets were tested in a technical scale pulverized fuel combustion rig with a thermal power of up to 300 kW. The experiments were carried out for different fuel types (hard coal, lignite, biomass) at varying operating parameters such as air to fuel ratio, thermal load and arcjet lance position in order to determine the optimal conditions for ignition and maintenance of a stable flame.

Keywords
arcjet
coal powder ignition
OES
highspeed camera
Microwave Plasma reactor for CO2 decomposition

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Since electricity from renewable sources of energy is subject to fluctuations, energy storage on demand plays a crucial role to create a reliable grid system. The CO\textsubscript{2} conversion into syngas or higher hydrocarbons via a plasma assisted gas conversion powered by renewable energy is one promising approach towards energy storage. To make this power to gas concept beneficial over other technologies it is of critical importance to improve the energy and conversion efficiency of this process. On the basis of preliminary tests and technological requirements for a microwave plasma unit for CO\textsubscript{2} conversion a modular plasma torch consisting of a cylindrical and a coaxial resonator has been constructed. This plasma torch enables a self-ignition and stable operation of a CO\textsubscript{2} plasma over a wide range of parameters as well as a flexible rearrangement of the different components to ensure the possibility to adapt to different requirements. Via the FEM-Simulation program COMSOL Multiphysics a model of this plasma torch has been developed and the electric field distribution and the gas flow inside the plasma torch have been investigated to optimize the configuration and hence establish the most suitable operation conditions. While improving the energy and conversion efficiency, it is also important to remove the oxygen contained in a CO\textsubscript{2} plasma in order to produce syngas, which is a mixture of e.g. carbon monoxide and hydrogen. For this purpose a tubular reactor, which can be connected to the microwave plasma torch, has been constructed, such that a ceramic capillary can be placed in a gland sealing inside the reactor. The capillary is flushed with Argon and the oxygen concentration is measured as a function of time for different volume flow rates of the carrier gas, different microwave powers and a wide variety of ceramic capillaries to identify the best operating conditions for the decomposition of CO\textsubscript{2} in an oxygen-permeation membrane reactor.

Keywords
microwave plasma torch
oxygen-permeation membrane reactor
CO\textsubscript{2} decomposition
modelling and simulation
Behavior of NH Radicals in Atmospheric-Pressure Plasma Jet Nitriding

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We use the pulsed-arc plasma jet for developing a novel atmospheric-pressure plasma nitriding. Although nitriding of steels and titanium has been succeeded, research on elementary process has not been performed yet. Therefore, we measured the behavior of NH radicals as the key radical in our technique. In our nitriding process, we introduce nitrogen hydrogen gas mixture into as operating gas. By performing emission spectroscopic analysis, we found that the hydrogen-dependent characteristics of NH radicals are different between the pulsed-arc discharge and the jet plume. In the pulsed-arc discharge, we observe that as the ratio of hydrogen increases, the emission of the NH radical monotonically increases. On the other hand, in the jet plume, the emission of the NH radical increases until the ratio of hydrogen reaches a certain level, but it decreases with further increase in the ratio of hydrogen. These experimental results may provide the following scenario. It is well known that NH$_3$ thermally dissociates under high temperature. The temperature of the pulsed-arc discharge is several thousands Kelvin and that of the jet plume is approximately or less than 1000°C. Since the temperature of the jet plume is much lower than that of the pulsed-arc discharge, we consider that NH radical is stabilized in the state of NH$_3$ in the jet plume as the ratio of hydrogen increases. On the other hand, the produced NH cannot become NH$_3$ in the pulsed-arc discharge. We concluded that the temperature difference results in the difference of the hydrogen-dependent characteristics of NH radicals.

Keywords
nitriding
pulsed-atmospheric plasma jet
NH radical
elementary process
Controlling Supplied Nitrogen Concentration in Atmospheric-Pressure-Plasma Nitro-Quenching

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Nitro-quenching (NQ) is a new surface-hardening technology by nitrogen-assisted martensite transformation. This process provides low distortion than carburizing. This technology has been used in automotive companies recently to obtain deep hardened layer after a short time treatment. In this laboratory, we have developed original nitrogen diffusion techniques using pulsed-arc plasma jet generated under atmospheric pressure. With this technique, we have demonstrated atmospheric-pressure plasma NQ. In this technique, hardening of low alloy steel is possible through the formation of iron-nitrogen martensite. Optical Emission Spectroscopy suggested that nitrogen supply into steel surface is carried out via NH radicals present in the jet plume. For now, the atmospheric-pressure plasma NQ has a problem that treated surface were excessively nitrided, which leads to undesirable formation of voids and iron nitride. This excess of nitrogen supply is likely due to the use of atmospheric-pressure plasma. In order to solve this problem, we attempt to decrease NH radical density to suppress the formation of voids and iron nitride. The detail of our method is as follows. According to previous research, the emission intensity of NH radical were decreased by increasing the hydrogen flow ratio of the working gas mixture ($N_2 / H_2$). Therefore, we examined the method of increasing the hydrogen flow ratio to decrease NH radical density. As a result, the concentration of nitrogen into steel surface was decreased. Consequently, we succeeded in suppressing the formation of voids and iron nitride in steel surface. In summary, we have developed the method to control NH radical density in our technique. This result also indicates that NH radical plays an important role in our technique.

Keywords
nitro-quenching
pulsed-arc plasma jet
martensite transformation
nitrogen concentration
Biological sources of air pollution like animal farms, food processing, waste water and solid waste treatment industries are areas of increasing concern as the risks posed by the pollutants from these sources are understood more profoundly. The current method investigates the possibility of using a low temperature plasma for treatment of pollutant gases. Multiple parallel powered steel electrodes are separated with ceramic plates to create a dielectric barrier discharge (DBD).

However, studies on DBD treatment of waste gases with high levels of methane show an inadequate decomposition efficiency of only a few percentage. The highly symmetric methane molecule withstands the chemical reactions of the plasma produced ozone.

Spectroscopic investigations show that the blue-violet light emission origins from the 2nd positive system of nitrogen as the rotational-vibrational band from the state C₃Πᵤ to B₃Πₒ. This emission between 300 an 400 nm is sufficient to activate photokatalytic materials like titanium dioxide or other metal oxides. In combination with adsorber materials a long residence time in the reactive area for an improved de-polluting can be achieved.

The first set-up with photokatalytical equipped barrier plates will be presented. The effect on the plasma generation and first investigations on the methane reduction efficiency will be shown.

Keywords
Dielectric barrier discharge
photo catalysis
waste gas treatment
optical emission spectroscopy
In order to generate the three dimensional atmospheric plasma for various application, plasma treatment of various products, sterilization or plasma treatment of the fruits or foods, development of discharge method were carried out. Since the localization of the electric field around the discharge electrode, the generation of the atmospheric pressure plasma with complicated three-dimensional shape is difficult. The discharge method of the complex shaped plasma using water-dielectric multi-layer electrode [1-2] was developed. To clarify the property of plasma using water dielectric multi-layer electrode, observation of discharge structure of atmospheric plasma using simple shaped electrode was carried out. In the case of using the coaxial electrode constructed by strait shaped cooling tube, the comparatively uniform plasma beside of inner surface of inner glass tube was generated. The water temperature in the coaxial glass cooling tube was controlled up to 70 °C by water bath. The rod electrode with ceramic tube and outer electrode were placed in the inner tube and outside of outer tube. Ar gas (1 atm, 3 L/min) is supplied from the gas inlet connected with inner glass tube. AC high voltage (10 kHz, 9 kVp-p) was applied between the electrodes. The structure of electric discharge along inside surface of inner glass tube was observed using digital camera. The filamentary discharge structure moves at high speed with the rise in the temperature with the increase of water temperature, and, it is seen uniform plasma in the macroscopic observation. In the case of 70 °C, it was observed that the filamentary structure by the high shutter speed observation of 1/1000[s], and moving speed was 200-500 [mm/s]. In the case of using the complex shaped glass electrode, the sterilization performance for actual agricultural products was evaluated.


Keywords
atmospheric plasma
three dimensional plasma
plasma sterilization
Deposition of metallic nanoparticles on polymers by atmospheric plasma for further metallization

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This study presents results obtained by applying an environment friendly plasma technology for deposition of metallic particles layer (Ag, Pd, Pt etc.) on polymer and composite surfaces at atmospheric pressure and ambient temperature. One of the major advantages of the developed technology is its applicability to the thermosensitive materials, which was successfully demonstrated for a wide range of polymers.

