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Abstracts
(as at August 25, 2020)
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CO2-neutral mobility as a challenge and opportunity for plasma surface technology throughout the energy chain

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For tomorrow's sustainable mobility, we will need to develop new technologies that are more efficient and, above all, less pollutant while consuming fewer fossil resources. There exist three basic paths to sustainable mobility in the future: Battery electric mobility, fuel cells powered by green hydrogen, and hydrogen-based e-fuels for already existing fleets using combustion engines. Over the next years, our challenge as an industry is to industrialize all three types of solutions. These developments will, in turn, lead to a sharp increase in renewable energies and the respective impact on the energy system.

Therefore, the mobility transition requires an energy transition. Plasma technology plays an important role not only in the mobility transition but also in the energy transition. Schaeffler has already successfully developed completely new coating systems particularly in the field of system components for energy storage and conversion. For instance, plasma technology coated metallic bipolar plates offer increased performance in terms of lifetime and operation modes at different voltage levels. This improvement has been achieved with a coating system using a nanostructured architecture combining different material groups of metals, nitrides and carbides. Energy efficiency still remains of central interest across all energy-related applications, including both traditional combustion engine technology and new propulsion concepts. Schaeffler has developed several thin film solutions that focus on the improvement of energy efficiency by improving friction performance and wear resistance. These coatings are already being used today in a wide variety of products. A key aspect for future improvements is the challenge of the development and application of tailored coatings which can interact adaptively with the lubricants and their additives. For a successful mobility and energy transformation the close cooperation between science, industry and politics, as well as a fast transfer of research and development results into economic and robust mass production, is of critical importance.

Keywords
mobility and energy transition
energy storage
tribology
Plasmas and polymers have surrounded humans since ancient times, although the appearance of these terms themselves is relatively recent: the term ‘plasma’ was introduced by Langmuir in 1928 and the term ‘polymer’ originates with the Berzelius’s work from 1832. Even earlier and entirely unaware, Mr. Lane may have been the first experimentalist to bring together plasmas and polymers when, in 1767, he investigated the spark discharge in various liquids, including water solutions of wheat flour. We know nowadays that plant-derived flour consists of starches which are natural polymers belonging to a polysaccharide class. The first deliberate studies date back to 1873 when the Thenards published an earliest known report on the condensation of an organic solid from hydrocarbon vapors upon the action of what we know now as dielectric barrier discharge. Since then, the field has witnessed tremendous progress, particularly in the period starting from the mid-20th century.

Spanning over decades of research, this talk reviews the state-of-the-art in the field of plasmas and polymers with the focus set on the synthesis of nanomaterials. Current ideas about the structure and molecular dynamics of single-component plasma polymers will be given in the context of the formation of nanostructured platforms (nanoparticles, thin films). These considerations will be further extended to plasma copolymers, covering thin films with molecular-scale component mixtures, nanophase-separated coatings and nanofluids. Plasma in contact with the liquid phase will be also considered as a tool for the synthesis of organic nanoparticles and, possibly, doped graphene as well as for solution processing of natural polymers. Finally, current views on hybrid plasma polymer/inorganic nanomaterials will be presented.

Keywords
plasma polymer
copolymer
nanoparticles
thin films
Plenary Lecture

Wednesday, September 9, 2020

PL0003

High-Temperature and Aerospace Coatings

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In high performance products, engineering coatings are often pushed to their mechanical, physical and/or chemical limits. For a wide spectrum of applications, tailored coatings made of metals, ceramics and polymers (and sometimes combinations thereof) are produced by various deposition techniques. The plenary talks will shed some light on recent developments in the field of high temperature and high performance coatings, some of which are being used in or designed for demanding aerospace applications. High-temperature resistant thermal barrier coatings (TBCs) produced by thermal spraying and/or EB-PVD are state of the art for both, industrial gas turbines and aeroengines. However, more recently the present authors have developed a new generation of TBCs and CMAS-resistant coatings using suspension spraying which demonstrate high performance at relatively reasonable cost. Moreover, thermodynamic modelling has proven beneficial for lifetime assessment of TBC bond coats. PVD Cr₂AlC MAX phase coatings were developed using magnetron sputtering and HPPMS, and were tested by the authors towards residual stresses, oxidation behavior and erosion resistance – a threat particularly posed to aeroengines. Also high entropy alloys were investigated as either metallic or nitride PVD coatings indicating great potential for high temperature applications combined with mechanical loads. Laser-arc deposited superhard ta-C coatings show a unique combination of high wear resistance and low friction coefficient, making them ideal candidates for sliding wear applications, not only in aerospace industry but also automotive industry where these coatings have matured to series products.

Keywords
thermal barrier coatings, high entropy alloys, ta-C coatings, MAX phase coatings, thermal spray, PVD, HPPMS, laser arc deposition
Plenary Lecture
Thursday, September 10, 2020

PL0004

Stages in the progress of plasma assisted PVD since its discovery and challenges for coating processes in future manufacturing.

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Plasma assisted PVD (PAPVD) processes have seen considerable improvements over the past 60 years. This presentation identifies four distinct waves of development, starting with simple DC diode systems followed by enhanced plasma systems based on methods such as arc and electron beam evaporation. This stage was paralleled by improvements in sputter-based processes. More recently we have seen the emergence of coating processes tailored for the increased demands of practical product applications, included dedicated high throughput systems for many different types of products. At the same time, in recent years we have seen considerable developments associated with the rise of Industry 4.0, together with the increased digitalisation of coating processes and the coatings themselves. Many Manufacturing-based economies are now seeing a move to a "Made Smarter" approach. This has many implications for advanced coatings. Not only must digitalisation be implemented but coatings and coating processes must be integrated into the product design process, as required by all High Value Manufacturing (HVM) techniques. The presentation will explain some of the implications of this transformation, and will describe two initiatives taking place in the UK to bring together industrial and academic researchers to face the challenges of digitalisation in the coatings sector.

Keywords
plasma
PVD
Digitalisation
Industry 4.0
HVM
ORA101

**Development of a model to predict the s-phase thickness of plasma nitrided austenitic steels**

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Austenitic steels are known for their high corrosion resistance but at the same time possess low hardness which results in low wear resistance. A common way to improve the tribological properties of austenitic steels is plasma nitriding. The formation of the so-called s-phase leads to a strong lattice distortion in the surface area which leads to an increase in the hardness. At the same time, in order to retain the corrosion resistance, process parameters such as temperature and duration must not exceed a certain threshold, otherwise chromium nitrides may be formed.

The aim of this study is to develop a model which predicts the thickness of the s-phase in plasma nitriding processes. For this purpose, a number of processes were executed and analyzed under specific variation of temperature ranging from 360 °C to 450 °C and duration of 10 to 24 h. Other process parameters such as voltage, pressure, pulse-pause ratio and gas mixture remained constant. A temperature dependent growth rate could be determined after the analysis of the results. On one hand this allows to predict the thickness of the s-phase for any given treatment temperature and process duration in the given temperature window, while on the other hand one of the two process parameters regarding treatment temperature and process duration can be explicitly selected via iso-thickness progressions line and combined with the other to obtain the required thickness of the s-phase.

In this way a possible formation of chromium nitride by the plasma treatment can be avoided. The developed model was verified by control experiments and shows a maximum relative error of 5.5 %.