The new developed ARC-PVD atmospheric pressure plasma technology is aimed to replace the chemical bath process commonly used during the metallization of polymers at the stage of the polymer surface preparation by an ecologically neutral dry atmospheric pressure plasma process. This is essential as the currently involved surface preparation baths require a usage of toxic environmental unfriendly chemical compounds while the usage of some of these compounds, like Cr VI, is severely restricted by recent EU regulations.

Using the new technology for deposition of Pd catalyst nanoparticles on the polymer surface followed by an electrolessplating process, a successful metallization of PA66, PA6; PBT and other polymers was achieved. It produces a smooth metalized layer on a polymer surface with a typical thickness between 50 nm and 1 µm.

Keywords
metallic particles
metallization of polymers
atmospheric plasma
Arc-PVD
Pd catalyst
Chemical Structure of Plasma-Polymerized Organosilicones by FTIR

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Thin films in a form of plasma polymers can be prepared from organosilicon monomers using plasma-enhanced chemical vapor deposition (PECVD). In this study, the pure tetravinylsilane (TVS) monomer and mixture of TVS with oxygen (O₂) or argon (Ar) gas were used for deposition of thin films using power ranging from 2 W up to 150 W. The deposited material prepared from the pure TVS or TVS/Ar mixture was hydrogenated amorphous carbon-silicon (a-SiC:H). On other hand the deposited material prepared from the TVS/O₂ mixture was hydrogenated amorphous carbon-oxygen-silicon (a-SiOC:H). The thickness of thin films was about 700 nm. The chemical structure of plasma polymers was examined by Fourier-transform infrared (FTIR) spectroscopy (VERTEX 80V, Bruker Optics), which was working under vacuum in a range of wavenumber from 4000 cm⁻¹ to 400 cm⁻¹. Chemical structure of plasma polymer films was evaluated using FTIR spectra as a function of power and monomer/gas mixture. For example, the absorption bands in range from 3000 cm⁻¹ to 2800 cm⁻¹, assigned to CH₂ and CH₃ vibrations, had a decreasing trend with enhanced power for all the mixtures. This development can be explained by increasing level of dissociation of hydrogen from the TVS molecule with enhanced power during the plasma process. Characterization of plasma species by mass spectrometry can help to analyze changes in chemical structure of deposited films. Therefore, the deposition chamber was equipped by mass spectrometer (Process Gas Analyser HPR-30, Hiden Analytical) to evaluate the fragments of monomer/gas molecules for different deposition conditions.

Keywords
PECVD
FTIR
mass spectrometry
plasma polymer
tetravinylsilane
Differences in properties and oxidation behavior of amorphous and crystalline magnetron sputtered Zr–Cu alloys

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Metallic alloys are fabricated either as crystalline solids by a relatively slow cooling process or as metallic glasses by a rapid cooling. These different structures lead to different properties and behavior of metallic alloys. Therefore the present work is focused on a comparison of the properties and oxidation behavior of amorphous and crystalline Zr–Cu thin-film metallic alloys with an identical composition. The amorphous Zr$_{54}$Cu$_{46}$ films were deposited onto unheated rotating substrates by non-reactive magnetron co-sputtering of the Zr and Cu targets. The magnetron with the Zr target was operated in dc regime while the magnetron with the Cu target in high-power impulse regime. In order to obtain smooth and dense crystalline films of the identical composition, some of the as-deposited films were annealed slightly above the crystallization temperature for a few minutes in high vacuum.

The amorphous Zr$_{54}$Cu$_{46}$ film was found to be a metallic glass exhibiting the glass transition at 408°C while the annealed Zr$_{54}$Cu$_{46}$ film possessed a crystalline structure consisting of a mixture of the CuZr$_2$ and Cu$_{10}$Zr$_7$ phases. The crystalline film exhibited a higher hardness (7.7 GPa vs. 5.4 GPa) and elastic recovery (41 % vs. 35 %) and a lower electrical resistivity (0.7 μΩm vs. 1.7 μΩm) than the amorphous film. In addition, the amorphous film showed shear banding plastic deformation and partial shape recovery behavior. Dynamical thermogravimetric curves revealed that the onset of the oxidation of the amorphous film (= 475°C) was shifted by about 120°C to a higher temperature than for the crystalline film. Moreover, lower mass gains were observed for the amorphous film up to 800°C. As for oxidation kinetics, all isothermal thermogravimetric curves (400 - 575°C) showed parabolic dependencies, i.e. diffusion controlled oxidation. Lower oxidation rate constants and a higher activation energy of the oxidation (142.5 kJ/mol vs. 111.5 kJ/mol) were evaluated for the amorphous film.

Keywords
Zr–Cu metallic glass
Zr–Cu crystalline alloy
Oxidation behavior
Mechanical properties
Austenitic stainless steels (ASS) are widely used in many industrial fields owing to their superior corrosion resistance. However, they possess poor wear resistance. Such drawback can be overcome with the use of surface modification treatments. The plasma nitriding process offers the advantage that a pretreatment is not necessary since the passive film is removed by sputtering. Low temperature nitriding can improve the wear resistance of ASS without loss of corrosion resistance by producing a layer composed of a supersaturated nitrogen solid solution phase (S phase). However, since the S phase excellent in hardness and corrosion resistance is formed by low temperature treatment, it takes a long time to obtain a thick hardened layer. An S phase could be formed even at high temperature during a short time treatment, although a comparison between this S phase and that formed at low temperature during a long time was not reported. Therefore, in this study, the composition and corrosion resistance of the S phases formed by high-temperature short-time treatment and conventional low-temperature long-time plasma nitriding treatment of AISI 316L were compared. The high-temperature short-time treatment was carried out from 793–913 K for 5–120 min, while the low-temperature long-time treatment was performed at 713 K for 15 h. Other processing conditions were similar, including a pressure of 200 Pa under a 25% N\textsubscript{2} + 75% H\textsubscript{2} atmosphere. A metallic screen was installed as an auxiliary cathode. After nitriding, the XRD results led to the identification of the S phase for the low-temperature long-time treatment, and revealed that the intensity of the CrN diffraction increased as the nitriding temperature and time increased for the high-temperature short-time treatment. Pitting corrosion tests revealed that the samples subjected to the low-temperature long-time and high-temperature short-time treatments possessed better corrosion resistance than the untreated sample.

**Keywords**
- plasma nitriding
- surface modification
- stainless steel
- expanded austenite
- S phase
The contact mechanics of nano-abrasion of dental enamel

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Tooth enamel plays a critical role in the survival of mammals despite its inability to repair, however the mechanisms responsible for its abrasive wear are poorly understood. Specifically, what factors in the diet of a mammal, especially their hardness and elastic modulus, contribute to enamel wear? In this study the stresses that develop during sliding contact of small spheres with enamel are evaluated. Knowing the stresses allows prediction of abrasive wear with an analytical wear model. For metals a brittle oxide film may be present, which influences the resultant abrasion mechanism. Stresses that develop during normal plus tangential loading, to simulate the coefficient of friction (CoF) developed during sliding are presented with and without a thin brittle film on the metal sphere. Three boundary conditions are assumed for sliding contact, namely; normal, lateral and tilting of the surface for three CoFs. The higher CoF is closest to that for a ductile metal (aluminium) in sliding contact with enamel. The CoF influences the magnitude and location of the maximum stress as does the tilting angle. Under normal and low CoF the maximum stress is located subsurface while at high CoF the maximum occurs at the surface and is up to 3 times greater than for the normal loading. Tilting also increases the surface stress concentration and it is no longer symmetrical about the axis of sliding. In the presence of a thin stiffer oxide film on the surface of the ball the maximum stresses occur at the edge of the area of contact and for normal loading are comparable to the max stresses subsurface but not within the enamel substrate. However, a slight increase in the CoF results in much higher stresses within the film. The influence of the specific boundary conditions on the magnitude of the stresses developed is also presented. These results are completely scale invariant and are thus of use for similar problems in thin film and multilayer applications.