The model is currently being extended by an additional parameter, namely the chemical composition of the material, in order to enable transferability. A factor for the transfer of the nitriding depth to other microstructures or steel classes is also conceivable. Subsequently, additional factors for other process parameters, e.g. voltage, gas mixture or pressure, will be included.

**Keywords**
plasma nitriding
s-phase
model
The maximum N content in nitride films prepared by atom-by-atom growth is examined by combining molecular dynamics (MD) simulations with experimental data [J. Houska, Acta Mater. 174, 189-194 (2019)]. Structures of amorphous nitrides such as CN$_x$, Si-C-N and B-C-N are predicted by extensive ab-initio MD (over 9000 trajectories) in a wide range of compositions and densities. When and only when the simulation algorithm allows the formation and final presence of N$_2$ molecules, the predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the number of unbonded N$_2$ molecules, with the aim to predict and explain the maximum content of N bonded in the amorphous networks. There are significant differences resulting from different Si/B/C ratios, ranging e.g. from no N$_2$ at the lowest-energy density of a-Si$_3$N$_4$ to many N$_2$ at the lowest-energy density of a-C$_3$N$_4$ (≈50% of that of β-C$_3$N$_4$). Detailed analysis shows that the maximum content of N bonded in a-CN$_x$ networks is ≈42%. From the kinetics point of view, higher N contents lead to steeply increasing rate of N$_2$ formation during materials formation. From the thermodynamics point of view, networks with more than ≈42% of bonded N may be temporarily stabilized by N$_2$ molecules sitting in voids around them, but N$_2$ loss into the atmosphere makes them unstable. The increasing maximum N content in Si-C-N with increasing Si/C ratio is also shown to be in an excellent agreement with experimental results of reactive magnetron sputtering. While the N$_2$ formation at a given total N content and in a wide range of Si/C ratios is given by the packing factor, the lowest-energy packing factor increases with Si/C. The results are important for the explanation of contradictory literature data, design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

**Keywords**
maximum N content
CNx and C3N4
Si-C-N and B-C-N
Magnetron sputtering into deep grooves

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Magneton sputtering is a well-established technique to prepare various thin film coatings in wide range of industrial applications. However, deposition into the grooves, trenches or holes is complicated using this technique. Changes in process parameters can increase the penetration of the coatings into the grooves. Increase of pressure results in increase of scattering of sputtered atoms and higher number of sputtered atoms can enter the groove. However, they will soon hit the wall and do not penetrate deep enough. There are two reasons for this statement: 1. the atoms enter the groove at very broad angular distribution and 2. The atoms are scattered even inside the groove and their probability to hit the wall is high. On the other hand decrease of pressure and placing the sample far from the target can result in high mean free path, very well defined angular distribution of the sputtered atoms and deep coverage of the groove walls by the coating.

In this work influence of pressure and target-to-substrate distance in case of DC sputtering from Cr target is analyzed. Special fixtures were constructed in order to direct measuring of coating thickness on two Si substrates with distance between them 2, 4 and 6 mm up to 30 mm deep into the groove. Experiments were supported by Monte-Carlo simulation in SIMTRA, by discrete ordinates model developed in ANSYS Fluent and also by simple and advanced analytical model programmed in C#. Very good correlation was found for all three approaches (models), allowing optimization of the process parameters in order to achieve the best coverage of the groove walls.

Recently the HiPIMS with positive pulse after the main HiPIMS pulse was reported as a method that increases the homogeneity of the coating inside 3D geometry. In this study comparison between the samples prepared by HiPIMS and HiPIMS with positive pulse after the main HiPIMS pulse (using two different power supplies) were performed and positive influence of HiPIMS with positive pulse on the homogeneity of the coating in the groove were confirmed.

Keywords
coating homogeneity simulations
magnetron sputtering
Surface characteristics underpinning fretting wear performance of duplex chameleon/PEO coatings on Al under high contact loads

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Being a consequence of contact fatigue, fretting wear is detrimental to durability of many structural components. The application of solid lubricants can reduce the damage resulting from fretting. In this work, duplex coatings comprising MoS\textsubscript{2}/Sb\textsubscript{2}O\textsubscript{3}/graphite (‘chameleon’) layer deposited on the top of plasma electrolytic oxidation (PEO) treated 6082 series Al alloy substrates were subjected to a series of fretting wear tests against two different counterpart materials and under varying loads, displacement amplitudes and environments. XRD, instrumented indentation, SEM, energy dispersive spectrometry (EDX), laser confocal microscopy and Raman spectroscopy were employed to examine the surface phase composition, hardness, elastic modulus, as well as microstructure, elemental distribution and 3D surface topographies of the wear scars. The duplex coating was found to effectively enhance the wear performance of the Al alloy, with friction coefficients reduced from ∼0.9 to ∼0.08 in dry N\textsubscript{2} and from ∼0.6 to ∼0.1 in humid air against alumina counterpart. About an order of magnitude improvement over a single layer PEO coating was observed in specific stick-slip (∼3 mm amplitude), partial slip (5-10 mm) and gross slip (>10 mm) regimes. Importantly, in the latter regime, high normal loads (about 1.4 GPa contact pressure) affected the duplex coating performance against 440 stainless steel in oxidising atmosphere, with Fe/Al/Cr oxides/hydroxides generated in the contact region, leading to the formation of micro-cracks penetrating throughout the PEO coating. However, when the contact pressure was reduced to ∼1 GPa, the coating showed low friction and wear rate, with no appearance of fatigue cracks after 10,000 fretting cycles.

Keywords
Plasma Electrolytic Oxidation
Aluminium alloys
Chameleon coating
Fretting wear
**Thermal stability of nanoparticle thin films characterized by x-ray scattering methods**

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Thin films composed of nanoparticles are interesting because of their inherent high porosity which is important for gas sensing, efficient batteries or hydrogen storage applications. The thermal stability of nanoparticle layers depends on chemical and phase composition, configuration of nanoparticles or the atmosphere in which they are heated up.

In this study we investigated systems of homogeneous and heterogeneous metallic nanoparticles, and also thin layers containing two different types of homogeneous nanoparticles. Nanoparticles were in all cases prepared by magnetron sputtering from pure metal targets followed by aggregation of fragments to the metallic clusters. Samples deposited on silicon substrates were characterized at the ambient air atmosphere after preparation. Size distribution of nanoparticles and the inert structure of heterogeneous nanoparticles were determined by small angle x-ray scattering (SAXS) and confirmed by transmission and scanning electron microscopies measurements (SEM, TEM). Thickness of the layers, analysed by cross-section SEM and atomic force microscopy, was used to estimate the layer porosity from absolute intensity SAXS measurements.

Microstructure of nanoparticles and its thermal evolution were studied by in-situ x-ray diffraction (XRD) experiments realized in various atmospheres (vacuum, air, argon or nitrogen atmosphere). Evolution of phase composition, lattice parameters, sizes of crystallites, and microstructural defects in present crystalline phases were described in details up to 900 ° C. In-situ SAXS measurements were done to examine the temperature dependence of the layer morphology as well as the size distribution of single nanoparticles. Electron microscopy was performed to verify the models used for fitting of the SAXS scattering curves.