Keywords
stress
Dedicated grain-boundary design by glancing angle deposition for fracture toughness enhancement of brittle nanocrystalline films

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Hard and superhard ceramic nanocrystalline thin films are known for extraordinary strength as well as lack of plasticity. The dominant failure mechanism of these materials is intergranular brittle fracture associated with grain boundaries of low cohesive energy. This limits their usage in applications where both strength and toughness are required.

In this contribution, two sets of TiN films with a sculptured chevron like grain morphology differing in density were sputter deposited by glancing angle deposition technique under various conditions. The films were tested by in-situ bending of microcantilever beam specimens in order to evaluate (i) elastic modulus, (ii) fracture stress and (iii) fracture toughness. The repeatedly tilted grain morphology resulted in multiple crack deflections at kink planes of the tilted grains, yielding energy dissipation at the crack tip and an increase of the fracture surface area. Due to the dedicated grain boundary orientation design, the fracture toughness increased up to 150% with respect to the reference TiN film with common columnar microstructure. It is deduced that number of crack deflections as well as density of the deposited film are critical values for the improvement of its fracture toughness. Based on the experimental results, it is expected that by a dedicated design of grain boundary orientation, it is possible to synthesize novel types of materials with enhanced fracture resistance.

Keywords
grain boundary design
micromechanical testing
fracture toughness enhancement
Study on the origin of roughness increase on low-temperature plasma nitrided AISI420 martensitic stainless steel

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Low-temperature nitriding of martensitic stainless steels is generally applied aiming to enhance the tribological behavior of the steel treated surface. Surface roughness and hardness are among the important parameters influencing the tribological behavior of the treated surface and both can be modified by low-temperature plasma nitriding. Several works deal with the treated surface hardness but the number of works dealing with the nitrided surface roughness is limited. So, the objective of this work was to study the origin of the roughness increase observed after subjecting the AISI420 martensitic stainless steel to low-temperature nitriding. To achieve this purpose AISI420 samples were nitrided using a plasma nitriding apparatus with an auxiliary heating system, enabling independent control of plasma parameters and nitriding temperature. The nitriding treatments were carried out at 300, 350 and 400°C, in a gas mixture composed of 10% Ar + 20% H₂ + 70 N₂ at 3 Torr. Plasma was generated using a 4.2 kHz pulsed DC power supply, with peak voltage of 700V. For each temperature, treatments were carried out using pulse width of 10 and 20 μs, with auxiliary heating system. Treatments were also conducted using only plasma as heating source (auxiliary heating system turned off) with pulse width of 24, 27 and 31 μs for 300, 350 and 400°C, respectively. After treatment samples were characterized by microstructural analysis, X-ray diffractometry, and microhardness measurements. The surface roughness was measured using a laser confocal microscope. Results indicate that temperature and pulse width have influence in several characteristics of the treated layer, including hardness, thickness and phase composition. Considering the roughness, it increases with both the pulse width and the treatment temperature, and results indicate that, at least for the studied treatment conditions, the surface roughness increase is mainly due to structural modifications of the treated layer, being the sputtering only a secondary cause of roughness increase.

Keywords
Low-temperature plasma nitriding
Martensitic stainless steel
Roughness
VEX is an aluminium alloyed tool steel specifically designed for hot work applications that are typically plasma and gas nitrided. Due to the addition of aluminum, VEX shows higher hardness after nitriding than AISI H13 because of aluminum nitride formation. This study aims to characterize the effect of plasma and gas nitriding on the properties and performance of VEX and AISI H13 extrusion dies. For the tests, samples were quenched, tempered to work hardness level and plasma nitrided. Residual stress profile has been carried out by X-ray diffraction. The effect of the residual compressive stress difference on the surface due to nitriding was correlated with the microhardness profiles measured in both materials. Tempering resistance at 600 ºC of the plasma nitrided layer was also investigated for 1, 10, 30 and 100 hours and compared to AISI H13. The results showed that VEX performance was superior in severe wear applications due to higher hardness after nitriding, greater diffusion depth and higher resistance to softening.

**Keywords**

Hot work tool steel  
Nitriding  
VEX
Acoustic emission as a tool for extended tribo-mechanical characterization at nano/micro scale – application to nanoindentation and scratch test

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Nanoindentation and scratch test have been established as standard tests for exploring mechanical and tribological properties of thin films and coatings. Evaluation of these tests mainly relies on the analysis of depth-load-time records. This approach has been proven to be sufficient in most cases for a variety of materials (thin films, micro-objects, composites, bulk). However there are many situations where indentation curves or scratch depth-load-time records do not provide sufficient information for a complex understanding of the deformation response of the material. Although microscopic observation of the residual indents or scratches extends the tests’ evaluation it does not elucidate the dynamics of the process or phenomenon studied, especially for non/transparent materials. On the other hand the recording of the acoustic waves can overcome this drawback and offer a nondestructive way for obtaining complementary information. In general, acoustic waves emitted during the mechanical tests at the nano-micro scale are a rich source of information about the deformation behavior of the tested material. This holds especially for the initiation and propagation of cracks in the tested surface or coating in particular. Hence analysis of acoustic emissions (AE) provides a better understanding and more complex interpretation of the results obtained by the nanoindentation and scratch test. The strength of the AE based method will be demonstrated for hard protective SiC, SiCN, CrN and AlCrN coatings magnetron sputtered on silicon and tungsten carbide explored via scratch test. Combination of AE and nanoindentation will be presented for silicon and various types of glass. The complementary analysis of the time and frequency domain will draw the potential of the AE extended approach. Especially dynamics of the failure and fracture processes will be distinguished and elucidated. In both cases the analysis of AE events will be correlated with standard approaches.

Keywords
Acoustic emission
Scratch test
Nanoindentation
Thin films
PO4062

Mechanical characterization of silicon-containing plasma polymer coatings and the influence of environmental conditions

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Residual stresses in vacuum-deposited thin films is still a major cause for device failure. Deposition of stress free coatings requires an in-depth knowledge of the stress formation mechanisms. The residual stress is usually a combination in intrinsic stresses, process induced stresses and environmental stresses. Especially the latter one not always taken into account.

This research presents a novel method on the measurement of residual stresses for highly curved sample as well as the expansion and compression of coatings under influence of humidity. Hollow cathode based PECVD was used to deposit silicon-containing plasma polymer coatings with different carbon contents, which were analyzed regarding their residual stress and coefficient of hygroscopic expansion. The results show that the carbon content increases the residual stress whereas the coefficient of hygroscopic expansion decreases. All coatings expand with increasing humidity. The coating with the highest oxygen content (SiO$_2$C$_{1.5}$H$_x$) tested in this research has an expansion coefficient of 29.2 ± 1.9·10^{-6} (% R.H.)$^{-1}$. Increasing the relative humidity from 20% to 70% affects the total residual stress more than 20%.

Keywords
Stress
Humidity
curvature
PECVD
Polymer
Simultaneous carburizing and boronizing of a pure titanium surface using spark plasma sintering

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Titanium materials have been widely used in the aerospace, automotive, and biomaterial engineering fields owing to their superior properties. However, further applications of such materials are limited due to their low hardness, poor wear resistance, and reduced corrosion resistance to non-oxidizing acids. Therefore, methods to coat the matrix surfaces of materials with a hard ceramic coating layer made of titanium compounds have been described to improve their mechanical properties. Moreover, titanium composites composed of carbides and borides have attracted enormous interests due to their superior properties, such as high hardness, good wear resistance, high electrical and thermal conductivities, and high fracture toughness, compared to single-phase ceramics. In this study, attention was focused on a diffusion coating method that could lead to the formation of a hard layer with excellent adhesion through the creation of an interlayer and a gradient layer. However, in conventional diffusion coating methods, the deterioration of the mechanical properties of the matrix resulting from the long-term, high-temperature processing can be problematic. Therefore, in this study, the spark plasma sintering (SPS) method was used to form a ceramic layer, since it allows the suppression of the growth of crystal grains by rapid heating and enables low temperature and short processing time. Thus, carbides and borides were simultaneously formed on a titanium surface using the SPS method. Commercially pure titanium (CP-Ti) was used as substrate, while the B\textsubscript{4}C powder was utilized as both carburizing and boronizing source. The analysis of the sample surface subjected to the SPS processing indicated the formation of TiC, TiB\textsubscript{2}, and TiB. Since a ceramic layer was formed on the titanium surface, a surface hardness of $\sim$1700 HV was obtained, and the wear resistance and corrosion resistance in a 2\%HF-10\%HNO\textsubscript{3} aqueous solution were improved compared to those of untreated CP-Ti.