**Keywords**
nanoparticles
SAXS
XRD
thermal stability
High temperature stable ZrN-based thin films for plasmonic applications

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Silver and gold nanoparticles are well-known materials for plasmonic applications. However, their optical properties (of these metals) are strongly modified at high temperatures. To overcome this problem, metal nitrides (TiN and ZrN) are suitable materials for high temperature plasmonic applications. Recently, it has been demonstrated that the plasmonic response of TiN- and ZrN-based materials is tunable in the infrared region by addition of a third element. The present contribution aims to show the effect of Y addition on the optical and electrical properties of reactively co-sputtered (Zr,Y)N films. The maximal value of the Y/(Zr+Y) ratio has been limited to approx. 50 at. %. The progressive addition of Y atoms into the ZrN films does not induce any change in the film structure. A linear increase of the lattice constant as a function of the Y content has been evidenced by X-ray diffraction indicating that yttrium atoms substitute zirconium ones in the rocksalt-like cubic structure. A drastic change of the electrical and optical behaviors has been observed when the Y content exceeds 30 at. %. At low Y content the films exhibit a metallic-like behavior with low electrical resistivity and a strong absorption band in the visible range whereas a semiconductor-like behavior is evidenced at high Y content. For the films exhibiting a metallic behavior, the plasmon wavelength evolves linearly with the yttrium content. The spectra of the real and imaginary parts of the film dielectric function deduced from ellipsometry confirm the above conclusions. Finally, the evolution of the films’ optical properties as a function of the temperature in the 25-400 °C range has been studied. Even after air annealing at 400°C, there is no change in the films’ reflectance. The same behavior has been also noticed for the electrical properties. These results clearly show that (Zr,Y)N films are suitable for plasmonic applications.

Keywords
Plasmonic
Optical properties
Thermal stability
ZrN
Optical and gas sensing properties of LSPR-exhibiting Au-TiO2 nanocomposite coatings obtained by sputtering

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Nanocomposite coatings consisting of Au nanoparticles capped with TiO₂ overlayer were synthesized by pulsed DC magnetron sputtering. By varying the Au target deposition time, Au nanoparticles of different morphologies and concentrations were incorporated. The structure, microstructure, morphology, optical and gas sensing properties of the nanocomposites were studied. For lower deposition times the Au nanoparticles were mainly spherical, giving rise to narrow localized surface plasmon resonance (LSPR) absorption peaks. With the increase in the Au deposition time ellipsoidal Au nanoparticles with decreasing aspect ratios were obtained, giving rise to wide red-shifted LSPR absorption bands. The peculiar LSPR extinction bands were simulated and related with the nanoparticles’ size and shape distribution in the coatings by using the Generalized Maxwell Garnett theory extended for shape distribution functions. The gas sensing properties were related with the microstructure of the coatings.

Keywords
Au-TiO₂
localized surface plasmon resonance (LSPR)
optical sensors
gas sensing
shape distributed Generalized Maxwell Garnett theory
ORA204

**Adhesion of Coatings vs. Strength of Composite Materials – A Review of Applications Evaluated by Centrifugal Adhesion Testing (CAT)**

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Sufficient adhesion/tensile strength are basic requirements for any coating/composite material. For coatings, adhesive strength in N/mm² is of major interest for various applications such as decorative and water-repellent coatings on wood (paints and varnishes), optical coatings on glass and polymers (reflectors and filters), electrical coatings on semiconductors, glass and polymers (conducting and bondable layers), mechanical coatings on metals and polymers (wear-reduction, scratch-resistance) and adhesion-promoting layers. For composite materials, tensile strength in N/mm² is also a key quantity for carbon fiber reinforced composites (CFC), laminates and adhesive-bonded joints. Centrifugal adhesion testing (CAT) transfers the single-sample tensile test from a tensile or universal testing machine into an analytical centrifuge as multiple-sample test of up to eight test pieces. The one-sided sample support instead of a two-sided sample clamping and the absence of mounting- and testing-correlated shear forces provides fast and reliable results both for adhesive strength and bonding strength by means of bonded test stamps. For bonding strength, the evaluation of failure pattern from microscopic inspection is required in order to determine the failure pattern according to ISO 10365 such as adhesive failure (AF), delamination failure (DF) and cohesive failure (CF). Hence, one test run by CAT-technology provides either statistics or ranking of up to eight samples at once. For adhesive strength of coatings, a variety of examples is discussed such as ALD-Al₂O₃ layers as adhesion promoters, evaporated Ag-layers on N-BK7 glass, sputtered Cr- and Al-layers on Borofloat 33 glass, evaporated Au-films on N-BK7 glass and sputtered SiO₂-layers on CR39 Polymer. Provided adhesive or bonding strength are high enough, the substrate or the joining part may also fail.

**Keywords**

adhesive strength  
pull-off test  
centrifugal adhesion testing  
failure pattern
Time-resolved optical emission spectroscopy of a unipolar and a bipolar pulsed magnetron sputtering discharge operated in an argon/oxygen gas mixture

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Reactive high power impulse magnetron sputtering (HiPIMS) of a cobalt cathode in pure argon gas at a gas pressure of 1 Pa and with different oxygen admixtures was investigated by time-resolved optical emission spectroscopy and time-integrated energy-resolved mass spectrometry. The HiPIMS discharge was operated at a repetition frequency $f = 100$ Hz with a duty cycle of 1%. A bipolar pulsed power supply capable of providing a large negative voltage (up to -1000 V) with a typical pulse width of 100 µs followed by a long positive pulse (+60 V) with a pulse width of about 350 µs was employed. The HiPIMS plasma in pure argon is dominated by Co$^+$ ions. With the addition of oxygen, O$^+$ ions become a prominent positive ion species. Optical emission spectroscopy reveals the presence of Ar I, Co I, O I, and Ar II emission lines. The transition from an Ar-burning to a Co-burning discharge is inferred from time-resolved OES. The enhanced intensity of excited Ar$^{+\ast}$ is explained by simultaneous excitation and ionization induced by energetic secondary electrons from the cathode. The intensity of violet Ar I lines is drastically reduced during HiPIMS. The intensity of near-infrared Ar I lines resumes during the positive pulse indicating an additional heating mechanism.

Keywords
magnetron
HiPIMS
bipolar pulse
optical emission spectroscopy
energy resolved mass spectroscopy
Scaling Particle-based Simulations of Plasma Processes to Industrial Applications using HPC

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Significant physical insight into the relevant industrial processes that are related to thin film deposition can be obtained from particle-based numerical simulation tools. Due to their heavy computational demand, however, numerous large-scale technical applications are still infeasible to examine via simulation. Different generic test cases for low-pressure plasma, such as magnetron sputtering or plasma source devices, can bridge the gap between academic desktop-scale and industry-relevant scales. The considered benchmarks serve as demonstrators showing the advantages of high-performance computing for industrial applications. The simulations are performed using the open-source code PICLas (https://github.com/piclas-framework/piclas), which is a parallel, three-dimensional PIC-MCC/DSMC solver that is developed cooperatively by the Institute of Space Systems, the Institute of Aerodynamics and Gas Dynamics at the University of Stuttgart and the spin-off boltzplatz. The software is fully parallelized for distributed memory systems via Message Passing Interface (MPI) and optimized to run on modern high-performance computing (HPC) architectures. Domain decomposition is performed using space-filling curves and the sub-domains can be dynamically re-distributed among the available MPI processes during run-time. Important HPC aspects, such as dynamic workload balancing approaches, are highly crucial when efficient simulations are required. With increasing number of processors or high heterogeneity within the simulation domain, workload imbalances can heavily decrease the overall simulation efficiency. This can be encountered by improved algorithms, which detect and reduce workload imbalances. Previously, different strategies have been implemented in PICLas for measuring and re-distributing workloads. In future, these schemes continues to play a critical role, e.g., when complex three-dimensional simulations of industry-relevant applications are considered, where strong workload imbalances are present.

Keywords
PIC-MCC/DSMC
Simulation
HPC
Computer-aided engineering of industrial PVD and PECVD coating chambers: past victories, future challenges

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Computer-aided engineering (CAE) is the go-to engineering tool in many fields of industry. In recent years, the growing availability of high-performance computing and scientific advancements in coating fundamentals enabled predictive industry-grade simulation of some coating processes. We discuss, from the perspective of an industrial coating CAE provider, what computational models are available, what are their predictive capabilities and what level of 2D/3D geometrical detail can be simulated. This is done for the most common vapor deposition techniques - reactive and non-reactive DC sputtering, arc evaporation, HiPIMS and DLC PECVD. Apparently, some process models are already so mature that they enable ab-initio prediction of coating uniformity, composition or even properties. Concerning the less mature models, we discuss the technical and scientific challenges, standing in the way of reliable CAE of coating systems.

**Keywords**
coating
simulation
model
pvd
pecvd
Collisional-radiative model of argon plasma for industrial PECVD tool for solar cells production

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Surface wave-sustained plasma discharge is produced by microwave sources around a quartz tube in a low-pressure reactor. This plasma is extensively used in industry for thin layer deposition by plasma-enhanced chemical vapor deposition (PECVD). Optical emission spectroscopy (OES) is an established characterization technique to determine plasma parameters such as electron temperature and density. The advantage of OES is being a fast, easy-to-set-up and non-intrusive technique, ideal for industrial tools if the right models are applied to interpret the emission spectra.

In our study, a collisional-radiative model (CRM) was developed for low-pressure, low-temperature argon plasma to calculate the electron density and the electron temperature in an industrial PECVD tool for solar cell production. The model describes the kinetics of 15 argon excites states (1s and 2p). The plasma parameters were solved for different pressures as well as at different positions from the quartz tube in order to study the plasma homogeneity. To ensure a high sensitivity for the electron density and temperature, a careful attention was taken while choosing the OES lines used for fitting the model to the experimental data. Electron temperature and density are in the range of what is reported in literature for these types of plasmas. Results from CRM are compared to a rather simple corona model, the latter known to be valid for low-pressure plasmas. Radiation trapping was found to play a very important role for excited states population in CRM and for line intensities emitted in OES. Kinetic processes of 1s and 2p levels have been investigated in order to evaluate the importance of every considered reaction in our model.

As a next step, argon was used as a trace gas for the characterization of a real process of silicon nitride SiNₓ deposition (using a mixture of silane SiH₄ and ammonia NH₃) for the passivation and anti-reflective coating of crystalline silicon solar cells. The effect of the depositing gases quenching on the argon excited states has been carefully investigated.

Keywords
PECVD
Surface-wave plasma
OES
CRM
Protective coatings for high-performance components – such as blades or powertrain systems in aero engines – constitute an important role for achieving further milestones with respect to carbon emission and environmental sustainability in general. Next to the well-established nitride-based coatings are boron containing systems an upcoming and highly promising class. Here, ternary transition metal diborides are relatively unexplored compared to their binary counterparts such as hard and inelastic TiB$_2$ or ZrB$_2$. In the design of novel ternary transition metal diborides diverse challenges arise, whereas the following are major factors: (i) composition-controlled crystallization in PVD based deposition techniques, (ii) limited fracture tolerance and brittle behaviour, as well as (iii) formation of non-adherent and volatile oxide scales.

Within this study, we want address these specific challenges on various ternary model systems within group IV to VI transition metal diborides. The phase formation of two competing hexagonal structure types ($\alpha$-AlB$_2$ vs $\omega$-W$_2$B$_{5-x}$), with respect to target composition and ionization degree within the plasma, has been investigated for non-reactive DCMS, HiPIMS, as well as arc evaporation. In addition, different alloying concepts for enhancing the ductile character as well as oxidation resistance of these superhard ternary diborides will be discussed in detail (e.g. W$_{1-x}$Ta$_x$B$_2$ and others). To describe all these relations comprehensively, we correlated the synthesis parameters with structural and morphological evolution using XRD, HR-TEM, APT, as well as micro-mechanical testing methods. Furthermore, specific aspects have also been described by atomistic modelling (DFT).

**Keywords**
Ternary Borides
Protective Coatings
Influence of the compound layer composition of steel to the adhesion of DLC films

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DLC films have special properties, which are of great interest in fields of tribology, including the high hardness and the low coefficient of friction. These properties are limited because of shortcomings in adhesion of DLC films on steel. So far, metallic adhesive layers like titanium and chromium are established options for the improvement of the adhesion of DLC films on steel. Past investigations show that plasma nitriding of the surface can strongly improve the adhesion.

Starting point is the overview of the different surface modifications, which can occur through plasma nitriding and how they influence the adhesion of DLC films. The surface can consist of a compound layer of γ'-nitride and/or ε-nitride or it is also possible that there is no compound layer. These surface modifications differ in their composition, crystal structure, bond type, as well as their solubility and diffusion velocity of carbon. One hypothesis is that the carbon solubility has a significant influence on the adhesion of DLC films.

First, the influence of nitriding parameters to the compound layer composition was analysed. After investigation of the surface composition by XRD it is concluded that the temperature (ranged between 480 °C and 560 °C), gas composition (ranged between 10 % and 80% N₂) and pulse-pause ratio (ranged between 1:3 and 1:7) seem to be factors with great influence on the composition of the compound layer.

By means of a two-stage nitriding process it was ensured, that the hardness depth profile of all three surface modifications were similar. Thus, the “eggshell” effect should have no significant influence on the adhesion differences between the surface modifications and can be ignored. Further, the influence of the surface composition on the adhesion behaviour was analysed. For these purposes, the nitrided specimens were DLC coated by PACVD. First tests, executed on a scratch test rig, indicate that there is a correlation between compound layer composition and adhesion properties. The LC2 value of the ε-nitride surface was 41 N, γ'-nitride 19 N and without compound layer 30 N. Typical values of LC2 DLC films with metallic adhesive layers are about 25 N.

Keywords
surface modification
ORB102

**Analysis of the MoS$_2$ supply mechanism of triboactive (Cr,Al)N+Mo:S coatings**

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The demands on the performance of components in industrial applications are steadily growing in order to meet current and future expectations of politics and society. The intention is to achieve higher degrees of efficiency while simultaneously lowering costs through longer maintenance intervals. The application of wear resistant and self-lubricating triboactive (Cr,Al)N+Mo:S coatings is a promising approach to ensure a sufficient lifetime of highly loaded components in vacuum and applications under extreme thermal conditions, not allowing the usage of lubricants. The aim of this paper is to analyse the supply mechanism of MoS$_2$ of (Cr,Al)N+Mo:S coatings in highly loaded tribological contacts under dry-running conditions. The study was conducted using different (Cr,Al)N+Mo:S coating architectures deposited at T ≤ 200 °C on case hardened steel 16MnCr5E (AISI 5115) by using a combination of high power pulse magnetron sputtering (HPPMS) and direct current magnetron sputtering (dcMS). Thereby, Mo and S are present separately in the coating matrix and are supposed to form the solid lubricant MoS$_2$ in the tribological contact.