Keywords
spark plasma sintering
diffusion coating
carburizing
boronizing
surface modification
Evaluation and Visualization of Surface Coating Strength Properties by a Micro Slurry-jet Erosion (MSE) Test Method

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New coatings with improved performance are rapidly being developed, and thus it is very important to clarify the mechanical characteristics of coatings and coated components. However, it is difficult to evaluate the surface strength of thin coatings by common experimental techniques. From this background, we have developed a new evaluation method based on a micro slurry-jet erosion (MSE) test [1, 2]. In this study, we are reporting on research on the MSE method, focusing on the accumulation of data for hard thin coatings (mainly TiN, TiCN, AlCrN), DLC films and so on. The MSE tests were mainly conducted impacting a slurry-jet containing 1.2 μm angular or 3 μm square alumina particles perpendicular to the specimen surface; the variation of the erosion depth on the eroded surfaces was measured, and finally the erosion rates were calculated from the measured data as an evaluation parameter. Based on the MSE test results, we propose to position each material in a diagram, which we designate as a MSE Map, with two axes, i.e. the erosion rates obtained by 1.2 μm angular or 3 μm square particles impacts; we discuss this proposed MSE mapping. We conclude that the MSE Map is useful to evaluate various characteristics of coating strength influenced by different failure mechanism.


Keywords
coating evaluation method
micro-slurry-jet erosion (MSE)
MSE Map
mechanical property
Increasing the ductility of single crystalline silicon treated by hydrogen plasma

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This study aims to investigate the effect of hydrogen and defect on ductility of single crystalline silicon. Silicon MEMS with mechanical structure was susceptible to fatigue fracture. Fatigue lifetime of silicon in hydrogen was extremely shorter than that in air. Recently, silicon fatigue failure was found to cause mechanically accumulate damage by cyclic loads because striation-like pattern and dislocation on fatigue fracture origin was observed by transmission electron microscopy. These results suggested that dislocations in silicon moves easily under hydrogen environment even at room temperature. Meanwhile, reactive ion etching (RIE) has used as standard microfabrication technique of MEMS structure. However, ion bombardment during RIE process induces damage on silicon surface. The presence between hydrogen and defect on silicon surface were closely related to plastic deformation and fatigue behavior. Different four types of specimens, which are made of p-type single crystal silicon with polished (100) surface, were prepared to evaluate the relationship between defects, hydrogen and combination of defects and hydrogen by nanoindentation test. Specimen were exposed to SF$_6$ plasma for 10 sec to induce defect into silicon surface. Hydrogen was diffused into silicon by CVD plasma which is excited by 400 W microwave for 1 hour. Hydrogen depth distribution and trapping state on each specimens were measured by Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and Thermal Desorption Spectroscopy (TDS), respectively. Either defect or hydrogen does not have effect on indentation depth under same load level. Surface defect and hydrogen had significantly deeper indents than the other cases. In case of shallow indentation depth, change rate of plastic deformation become relatively larger than deep indentation depth. These results showed that silicon surface in the presence of defect and hydrogen was softer than silicon bulk even at room, and suggested correlation with defect accumulation of silicon fatigue fracture.

Keywords
Silicon
Ductility
Hydrogen
Defect
Application of Calotest and Scratch test for evaluation of structure and quality of multilayer coatings - the Recatest method

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The examinations were discussed of selected properties of hard coating materials obtained in PVD processes. Three examination methods were used: spherical microsection (Calotest), scratch test and Recatest (scratch test + spherical microsection). The author presents the methodology for revealing thin coating structures on spherical microsection surface, particularly in the scratch area and the method for evaluation of their quality. Based on the example of TiN and CrN/CrCN WCC/TiAlN coatings strained during scratch test, the measuring methodology is presented along with the analysis of information that can be obtained from the surface of spherical microsection.

The method is applicable to areological systems like coating – substrate, multilayer coating – substrate and coating – diffusion layer – substrate, obtained using PVD and CVD techniques and thermal, thermo-chemical and electroplating processes. The core of Recatest method is that the spherical microsection on the examined material is made in the area of previously made scratches. The spherical microsection within the scratch area allows performing precise analysis of selected structural features of strained and unstrained areological system as a function of distance from the surface.

Quantitative data are provided by accurately defined points and geometry of analysed images of structures. The analysis of coating structure on spherical microsection within the area of scratches.

The combination of scratch test and spherical microsection techniques offers new methods for precise quality evaluation of coatings and layers subjected to strong elastic and plastic strains.

The capability of quick quality assessment of coatings and layers obtained in thermo-chemical and electroplating processes indicates that the examination methods based on Recatest technique should be implemented.

Keywords
Recatest
Scratch test
Calotesty
CrN/CrCN
WCC TiAlN
Optical and electrical properties of silicon carbonitride thin films deposited by sputtering on Si (100) and nitrided Si (100): Effect of the interface

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Improving the efficiency of photovoltaic cells, especially those of the 1st generation and decreasing the production costs are more than ever required regarding the world’s energy demand. In this context, thin coatings such as hydrogenated silicon carbonitride (SiC$_x$N$_y$:H) have attracted lot of attention. In this work, we elaborated SiC$_x$N$_y$:H thin films on silicon using a process combining RF sputtering and ECR plasma excitations, by sputtering a Si target under an Argon-N$_2$-CH$_4$ gas mixture, and four coaxial microwave sources while the reactive gas flow ratio $R = [F_{N_2}]/ ([F_{N_2}] + [F_{CH_4}])$ was varied. On one hand, we proved that SiC$_x$N$_y$:H are an interesting candidate as antireflective coating for silicon PV devices thanks to their optical properties. Indeed, their band gap and refractive index could be easily tailored as a function of the reactive gas ratio. On the other hand, high defects level and interface state density are one of the main causes of PV cells efficiency decrease. One of the known methods to reduce the recombination of charge carriers at the interface between SiC$_x$N$_y$:H and the Si substrate is surface passivation. A passivating treatment of the silicon has been performed. These SixNy passivated films were elaborated in UHV chamber by two N$_2$ plasma sources (ECR and GDS at 10$^{-4}$ Pa) and monitored by XPS. To perform electrical capacitance-voltage (C-V) measurements, a metal insulator semiconductor (MIS) structure was elaborated by sputtering Al on the front and back side of the SiC$_x$N$_y$:H/Si films. The effect of the interface preparation on optical and electrical properties has been pointed out.

Keywords
SiC$_x$N$_y$:Hz
Sputtering
Passivation
Electrical properties
Nitridation
Effect of bias on layer formation during two-step plasma nitriding using a cathodic screen

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Recently, considerable efforts have been devoted to the development of alternative nitriding methods such as active screen plasma nitriding (ASPN). ASPN offers several advantages over conventional direct-current plasma nitriding (DCPN) since the plasma is produced on a screen and not directly on the samples. In recent studies, it became clear that S phase (nitrogen supersaturated solid solution), which enables to improve the surface hardness, can be produced by subjecting austenitic stainless steels (ASS) to low temperature nitriding. However, it has been reported that the deposited layer formation on the surface of a nitrided sample may suppress the nitriding layer growth. Since the S phase is formed at a low temperature of 723 K or less for ASS, a long time is required for the nitrogen to diffuse and it is difficult to obtain the thickening of the nitriding layer in a short time. A two-step plasma nitriding constituted of a low-temperature long-time treatment followed by a high-temperature short-time treatment was attempted in order to thicken the S phase during a short time. The samples were nitrided using a cathodic screen with either an insulation state (ASPN) or voltage application state (S-DCPN), and the results were compared. AISI 316L was treated for 14.4 ks at 673 K followed by 1.8 ks at 673 K–873 K at 200 Pa under a 25% N$_2$ + 75% H$_2$ atmosphere using a 316L steel screen. After nitriding, the surface hardness tests revealed that the surface hardness increased with an increase in the second step temperature for S-DCPN, whereas decreasing during the second step processing at the temperatures of 823 and 873 K for ASPN. The GD-OES results revealed that the nitrogen diffusion region tended to increase with the increasing of the second step temperature, and the thickness of the layer formed in the case of S-DCPN was wider than that formed in the case of ASPN.