The goal was to understand the formation process of the tribochemical reaction layers and the decisive steps of the supply mechanism of MoS$_2$ on the tribological behaviour. Therefore, the pairing (Cr,Al)N+Mo:S/steel was chosen for tribological analyses. The tests were carried out in a pin-on-disk (PoD) tribometer under dry-running conditions at T = 25 °C and varying contact pressures from 400 MPa ≤ p ≤ 1,300 MPa regarding the application of (Cr,Al)N+Mo:S coatings on gears. In a next step, the wear tracks of the (Cr,Al)N+Mo:S coated specimens were analysed by means of Raman spectroscopy regarding the formation of tribochemical reaction layers. Hereby, there formation and chemical composition are significantly influenced by the contact pressure. The results of the supply mechanism of MoS$_2$ are correlated with the wear rate and the coefficient of friction.

**Keywords**
Nitride hard coatings, Wear, Raman spectroscopy, Solid lubrication, PVD
Low temperature PVD hard coatings

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PVD hard coatings are well established to improve the properties of tools and components, especially with regard to mechanical wear resistance. One advantage over CVD coating procedure for example is the lower coating temperature (normally 400 - 500 °C). But there are also materials which need a lower process temperature. Especially during the coating deposition on light metal alloys or low tempered steels there can lead to a change of microstructure which influences the material properties negatively. Furthermore, bonded tools are now more and more state of the art, in which the organic or inorganic adhesives have a limited temperature resistance. For these applications, it is necessary to reduce the deposition temperature down to about 200 °C to improve the applicability of the PVD deposition process. In various investigations, process analysis and adaptation were used to determine the effects of deposition temperatures on layer formation and coating properties. Goal was to develop a coating strategy/technology with a significantly reduced deposition temperature. The challenge here is the limited particle mobility and diffusibility of the adatoms, which leads to a higher error density and lower crystallinity. In many layer systems that were deposited at a reduced temperature an increase in microhardness and elastic modulus can be reached, but also an effect of embrittlement can be detected. This effect is not only based on the thermal conditions, but also correlates with the lowering of the cathode currents and reflects the effect of the reduced particle mobility. Based on the investigations, the deposition temperature of PVD-multifunctional coatings can be reduced to temperatures < 200 °C. With an optimized deposition strategy high-performance AlTiCrN multilayer coatings with a high hardness (> 40 GPa) and increased coating adhesion (Lc2 > 70 N) were successfully deposited on carbide tools and tested in milling applications.

Keywords
PVD coating wear resistance low temperature process
Tribological properties of diamond-like carbon coatings deposited by deep oscillation magnetron sputtering in Ar-Ne discharges

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Diamond-like carbon (DLC) films have been the paramount solution to reduce friction during operation of internal combustion engines for the automotive industry because they offer excellent surface properties, including very low coefficient of friction (<0.2) and wear rate (<$10^{-16}$ m$^3$/Nm), even under high load/pressure. The authors have shown that a recently developed variant of high power impulse magnetron sputtering (HiPIMS), called deep oscillation magnetron sputtering (DOMS), was suitable for the deposition of hydrogen-free DLC coatings comparable to those of the DLC films deposited by other state of the art deposition processes. Adding Ne to the discharge gas has been shown to be an effective method to increase the ionization fraction of the sputtered carbon species in an HiPIMS discharge. In this work, the properties of the DLC films deposited by DOMS are characterized in order to investigate the effect of adding Ne to the discharge gas on the film growth processes and on the tribological performance of the films.

On the overall, the substitution of Ar by Ne in the discharge gas up to 50 % results in changes of the DLC films properties similar to those observed when the substrate bias is increased from –80 to –100 V. However, the addition of Ne to the discharge gas results in much lower specific wear rates, reaching a minimum value of $4 \times 10^{-17}$ m$^3$/Nm, without any significant increase of the films residual stresses. Moreover, the higher wear resistance of the Ne films is achieved with only a small increase of the coefficient of friction, which remains close to 0.15, i.e., within the range of typical values for DLC films tested in relatively humid conditions. Thus the tribological properties of the DLC films deposited in this work are very interesting for many applications in the automotive industry, such as for the replacement of the CrN coatings nowadays standardly deposited onto the piston rings of internal combustion engines.

Keywords
DLC
DOMS
Ne
Hardness
Wear resistance
Effect of HiPIMS impulse shape on DLC films deposition: process and mechanical properties

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The deposition of hard diamond like carbon (DLC) films, such as tetragonal amorphous films (ta-C), relies on the subplantation of C ions into the subsurface region of the growing film and subsequent formation of sp$^3$ sites. In HiPIMS the sputtered species are ionized in their path towards the substrate. Thus, ionized C species can be used to bombard the growing film allowing for a more efficient formation of sp$^3$ than in dcMS, as bombardment with energetic ions from the background gas (Ar) causes additional compressive stresses without significantly contributing to sp$^3$ site formation. However, the ionization fraction of C in HiPIMS is rather low compared to metallic species. The ionization fraction can be improved by adding Ne to the discharge gas as previously shown by the authors. In this work, the effect of the shape of the HiPIMS pulses is investigated in order to increase the ionization fraction of the C sputtered species. DLC films were deposited using long pulses (up to 140 μs), with a HiPIMS Hipster power supply, and packets of oscillating pulses with less than ≈20 μs, using a Cyprium power supply in deep oscillation magnetron sputtering (DOMS) mode.

The effect of substrate biasing has been studies for both power supplies. Time resolved substrate current density measurements, carried out in pure Ar plasma using a specifically designed flat probe, clearly show an increase of ionic current for DOMS. Denser DLC films are deposited with increasing bias, resulting in an increased hardness, although with a decreasing deposition rate. However, for the same bias, harder and denser films are obtained when using packets of short oscillating pulses. The harder films are obtained with a bias of -100 V for short pulses while similar films are only deposited at a bias of -160 V when using long pulses. However, in the latter case, lower maximum compressive stresses are obtained (~ 1.5 GPa against ~ 2.5 GPa)

Keywords
HiPIMS
DOMS
Hard DLC
Carbon ion
Current density Probe
ORB202

**Tribomechanical properties of 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 a novel deposition technique of hard DLC coatings doped with various elements (e.g. W, Cr, Ti, Si) using HiPIMS by incorporation of positive pulses. Highly ionized plasma discharges were obtained during HiPIMS deposition. The high ion energy bombardment resulted in a higher sp³ to sp² bond ratio. EELS and Raman spectroscopy were used to characterize the sp³ and sp² structures in the deposited films. Nanoindentation tests revealed improved mechanical properties (hardness up to 35 GPa) in the range of 27 °C to 450 °C. Micropillar splitting were used to evaluate toughness of the coatings. Pin-on-disk tests were carried out both at room and high temperature. Finally, micromilling trials were carried out to assess the performance of these doped DLC coatings in micromachining of Ti6Al4V samples.

**Keywords**

DLC
HiPIMS
Tribology
Hard coatings
Wear
**Tribological Study of Tribocatalytically Active PVD Mo-X-N Coating**

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Due to the globally growing demand for reduction of CO₂ emissions, the reduction of energy losses from tribological contacts on sectors such as transportation, manufacturing and power generation becomes more and more important. One application is the tribological contact bucket tappet/cam or roller finger follower/cam in valve train system of passenger cars that offers potential for friction reduction but also places high requirement for coatings due to its complex kinematics and high contact pressures. A new approach is the use of a nanostructured tribocatalytically active PVD nitride coating system, which is composed of Mo-X-N (X = catalytic element) and interacts with the base oil and its additives. The tribological investigations of this new tribocatalytically active coating were carried out using two different ball-on-disc tribometers and fully formulated low viscosity engine oils with and without molybdenum containing additives. The tribofilms on this coating were investigated for the first time by in-situ Raman spectroscopy measurements during the tribological tests. In terms of friction behavior of the Mo-X-N coating, a friction reduction up to 35% was achieved with engine oil containing molybdenum additives compared to uncoated polished steel surface. The results of the in-situ Raman investigations pointed out the formation of a tribo-film on the coating consisting of molybdenum disulfide. The results reveal the high potential of this new tribocatalytically active Mo-X-N coating as major enabler to increase energy efficiency in the field of the “Mobility for Tomorrow”.

**Keywords**
Tribocatalytically active coating  
Nanostructured coating system  
friction reduction  
energy efficiency  
engine components
Coating thickness nonuniformity on cutting tools, deposited using different PVD techniques

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Standard industrial PVD deposition systems incorporate a substrate rotation mechanism to insure proper coating uniformity on complex-shaped substrates such as cutting tools. Though the rotation system and mounting geometry may be well optimized, the coating thickness in holes or other shaded areas will inevitably be lower. An opposite effect can happen on sharply pointing parts, which is of particular concern in processes with a high ionization rate. The term "antenna effect" is also used to describe this phenomenon. It may have a benefit to increase the thickness where the coating is most prone to wear, such as the cutting edge. On the other hand, it may cause a blunting of the cutting edge, or even increase the diameter of the tool, which can be detrimental at micrometer-sized tolerances, for instance in reamers. The effect has been well studied on simple geometries, however, the purpose of this study is to evaluate it in real industrial batches. Standard drills were put in the deposition chamber, accompanied by rods of different lengths and diameters. Both types of substrates were placed in varying geometrical environments (stand-alone or in a row) and at different heights. Two deposition systems were evaluated: cathodic arc evaporation and magnetron sputtering; in both cases standard TiAlN coating was deposited. After deposition, cross-sections were made at several positions and angles to evaluate the thickness enhancement as a function of geometry.

Keywords
arc evaporation
magnetron sputtering
antenna effect
thickness
coating
Adhesive-free bonding of web-like plastic-metal combinations at low temperatures

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Innovative materials often form the basis of modern industrial products in all areas of life. One example are special films, such as films for food packaging, flexible circuit boards, decorative and protective films, whose markets are constantly growing. These materials must meet a wide range of requirements, such as permeation to oxygen and water vapor, optical transparency, temperature stability, easy processability. Laminated films are particularly suitable for such complex functions because the different layers of which they are made of combine different material properties. These composites are often made of plastics and metals and are currently being joined using various adhesives. In addition to the high quantities of adhesives, long-term stability, creep tendency and migration are often problematic.

In this paper, a new adhesive-free low-temperature bonding process is presented as an interesting alternative for joining plastic and metal foils. Thin coatings were applied on the polymer and metal surfaces using an Atmospheric-pressure Plasma enhanced CVD process (AP-PECVD). 3-Aminopropyltrimethoxysilane (APTMS) forms a nm-thick adhesive layer, which covalently bonds to the activated webs. Besides polyethylene and aluminium, on which the focus was placed, the adhesion between polyvinylchloride and aluminium was also investigated. In a subsequent step the materials were bonded using a thermocompression bonder at moderate pressure (1,85 N/mm\textsuperscript{2}) and low temperature (< 100°C). Best results were achieved for the bonding of polyethylene with aluminium with adhesives forces up to 2.2 N/mm. By an optimal adjustment of the parameters, such as pre-treatment time, precursor concentration, plasma power and layer thickness, it was possible to generate composites with a high long-term stability. The deposited layers and composites were examined in a basic and application-specific manner by FTIR spectroscopy, contact angle measurements and peel tests on fresh and aged samples.

Keywords
adhesive-free bonding technology metal-polymer-compounds surface treatment thin film coating
Deposition of plasma polymer films (PPFs) occurs via plasma activation of a monomer (here: hexamethyldisiloxane) creating excited intermediates and highly reactive film-forming species. Such processes are governed by the available energy per monomer molecule in the gas phase, $E_{pl}$, which holds both for low and atmospheric pressure plasmas. Up to a threshold energy, $E_{th}$, of $\sim 15$ eV, the deposition rate is linearly increasing with $E_{pl}$ yielding PDMS-like coatings with low film density ($\sim 1.2$ g cm$^{-3}$) and good hydrophobicity. Increasing $E_{pl}$ accompanied by increasing energy deposited during film growth enables denser films up to about 1.8 g cm$^{-3}$ with reduced hydrocarbon content. Maximum conversion of the monomer into film growth can be reached depending on the used plasma source. The film growth at highly non-equilibrium conditions can be controlled starting from a thickness range as low as 1 nm. Hence hydrophobic nanolayers with defined density can be deposited on similar materials such as PDMS or SiOx fully covering their surface. 2 nm-thick hydrophobic cover layers on PDMS substrates of different crosslinking degree are used to clarify the role of viscoelastic properties on bacterial growth indicating the lack of mechanosensing abilities. Likewise, hydrophobic cover layers with varying film density are explored to control water intrusion. Thus, barrier properties of dense SiOx films can be enhanced or a defined volume of water can be allowed to penetrate a porous SiOx base layer. Protein adsorption of BSA is found to be affected by this hydration effect due to orientation of water molecules in the subsurface. Moreover, controlled drug release from a Ag reservoir is enabled for long-term antibacterial properties.

Recent progress in the understanding of plasma polymerization processes enables increased control and usability of functional plasma polymer films at the nanoscale. Dry and environmentally friendly processes can thus be implemented meeting the requirements for industrial applications.