Keywords
active screen plasma nitriding
plasma nitriding
surface modification
deposition, diffusion.
S phase
Can the normalized energy flux at the substrate control the microstructure of reactively sputtered TiO$_2$ thin films?

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In order to answer the question “Can the normalized energy flux at the substrate control the microstructure of reactively sputtered TiO$_2$ thin films?”, we have compared the properties of the TiO$_2$ films synthesized in different working conditions and used the Normalized Energy Flux at the substrate (NEF) as a standardization parameter. The NEF is expressed in eV/deposited Ti atom and was obtained by combining energy flux probe data (mW/cm$^2$) and Rutherford Backscattering Spectroscopy results (Ti at./cm$^2$). The NEF was calculated for various sputtering powers and pressure x cathode-substrate distances (p x d) in two different vacuum chambers. Among other discrepancies, one could note that the chamber of the University of Mons was furnished with a single circular (7.5 cm in diameter) magnetron sputtering target while the one located at the University of Namur was furnished with two sputter targets (5.1 cm in diameter) set in a closed – field configuration. Despite the discrepancies highlighted for these two deposition systems, similar values of the NEF were obtained by varying the sputter power and the p x d values. The microstructure of the TiO$_2$ films deposited in these NEF conditions was obtained from Scanning Electron Microscopy and X-Ray Diffraction. Those results are discussed and atomistic kinetic Monte-Carlo simulations are performed to support the findings.

Keywords
energy flux
titanium dioxide
magnetron
phase formation
microstructure
Thin films polymerized from diethylene glycol dimethyl ether (diglyme) low-pressure discharges are very attractive for several industrial applications. Under a certain conditions they can have high biocompatibility and non-fouling properties. Though films with similar properties can be produced by conventional chemistry; the chemically produced films are soluble in acid or basic solutions, which is a great disadvantage for biomedical applications. Material properties of diglyme films were extensively studied, but due to complex nature of plasma medium the deposition process and its kinetics is still not well understood.

In order to understand deposition mechanisms of diglyme plasma polymers it is important to correlate plasma properties (using plasma diagnostic techniques) with material characteristics.

In this work diglyme plasma was produced in a cylindrical stainless steel reactor with two parallel plate electrodes excited at 13.56 MHz. The discharge was operated from 1 to 30 W applied power with total pressure inside chamber ranged from 10 Pa to 30 Pa. The plasma was investigated using optical emission spectroscopy in actinometric method (A-OES) and electrostatic measurements with RF-compensated Langmuir probe technique. The principal transitions investigated by A-OES were CH (431.2 nm), CO (519.7 nm) and H (656.5 nm). It was observed that the relative intensity of all transition is proportional to applied power while is disproportional to the operating pressure. Electron temperatures were calculated and for RF power varying from 1 W to 30 W electron temperature varied from 0.20 eV to 1.60 eV. The value of electron temperature was increasing for higher applied power or lower operating pressure.

Keywords
Plasma
optical emission spectroscopy
diglyme
Langmuir Probe
low pressure
Mass spectrometry is an important technique to investigate vacuum and discharges maintained in low or high pressure. Mass spectrometry has been used to investigate discharges from organic compounds, due to them being precursors of organic solid materials used in several technological applications. In this work the mass spectrometry technique was used to investigate the fragmentation process of diethylene glycol dimethyl ether (CH₃O(CH₂CH₂O)₂CH₃) (diglyme here in) molecule in low pressure RF excited plasma discharges. The study was carried out using mass spectrometry. The results showed that for a fixed pressure, the increase of the RF power coupled to the plasma chamber from 1 to 35 W produced a plasma environment much more reactive which increases the population of the ionized species like CH₃⁺ (15 amu), C₂H₄⁺ (28 amu), CH₃O⁺ (31 amu), C₂H₄O⁺ (44 amu), CH₃ OCH₂CH₂⁺ (59 amu) and CH₃OCH₂CH₂O⁺ (75 amu). This fact may be attributed to the increase of the electronic temperature that makes predominant the occurrence of inelastic processes that promotes molecular fragmentation. For a fixed value of RF power the increase of pressure from 10 Pa to 30 Pa produces the decreasing of the above mentioned chemical species due the lower electronic mean free path. These results suggest that if one wants to keep the monomer's functionality within the plasma deposited films resulting from such kind of discharges one must operate in low power conditions.

**Keywords**
Plasma
mass spectrometry
diglyme
chemical species
low pressure
Formation of Ar\(^{2+}\), ArTi\(^{+}\), and Ti\(^{2+}\) dimer ions in a dc magnetron discharge

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Formation of Ar\(^{+}\) and Ti\(^{+}\) monomer and of Ar\(^{2+}\), ArTi\(^{+}\), and Ti\(^{2+}\) dimer ions in a magnetron discharge with a Ti target at argon gas pressures of 0.3–2.1 Pa was investigated by energy-resolved mass spectrometry. An unbalanced magnetron with diameter 50 mm was operated in direct current mode with a power of 150 W. Energy spectra of Ar\(^{+}\) and Ti\(^{+}\) ions show distinct features which are related to the specific formation processes taking place in the plasma region and during ion bombardment of the Ti cathode. Our observations proved that low-energy Ar\(^{+}\) ions are produced inside the plasma region. The high-energy component of argon ions is attributed to sputtered or back-sputtered Ar atoms which subsequently become ionized in the plasma region. Ti\(^{+}\) ions originate from sputtering events and the subsequent ionization far away from the cathode. The measured energy distribution of titanium ions does not follow Thompson's formula but at the lowest gas pressure the measured energy distribution can be modelled by a shifted Maxwellian distribution. Formation of Ar\(^{2+}\), ArTi\(^{+}\), and Ti\(^{2+}\) dimer ions show pronounced pressure dependence which is attributed to various formation and loss processes inside the plasma region. Estimates show that associative ionization with excited argon atoms is the dominant formation mechanism. Ti\(_2\)^{+} ions are formed by sputtering of Ti\(_2\) dimers and the subsequent ionization in the plasma region. Ti\(_2\)^{+} ions quickly thermalize with increasing gas pressure leading to an enhanced loss presumably due to reactions leading to particle growth.

The work was partly supported by projects 17-08389S and 16-14024S of the Czech Science Foundation and by the German Academic Exchange Service (DAAD).

**Keywords**
dimer
magnetron
mass spectroscopy
cluster
titanium
Titanium Atom and Ion Number Density Evolution in Reactive High Power Impulse Magnetron Sputtering

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The hysteresis curve in R-HiPIMS generally exhibits a narrower shape compared to dcMS, or it can even be entirely suppressed, which is beneficial for high-rate deposition of stoichiometric compound films. However, the main effect behind the hysteresis suppression is not yet completely understood. We report on evolutions of titanium atom, and ion ground state densities in R-HiPIMS discharges in oxygen for constant mean power and pulse duration, when varying the repetition frequency. A fast feedback system is employed to allow working in the transition region of the hysteresis curve in a well-controlled manner. A recently developed effective branching fraction (EBF) method is utilized to determine absolute ground state number densities of sputtered titanium species from the optical-emission signal. The ionization fraction of sputtered species increases with the partial pressure of the reactive gas. The increased ionization of titanium is attributed to the combination of the following effects: a longer residual time of sputtered species in the target vicinity; a higher maximal discharge current attained at the end of the pulse; enhanced ionization. It is furthermore found that the hysteresis curve shape changes when varying the repetition frequency at the same mean power. The difference is more pronounced for R-HiPIMS with higher sputtered species ionization fraction. The experimental results are compared to the results obtained by a reactive ionization region model (R-IRM). The absolute ground state number densities of Ti atoms and Ti ions measured at the target vicinity are also substituted into the Berg model. The Berg model is modified to include ion back attraction, and a rather good match between the measurements and simulation results for different experimental conditions is found. This research has been financially supported by the LO1411 (NPU I) funded by Ministry of Education Youth and Sports of Czech Republic. Matej Fekete is a Brno Ph.D. Talent Scholarship Holder – Funded by the Brno City Municipality.