Keywords
diffusion control
bacteria adhesion
protein adsorption
Plasma polymerization from Ar-HMDSO mixtures by single-filament dielectric-barrier discharges

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Hexamethyldisiloxane (HMDSO) has been used for plasma deposition of organosilicon thin films for several decades. Plasma polymerization from single-filament dielectric-barrier discharges (SF-DBDs) may be used to test and advance models of the deposition process and to develop new deposition methods. In the present study Ar-diluted HMDSO is used to deposit thin films from SF-DBDs between a tip electrode, covered by a plane dielectric, and silicon wafer pieces serving as substrates. Owing to the dominance of Penning ionization for HMDSO fractions larger than x ≈ 10 ppm, discharge durations are in the microsecond range and relatively wide truncated-cone-shaped microdischarges are visible with diameters of several millimeters close to the dielectric and typically 1 mm near the Si substrate. Thickness distributions and IR spectra of the deposits are measured using an FTIR microscope. For average cross-flow gas velocities $v_{av} \geq 100 \text{ cm/s}$, nearly circular-symmetric bell-shaped deposits with widths of the order of the filament diameter are obtained. We attribute this observation to the rapid drift and deposition of ions such as $(\text{CH}_3)_3 \text{Si-O-Si(CH}_3)_2^+$, formed by about 30 % of reactions between energetic Ar species and HMDSO, while neutral products of these reactions are carried away by the gas stream without being deposited. It is found that the deposition profiles are virtually not affected by the gas flow. FTIR spectra show characteristic differences with respect to typical spectra of plasma-polymerized (pp) HMDSO films deposited from DBDs with extended electrodes. These differences consist of e.g. a shift of the $\nu_{as}(\text{Si-O-Si})$ mode to short wavenumbers even below 1000 cm⁻¹, and a pronounced band from 2120 to 2130 cm⁻¹ due to the $\nu(\text{Si-H}_x)$ mode. These features are generally observed in low-pressure pp-HMDSO spectra, but absent in spectra of pp-HMDSO deposited at 1 bar.

Keywords
DBD
Single-filament
HMDSO
Plasma polymerization
Analysis and control of the nanoporosity of PE-ALD and PE-CVD SiOx-films on polydimethylsiloxane (PDMS) membranes

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The aim of the here presented work is the correlation of fundamental plasma parameters with surface chemical changes of plasma modified PDMS membranes and the resulting membrane properties. The goal is to be able to control the selectivity and permeability of the composite membrane, through tailoring of the micropores within the SiOₓ film. The parameters that control the micropore size distribution are determined both by the plasma characteristics, and the characteristics of the PDMS surface. Plasma process characteristics i.e. oxygen fluence and average incorporated ion energy are separately controlled; additionally, the deposition is performed onto differently pre-treated PDMS membrane films. The plasma-pretreated PDMS and the SiOₓ-coated membranes were investigated by means of surface spectroscopy (XPS, FTIR, ToF-SIMS) and AFM. The film structure was later correlated with the intrinsic pore structure as determined by Positron Annihilation Lifetime Spectroscopy (PALS) and electrochemistry. The analysis revealed the existence of micropores in the nanometer and subnanometer range with silanol groups terminating the relevant interfaces. Moreover, the results illustrate how the gradual conversion of siloxane groups to a SiOₓ network during plasma oxidation as a pretreatment step influence the nanoporosity and therefore the permeation of small molecules. Additionally, plasma-enhanced Atomic layer deposition (PE-ALD) was used for the deposition of SiOₓ on the PDMS and a comparison to the PECVD-deposited SiOₓ was done in terms of size distribution of micropores in the thin SiOₓ films and the film/substrate interphase. The PALS investigations proved to be an essential approach to understand the membrane properties of plasma polymer films.

Keywords
PDMS
SiOₓ
PECVD
PEALD
membrane
Plasma polymerization on porous materials: role of sticking coefficients on the penetration depth

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Plasma polymerization applied to the deposition of thin functional coatings on planar substrate reached its maturity because dozens of precursors and plasma conditions have been already tested. Anyway, it is inherently a very complicated process involving a plethora of particle species and numerous effects governing their production, transport, deposition, and possibly etching. For many applications, the substrates are not planar and we can encounter necessity to deposit films inside porous materias. In this paper we highlight some aspects which need to be considered for successful optimization of a low-pressure plasma polymer deposition process on non-planar substrates relevant for bioapplications such as biological tissue cultivation wells, porous scaffold and nanofibrous mats. It is clearly shown on example of cyclopropylamine/argon discharge that geometry different from the standard piece of silicon placed on the electrode changes the film deposition rate and thin film chemistry through altered diffusion pattern and different sticking probabilities of various film forming species.

\textbf{Keywords}
amine plasma polymers
porous scaffolds
nanofibrous mats
Wetting, de-icing and anti-icing behavior of roll-to-toll structured and plasma coated PU-films

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Ice formation on surfaces affects the functionality of means of transport, e.g. the wings of airplanes, or technical installations, such as rotor blades of wind turbines, and reduces their safety. This project in particular is researching a new approach to passive de-icing in flight operations of small and medium-weight helicopters. In addition to extending the operational availability (e.g. mountain rescue in winter or in bad weather), an active contribution to CO₂ and NOₓ savings is being made within the framework of environmentally friendly aviation. Furthermore, the safety of passengers, crews and third parties in aviation can be increased.

The passive de-icing system consists of microstructured, ice-repellent, self-adhesive PU films. These super-hydrophobic surfaces, with microstructure diameters of 35 µm or more, reduce wetting by water and at the same time reduce or delay ice formation. In addition, these films exhibit low ice adhesion.

The innovative approach is to combine a hot stamping roll-to-roll process to create different surface structures with plasma enhanced chemical vapor deposition (PECVD) for a coating. The layers consist of hydrophobic plasma polymers, mainly fluorocarbon (CF) precursors or hexamethyldisiloxane (HMDSO) are used as precursors.

The basics of the investigations focus on ice formation and ice adhesion on the functionalized films. Different chemical compositions of the deposited plasma coatings in combination with different structures are investigated for their anti-ice effect and the manufacturing process is optimized. The aim is to achieve the lowest possible wetting with water by hydrophobic surfaces in advance. If ice freezes out on the surfaces, the ice adhesion force for removing the ice must be as low as possible in order to achieve effective de-icing. The anti-ice foils can be applied flexibly on particularly relevant surfaces on the helicopter (skid landing gear, tail boom, Fenestron tail rotor) or on other surfaces susceptible to ice (e.g. ski lifts).

Keywords
PECVD
PU-film
de-icing
wetting
Additive manufacturing methods, such as direct metal deposition, are becoming increasingly important. Spraying technologies such as thermal or plasma spraying [1], but also laser cladding or laser metal deposition (LMD) [2] [3] play a central role for additive metal direct deposition. However, these spraying technologies itself are not suitable for the field of micro structuring. At the other side specific direct metal deposition technologies are more and more used for MEMS production. The inkjet and aerosol printing processes are particularly noteworthy here. The printing of nanoparticles is progressively applied to produce electrical leads and contacts on the desired surfaces. Both processes work with prepared nanoparticles that are generated from a dispersion or an aerosol from a dispersion. [4] [5] However, these established technologies have some disadvantages, as handling and cost-efficiency. In this paper a new production process is presented, which uses the novel technology of atmospheric pressure sputtering [6] [7] to apply directly metallic conductors onto three-dimensional substrate surfaces. It is based on thin film direct coating of gold and platinum for high temperature interconnection technology. Other process able materials are palladium and silver. The advantages of this new production process compared to similar conventional technologies will be explained. These advantages are for instance lower raw material consumption, lower technology costs, higher electrical conductivity and a higher flexibility of production. Furthermore, layer thicknesses below 100 nm and above 10 μm can be realized with this new technology. Maximum static deposition rate of the standard material gold depends on the final layer porosity and lies between 500 nm/s for 90% and 50 nm/s for less than 1% porosity. Limitations are until today, the structural widths of at least 700 μm. The reasons for this characteristics and how it may can be improved in the future will be also explained in this paper.