Keywords
density of sputtered species
reactive HiPIMS modelling
reactive HiPIMS
Determination of the deposition and energy fluxes in the industrial deposition system

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High efficiency of the sputtering process and good homogeneity of the deposited layers are among the most important issues being solved in the industry. Understanding the effects which influence both characteristics has therefore a high importance. Generally, in direct current magnetron sputtering (DCMS) higher deposition rate is provided compared to the high power impulse magnetron sputtering (HiPIMS). However, in HiPIMS higher homogeneity and overall quality of the coatings is achieved. Here a study is presented, where the influence of the process parameters on the deposition fluxes of atoms and ions in both DCMS and HiPIMS is investigated within the state of the art industrial deposition system. The direct comparison is made for the same deposition parameters such as working pressure and average power. To monitor the deposition rate and fluxes the quartz crystal monitor with biasable grids or gridless sensor with electron magnetic filter is attached on substrate holder. Measurement of the deposition flux itself is conducted by adjusting the bias voltage on the quartz crystal monitor grid. Increasing the voltage, more ions are repulsed from the grid up to the point where the whole deposition flux consists only from atoms. The energy resolved ion flux and total atom flux is obtained. By changing the position of the quartz crystal monitor spatial atom and ion flux resolution is obtained. Additionally, to directly measure the global energy transfer of the plasma to a surface, the heat flux microsensor (HFM) was employed. Such combination of diagnostic tools helps us to optimize the deposition process leading to the creation of thin films with the high quality and reproducibility.

This research has been supported by the project TJ01000157 funded by Technology Agency of the Czech Republic.

Keywords
HiPIMS
Mass flow density
Deposition flux
Space-resolved evolution of sputtered species number densities in HiPIMS and DCMS discharge

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Magnetron sputtering is a physical vapor deposition technique used in the whole spectrum of industrial applications; thus, it is crucial to characterize the process behavior thoroughly. The analysis of non-reactive Direct Current Magnetron Sputtering (DCMS) and High Power Impulse Magnetron Sputtering (HiPIMS) in the presented study is performed using a Quartz Crystal Monitor (QCM) and Optical Emission Spectroscopy (OES). The QCM system can be equipped with biasable grids or a gridless sensor with magnetic electron filter, and it is used to measure separately the flux of atoms and of the ionized particles impinging the substrate. A spectroscopic method utilizing self-absorption of the plasma and Effective Branching Fractions (EBF) is employed to evaluate the absolute ground state titanium atom and ion number densities. A systematical study on three discharge parameters – working pressure, duty cycle and distance from the titanium target - is presented. The study is realized at three different distances from the target – in the magnetized plasma region, between the target and the substrate and at the substrate level. The investigation is performed at a constant mean power and pulse duration. Both the titanium atom and titanium ion number densities are correlated with the overall atom and ion deposition fluxes at the substrate level, respectively. For instance, at the substrate level, the maximal sputtered species ionization fraction of 70% is obtained for 1.6% duty cycle. Increasing a working pressure and a duty cycle, ionization fraction of the sputtered species at the substrate level decreases, for example in HiPIMS, the ionization fraction of the sputtered species of 30% is attained for 4% duty cycle and maximal studied working pressure. However, in the magnetized plasma region, the ionization fraction of the sputtered species is almost independent on the working pressure and is always higher than 70% through the studied duty cycle range of 1.6% - 4%. The ionization fraction of the sputtered species decreases with the increasing pressure, the duty cycle and the distance from the target.

Keywords
HiPIMS
Ionization fraction of sputtered species
Deposition flux
Quantitative determination of the species produced in low pressure N2-H2 plasmas by in-situ mass spectrometry

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Plasmas created from N₂-H₂ gas mixtures are extensively applied in surface treatment and functionalization processes. Amongst these processes, plasma nitriding is a well-established process during which a nitrogen diffusion layer is created inside a bulk material. The aim of this process is to modify surface properties of the treated material such as mechanical properties (hardness, wear resistance, ...), corrosion resistance, surface roughness, surface patterning, ... However, in the case of plasma created in N₂-H₂ gas mixture, the exact role played by H₂ addition is not clearly yet understood. A better understanding of the fundamental mechanisms inherent to these discharges could increase their potential. In this work, N₂-H₂ plasmas were generated by Distributed Electron Cyclotron Resonance (DECR) in a reactor specially designed for low pressure plasma nitriding. When the N₂ gas flow is increased in a constant H₂ gas flow plasma, the presence of an unexpected minimum pressure is observed. In order to understand the origin of this pressure behavior, the neutral species composition of the plasma phase has been characterized by the means of Mass Spectrometry (MS). The MS measurements show that the pressure decrease is associated to the production of a high ammonia concentration (up to 20% in our experimental conditions). The ammonia signal increases to reach a plateau as the nitrogen gas flow rate increases. This plateau is reached when the pressure is minimum. Others results concerning the evolution of atomic nitrogen and hydrogen, and NHₓ species will be also presented. MS measurements have also been performed within nitriding process experimental conditions (90% N₂, 10% H₂). Comparison between plasma properties and nitrided layer properties obtained in these conditions will be presented.

Keywords
mass spectrometry
nitriding
**Time Resolved Optical Emission Spectroscopy Measurements during PIII High Voltage Pulses**

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PIII is characterized by a pulsed emission of secondary electrons and sputtered atoms is added periodically to the plasma. Whereas the majority of the secondary electrons, after being immediately accelerated to high energies in the plasma sheath near the substrate, are impinging into the chamber walls without interaction with the plasma, the sputtered atoms are much slower and more prone to interactions with the plasma. Compared to a more conventional experimental setup for GDOES, the PIII experiment is characterized by higher ion energies used for sputtering, lower pressures with a larger mean free path, shorter pulses and a higher relative energy density deposited by the passing secondary electrons. Using time resolved OES during PIII high voltage pulses, detailed insights into the interactions of sputtered atoms, secondary electrons and the low pressure plasma discharge are possible. The experiments were performed in an argon discharge powered by a 150 W ECR source at 0.3 – 0.8 Pa with 1.5 – 7.5 kV voltage pulses of 15 – 45 µs length. The main component of the additional observed, transient optical emission beyond the baseline plasma is observed 20 – 80 µs after the end of the high voltage pulse for already present Ar I lines. Moreover, neutral metal lines of Ag, Al and Cu – for the respective target materials – corresponding to low lying excited states are being detected. No emission of nitrogen or oxygen atoms sputtered from nitride or oxide materials have been observed. These effects scale with the mean free path of the secondary electrons, i.e. the more interaction of the secondary electrons with the background gas the higher the additional excitation of species. At the same time, a complex and varying peak shape points of the detected lines towards a behavior beyond a single excitation and thermalisation process inside the plasma with several time constants being involved. Thus, PIII cannot be used as a simplified GDOES experiment. Despite the wealth of data, a clear modelling of the active processes is presently not possible.

**Keywords**

OES

PIII
Energy influx measurements on an atmospheric pressure surface barrier discharge

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The energy balance of diffuse coplanar surface barrier discharge (DCSBD, Roplass) [1] was investigated by passive calorimetric probe measurements [2] to characterize the discharge and the interplay between energy influx and surface activation. Surface activation of polymers is a well-studied field [3], however, most experiments were done under vacuum conditions, while often atmospheric pressure discharges are desired by industry due to easier integration into process lines.

Energy influx measurements at atmospheric pressure discharges always come with some challenges and necessity to adapt the probe design due to high energy and gas fluxes [4]. After successful adaptation, measurements at different distances from the surface showed similar trends as surface activation measurements on polymeric material by contact angle analysis. These observations indicate a strong correlation between the energy influx from DCSBD plasma to the substrate and the resulting surface properties due to plasma modification.

Furthermore, energy influx measurements were performed in different atmospheres (air, nitrogen, oxygen and argon) and additional cooling effects which appeared inside the plasma have been studied, indicating gas transport within the discharge.


Keywords
atmospheric pressure plasma
DBD
energy influx
surface activation
Space-resolved analysis of hollow cathode discharges in blind holes

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The hollow cathode discharge can be used for deposition of amorphous hydrogenated carbon films in blind holes with an aspect ratio $>>1$. The high plasma density of the hollow cathode discharge leads to very high deposition rates up to 600 $\mu$m/h. The film homogeneity, i.e. film thickness or structure of these films, vary strongly due to the occurrence of different plasma states inside the blind hole, each of them resulting in very different growth conditions.

For the investigation of these plasma states and the understanding of the influences of the hollow cathode effect on the growth mechanism of thin films a space-resolved optical emission spectroscopy has been performed to determine the plasma species of an argon hollow cathode discharge. A hollow cathode discharge and a glow discharge inside the blind hole have been examined to devise the space-resolved differences of the plasma composition. Furthermore, the etching rates on a silicon substrate has been measured to estimate the ion energy in the collisional plasma sheath. Both results are discussed in the context of the different plasma states and Monte Carlo plasma simulation.

Keywords
hollow cathode discharge
optical emission spectroscopy
hollow cathode effect
Spatially resolved characterization of momentum transfer during sputter processes

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In this work, the momentum carried by reflected and sputtered particles in a sputter plume is characterized. A sputter target is mounted in front of an ion beam on a rotatable platform. For each angle on incidence, a different sputter plume is generated. These plumes are characterized using interferometric force probes [1]. In contrast to conventional diagnostics, a force probe does not rely on charged particles but measures also neutrals and supports a more comprehensive picture of the sputtering process. A double axis version of force probes is used to determine the momentum transfer onto the sputter target itself. A second force probe is used to circle around the target scanning through the resulting plume of sputtered target atoms and beam particles. The ejection distributions then compared with simulated data using SRIM [2]. For the experiment copper and silver targets have been used. Additionally, ion energy, gas type and gas pressure are varied.


Keywords
ion beam
sputtering
diagnostic
force probe
SRIM
Plasma Density Monitoring of long-term PIAD Processes

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Plasma Ion Assisted Deposition (PIAD) process is mainly characterized by common e-beam evaporation in conjunction with additional ion beam bombardment targeted on the substrate surface. This bombardment increases the mobility of ad-atoms at the surface and in the bulk during the growth process of the thin film to achieve energetically advantageous positions of atoms, leading to an improved layer quality. As the properties of the ion beam can be adjusted with high accuracy, the PIAD process is quite stable, providing high precision in high-end layer systems. Nevertheless, fluctuations of plasma conditions can occur due to short-term instabilities or long-term drifts of process parameters. In case of the hot cathode dc source APS, lifetime of the electrodes is a major issue. In complex layer systems with extended deposition times of up to 18 hours, changes in lateral distribution of the coating material at the substrate level can cause deviations of layer thickness. As the layer growth is directly correlated with the plasma conditions, plasma parameters must be stabilized to reach reproducibility in coating of a batch series for long-term view. For the monitoring of plasma conditions, we installed a multipole resonance probe (MRP). This diagnostic tool is based on active plasma resonance spectroscopy, whereby a radio frequency is fed into the plasma to make use of the resonance behavior of electrons that corresponds to the plasma density in low-pressure gas discharges. Results of the MRP measurements reveal instabilities during the coating process and give insight into the dynamics of the deposition conditions over run-times of up to several hours. At LASER COMPONENTS GmbH, PIAD is employed for the manufacturing of HfO₂ and Ta₂O₅ based optical interference coatings for IR applications. Process and plasma parameters have been compared to thin-film properties and lateral distribution at the substrate level. Within the study, the MRP monitoring has proven to be a promising approach towards an implementation of a phase lock loop controlling and balancing the plasma density. This work is based on funding by BMBF under grants 13N13208, 13N13212 and 13N13213.

Keywords
APRS
Properties and surface interaction of a low pressure microwave microplasma as an electron source for a MEMS device miniature mass spectrometer

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Micro-electromechanical systems (MEMS) have a broad area of application in modern technology. Lab-on-a-chip devices are enabled by the shrinkage of sensors to micrometer scale. The authors present a micro-fabricated mass spectrometer equipped with a low pressure plasma source driven at a frequency of 2.45 GHz. An antenna creates a cylindrically-shaped plasma volume of 250 μm in radius and 300 μm in height, surrounded by borosilicate glass and electrically conducting silicon. The low pressure microplasma is used as an electron source for electron impact ionization and therefore electron density, power efficiency and gas consumption are key parameters for optimization. Limited availability of inert materials in MEMS processing technology requires careful plasma process design. Change of surface composition by plasma etching, film deposition or ion induced sputtering degrades device properties over time.

Absolutely calibrated, space- and time-averaged optical emission spectroscopy (OES) is used to measure gas temperature, electron temperature and electron density in noble gas atmosphere with small additions of nitrogen. Space-resolved spectral line analysis is performed by a CCD-Camera equipped with a bandpass interference filter. The pressure inside the discharge chamber is estimated by the pressure drop induced by micro-capillaries. Surface changes over long periods of operation time are measured by SEM, EDS and XPS analysis and correlated with mass spectrometer measuring signals.

The authors would like to thank the financial support by the Bundesministerium fuer Wirtschaft und Energie (BMWi, FKZ: 03ET1314B)

Keywords
diagnostics
MEMS
mass spectrometer
surface
OES
Process characterization of reactive magnetron sputtering using two reactive gases for tuning the properties of TaOxNy thin films

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The reactive magnetron deposition technologies are widely used in research and industry, with an increasing interest over the past two decades for the synthesis of more complex compounds such as oxynitrides and carbonitrides. The aim of this study is to investigate the reactive sputtering process of Ta target in a mixture of Ar, O₂ and N₂. The use of two reactive gases increases the complexity of the process by the presence of competing surface and volume reactions. The Ar/O₂ and Ar/N₂ single reactive gas processes were investigated separately, in terms of hysteresis behavior resulting from variation of the reactive gas flow. The reactivity of the process is analyzed by using the electrical characteristics of the discharge, the total and partial pressure of the gasses and the optical emission intensity of selected spectral lines. The reactive gas flows corresponding to maximum reactivity of each process are chosen as reference, and used to calculate an optimum ratio of reactive gas flows. The so determined ratio (2.5) is used as a fixed parameter in the analysis of the hysteresis behavior of the two reactive gases process, as such an optimum process windows enabling maximum tunability was identified. The TaOₓNᵧ thin films were investigated in terms of microchemical, microstructural, mechanical and optical properties, the changes in the sputtering process being directly related to the changes of the obtained layers. Although the gas flow ratio is kept constant a modified chemical composition of the layers was observed, depending on the chosen setpoint in the reactive process. These changes determine corresponding modifications of the optical properties, with a tuning range of refractive indices from 3.3 to 2.15 and optical band gap variation from 1.7 to 3.6 eV.

This work was supported by the Romanian Ministry of Research and Innovation, National CORE Project 2018, and the Bilateral Cooperation South Africa –Romania NRF/RISA UID: 104018.

Keywords
reactive sputtering
oxynitrides
optical emission spectroscopy
PIC simulations of spoke structures in the dcMS and HiPIMS regimes of magnetron discharges

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Sputtering in magnetron plasma discharges remains one of the main technologies used for thin film deposition owing to relatively large deposition rates in the dcMS regime and high film density along with improved control over film properties in the HiPIMS regime, where plasma is highly ionized. Plasma dynamics is an essential part of this kind of technology, its understanding enables better control and forms a path for possible optimizations. One of the most prominent features of such magnetized discharges still lacking full understanding is the emergence of self-organized nonlinear structures dubbed spokes. The spokes strongly affect many important discharge aspects, such as electron transport and energy of the ions impinging on the substrate. The present work uses an implicit energy-conserving PIC code to self-consistently model the formation and dynamics of the spoke structures in the two basic regimes used for the film deposition, dcMS and HiPIMS, and demonstrates that although the spokes have a relatively large spatial scale, they are generated by much finer plasma instabilities. Differences between the spoke structures in the considered regimes are discussed.

Keywords
dcMS
HiPIMS
spokes
PIC
plasma instabilities
Plasma simulation of hollow cathode effect in a blind hole

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The hollow cathode effect can be used for deposition of amorphous hydrogenated carbon films on inner surfaces of blind holes. In dependence of the aspect ratio between blind hole depth and blind hole diameter, the plasma states vary within the geometry. Due to the different plasma states, it is difficult to deposit homogeneous thin films in terms of their structure and thickness. In the following, a simple argon hollow cathode discharge is considered to give an understanding of the various processes taking place.

In the present investigation, a probabilistic simulation based on the Monte Carlo methods has been used to develop a better understanding of the hollow cathode effect in blind holes with an aspect ratio $\gg 1$. First, pressure gradients inside the blind hole were investigated with a direct simulation Monte Carlo (DSMC) method. Then, the resulting pressure distribution has been used as input for a Particle-in-Cell Monte Carlo (PICMC) plasma simulation to determine the energy input to the hole wall and the charge carrier distribution along the tube. Subsequently, the results were compared to corresponding experimental results, such as pressure measurements, argon ion etching rate, substrate heating rate and results of space-resolved optical emission spectroscopy (OES), to verify the simulation.

Keywords
- hollow cathode discharge
- plasma simulation
- direct simulation Monte Carlo (DSMC)
- Particle-in-Cell Monte Carlo (PICMC)
- optical emission spectroscopy (OES)
Analysis of the sheath behavior of an analytic model for a capacitive discharge

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Global models are particularly suitable for incorporating the most relevant plasma characteristics. In comparison to spatially resolved simulations, e.g. PIC simulations, they are computational less demanding. They also need low computing times whereby results can be achieved faster. In this work the numerical modeling of a capacitively coupled discharge is shown. For this purpose, an existing global model [1] is extended by a sheath in front of the grounded electrode in order to be able to investigate the boundary sheath behavior in front of the driven and the grounded electrode. Particular emphasis is put for a variation of the area ratio of the driven to the grounded electrode. The obtained results allow conclusions about the effects of the nonlinearities as well as for the effect of the plasma series resonance. In addition, it can be said that the assumption of the DC-floating potential is suitable for large area ratios (AG ≥ 30•AE).

A first approach for the sheath model uses a constant ion density profile, which is called matrix sheath model. Additionally an experimentally determined ion density profile is used in the model and suitable parameter variations allow a comparison of the results using the two different density profiles.

As an outlook, a further improvement of the boundary sheath behavior can be achieved by incorporating thermal and dynamic effects. Moreover the ambipolar field which is particularly important for the ion dynamics is considered. This can be accomplished by using an improved sheath model.


Keywords
Global model
Sheath model
Area ratio
Artificial Neural Networks as Plasma-Surface Interface for Sputtering and Gas-Phase Transport Simulations

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Thin film processing by means of sputter deposition inherently depends on the particle interaction at the target surface and the subsequent transport of film forming species through the plasma. The length and time scales of the underlying physical phenomena span orders of magnitudes. A theoretical description which bridges all time and length scales is not practically possible. A unified approach which describes the dynamics of both the solid and the gas-phase, however, remains desired. In fact, advantage can be taken particularly from the well separated time scales of the fundamental surface and plasma processes by evaluating both independently. Initially, the surface properties may be a priori calculated and stored. Subsequently, the data may be provided to particle transport simulation models via appropriate interfaces (e.g., analytic expressions or look-up tables) and utilized to define insertion boundary conditions. Specifying accurate and computationally feasible interfaces in cases which involve only a few species (e.g., argon and metal) is straightforward. More complex surface and gas compositions, i.e., a higher order parameter space, complicate the interface models substantially. In this work, a potential remedy is demonstrated based on artificial neural networks (ANNs) [1,2]. As a proof of concept, a multilayer perceptron (MLP) is trained and verified with sputtered particle energy and angular distributions obtained from TRIDYN simulations [3] for Ar, Al, and Ti projectiles bombarding an Al-Ti composite. Subsequently, the trained network is used to predict the sputtering dynamics for arbitrary incident ion energy distributions. Consequently, the sputtered particle energy and angular distribution may be sampled quasi-continuously and to a sufficient accuracy also in scenarios which have not been previously trained.

Keywords
Plasma surface interaction
Analysis of a lumped element model for radio frequency magnetron discharges

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Magnetron sputtering is an established technology to deposit thin films with high quality. Employing RF power (instead of the conventional DC power) allows to sputter not only electrically conductive materials but also dielectrics like optical coatings or semiconductors. This work presents a global model for such an RF driven magnetron sputtering process which is an extension of a previously published lumped circuit description of unmagnetized RF discharges [1]. As its predecessor, the model represents the discharge by separate bulk and sheath zones which communicate via Kirchhoff relations. The extension accounts for the presence of a magnetized region with reduced electric conductivity. The model evaluates quickly and may be used for the purpose of model based control.

In addition, the underlying sheath model is considered. Various ion density profiles are incorporated into the model and the respective behaviour is studied.


Keywords
Magnetron sputtering
Lumped element model
Sheath modeling
A New Method for Measuring Chemical Composition with Hollow Cathode Discharges

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In this study a new spectroscopic approach for analysis of chemical composition using hollow cathode discharges is introduced. The influence of the physical dimensions as well as the ratio aspect (length/diameter) of the discharges on the measurements was investigated. Several spectral lines of some elements have been observed, especially those originated from decaying transitions to the ground state and metastable states. Our approach consist in select spectral lines, whose light intensity can be represent in terms of the invariant parameter associated with the discharge current density and pressure. Whenever a quantity can be represented in terms of an invariant parameter, it can be scaled up for other discharges with the same cathode material and filling gas, but with different dimensions and operated under different conditions. A correlation between the light intensities of spectral lines of some selected elements and their relative chemical composition on different samples was found by plotting these quantities as a function of the invariant parameter. The measurements were made for several commercial samples containing Fe, Cr, Ni, Ti and Al. A better overlapping of the experimental points occurs in the low current range, where the gas temperature is close to the room temperature and the density of sputtered metal atoms is low compared to the density of the gas atoms. In this case, the discharge is manly sustained by the ionization collisions of the beam electrons emitted by the cathode with the argon atoms. So far the sputtered metal atoms do not play a significant role on the discharge self-sustaining mechanism, deviations from the characteristic curves are small.

Keywords
Hollow cathode
chemical composition
emission spectroscopy
invariant parameter
PO4093

Investigation of Plasma Nitriding Process by Absorption Spectroscopy

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In this work the glow discharge of a plasma nitriding process was investigated using absorption spectroscopy. A small hollow cathode running inside the nitriding chamber was used as line light source in the absorption measurements. Density profiles of sputtered iron atoms were measured in the cathode fall and negative glow. In addition, the emission signals of the gas species were also monitored. The cleaning discharge, conducted in an Ar/H₂ atmosphere prior to nitriding, was also investigated. Samples of mild steel AISI 1020 and low alloy steel AISI 4340 were used as substrates for characterization of the treatments. They were nitrided at temperatures varying from 723 K up to 823 K for 1 h in N₂/H₂ atmospheres with different nitrogen contents. The treated surfaces were analyzed with respect to their composition, microstructure, crystallographic structure, surface roughness and Vickers microhardness. After Nitriding, a typical surface hardness of 430 HV₀.₁ and 820 HV₀.₁ was measured for the 1020 and 4340 steel, respectively. A hardness decrease was observed due to decarburization in the cleaning discharge for temperatures above 700 K. A correlation between the spectroscopic measurements, the process parameters and the surface properties at different stages of the process will be presented and analyzed.

Keywords
Absorption spectroscopy
emission spectroscopy
plasma nitriding
RF hollow feeder for ITER diagnostic mirrors cleaning system: breakdown risk assessment

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Ion sputtering in RF discharge is a primary candidate approach to periodic mirror recovery in ITER. Such discharge requires RF power of ~1 kW@10...100 MHz. The current approach to RF power transmission inside ITER vacuum vessel is mineral insulated cables. However, they are not acceptable as a full-fledged solution due to high insertion loss: up to 15% per meter. Rigid hollow feeder is considered as a solution alternative to the MI cables. Such feeder type has low insertion loss, but its power handling capability is limited by electrical breakdown. The conditions affecting the hollow feeder breakdown threshold in ITER are: pressure of 1...20 Pa in Ne, D₂, He, etc. and their mixtures, magnetic field of 0.1...5 T, DC-biased line conductors, complex 3D structure incorporating conductive and dielectric materials, exciting wave electromagnetic field configuration, background temperature and ionizing radiation. Breakdown simulation in hollow feeder described, aiming to reveal breakdown-free parameters area. The available software tools allow breakdown simulation not for all ITER-specific conditions, and its experimental study is quite challenging and time consuming. Thus, to assess the risk of hollow feeder breakdown in ITER conditions, a software tool is being developed, based on direct Monte Carlo electron cloud evolution simulation. The main breakdown mechanism considered in conditions of interest is an avalanche-like electron density increase, which can occur due to either volumetric gas ionization or to so-called “multipactor” effect governed by secondary electron emission. The report discusses physical statement, mathematical approach, ways of the code validation, and preliminary simulation results.

Keywords
Breakdown
Hollow feeder
Monte Carlo simulation
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