Keywords
Additive Manufacturing
Atmospheric pressure sputtering
Vanadium dioxide (VO$_2$) undergoes a metal-semiconductor transition at $T_c = 68^\circ$C. In the semiconductor state (temperature lower than $T_c$), VO$_2$ presents a monoclinic structure, high transmittance in the infrared region and high electrical resistivity, while as metal (temperatures higher than $T_c$) exhibits tetragonal rutile structure, low transmittance and low electrical resistivity. The abrupt change of these properties makes this material suitable for several industrial applications, such as near-infrared modulation in smart windows, thermal solar collectors and so many others. However, the numerous phases belonging to the V-O system still challenge the production of pure VO$_2$ with excellent thermochromic properties.

To obtain thermochromic VO$_2$, we have chosen to modify the sputtering oxidation coupling method [1] using another precursor: vanadium nitride (VN). We have already shown that polycrystalline VN is an interesting precursor to synthesize thermochromic VO$_2$ films. In this work, single crystallized VN thin films were deposited on MgO substrates by reactive magnetron sputtering. The epitaxial as-deposited VN films (50 nm thick) were annealed in a pre-heated furnace at different durations and three temperatures in the range of 450°C-550°C. Raman spectrometry, X-ray diffraction, SEM and TEM were performed for structural and morphological characterizations of the epitaxial VN films and the VO$_2$ ones. The thermally-induced properties of the oxidized VN films were analyzed, in the 30-120°C temperature range, in terms of their electrical resistance employing four-point probe method and their emissivity modulation properties by infrared camera. The choice of the correct values during the annealing process, altogether with the results from characterization techniques, provide us to identify the accurate parameters to achieve thermochromic VO$_2$ films.


Keywords
Vanadium dioxide, Thermochromic films, Epitaxial growth
Passive Sensor Coatings to Detect Critical Temperature-Conditions in High-Performance Fiber Applications

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Ropes and belts made of synthetic fibers are increasingly applied for hoisting, industrial tractions, and supporting elements in constructions, but also for mountain climbing robes and safety belts. Above a critical temperature, high performance fibers may lose their mechanical properties resulting in unexpected failure under load. Therefore, a passive 'structural health monitoring' sensing the temperature history of these ropes would be useful. In this study, we introduce a method to functionalize polymer fibers with thermochromic optical phase-change coatings by Magnetron sputtering that enable signaling of deterioration caused by thermal history. These smart coatings are comprised of an index-tunable anti-reflection coating based on chalcogenide phase change materials (PCM). In a first step, the optical contrast for the amorphous-to-crystalline transition of Ge₂Sb₂Te₅ (GST) structures upon heating to the critical temperature, $T_c$, were simulated on gold reflectors. In a second step, the GST coatings were applied on flat substrates comprising a silver reflector. We found, that the color change can be adjusted by the Ge content to the demanded temperature range. Finally, the results are demonstrated on two different polymer fibers with different deterioration temperature. Polyethylene terephthalate (PET) monofilaments ($T_c \sim 150°C$), and liquid-crystal aromatic polyester (LCAP) yarn ($T_c \sim 300°C$) were coated with the passive sensor system enabling the detection of thermal history by the color change of the PCM visible by eye.

Keywords
thermochromic
Ge₂Sb₂Te₅
synthetic fibers
sputtering
The piezoelectricity of aluminum nitride (AlN) is widely used in industry for MEMS sensors and actuators [1]. Besides, AlN can be utilized for energy harvesting from mechanical vibrations where it even succeeds the performance of lead zirconate titanate (PZT) due to its low permittivity [2, 3]. In recent years, AlN has gain much attention in the field of ultraviolet (UV) photonic devices due to its high band-gap (6.2 eV), large thermal conductivity and low thermo-optic coefficient [4].

In this study, AlN was deposited on a c-plane (0001) sapphire substrate by using reactive magnetron sputtering with a scia Magna 200 at an elevated substrate temperature of 450 °C. Detailed information about the sputtering system, process parameter settings and process monitoring are presented. It is shown, that optical emission spectroscopy is a powerful method to characterize the process at high N$_2$/Ar ratio and elevated substrate temperature. The crystal structure was investigated by using x-ray diffraction (XRD). The existence of the (0002) peak shows the epitaxial growth of the AlN on the (0001) sapphire. Further study of the crystalline lattice was done by rocking curve measurements. Atomic-field microscopy was used to extract the surface roughness. Further, optical properties were investigated by ellipsometry. As a result, the deposited 300 nm thick AlN layer is c-axis textured which is confirmed by a FWHM of 1.5° (rocker curve measurement) The surface roughness measurement yield 1.7 nm RMS. This investigation proves the excellent crystalline quality of the sputtered AlN which makes it suitable for UV photonic devices and MEMS.

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[3] C. Fei et al., DOI: 10.1016/j.nanoen.2018.06.062
[4] C. Xiong et al., DOI: 10.1142/S0129156414500013

**Keywords**
sputtering
reactive
piezoelectricity
epitaxial
crystallinity
**Tailored ITO deposition at room temperature for optical and electrochemical bio-sensors**

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Our work focuses on the investigation of nanostructured surfaces for advanced sensors based on optical fibre. Conventional, fibre sensors utilize concepts of intensity, phase or wavelength modulation. However, our novel approach aims at the development of a fibre sensor that is capable to combine not only the standard optical way of detection but an electrochemical way of detection as well. We used to employ a lossy mode resonance (LMR) effect for optical detection. Furthermore, in our concept, we also utilize the fibre sensor body as an active working electrode in cyclic voltammetry measurements for electrochemical detection. By other words, the surface of the optical fibre needs to be tailored to achieve an LMR effect together with a relevant response for cyclic voltammetry.

The LMR effect occurs when light propagating through the optical fibre core refracts at the film-core interface. The resonance conditions are determined by the layer properties (refractive index, dielectric constant) covering the fibre core and the medium being investigated. On the other hand, the film resistivity and mobility of carriers are the key parameters for the efficient working electrode in cyclic voltammetry. Both parameters can be achieved by tailored indium doped tin oxide (ITO) film deposited onto the bare fibre core. Hence, the contribution focuses on the characterization of plasma discharge and ITO films deposited by pulsed magnetron sputtering. Optical, electrical and structural properties were tailored as a function of reactive process gases, namely O₂ and N₂, using optical ellipsometry, UV-VIS, four-point probe method, AFM and XRD. Experiments show that proper introduction of reactive gases into discharge induces crystalline films with various preferred orientations without any post-deposition annealing. Beside film investigation, we carried out cyclic voltammetry and LMR measurements for detection of selected biomolecules. This study was supported by the Czech Science Foundation (Grant Number GACR 19-20168S).

**Keywords**
ITO, Optical fibre, LMR, Electrochemistry, Bio-sensors
Hybrid Reactive High Power Impulse Magnetron Sputtering System used for the Deposition of Semiconductor Thin Films for Photoelectrochemical Applications.

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A hybrid high power impulse magnetron sputtering combined with an electron cyclotron wave resonance plasma source (r-HiPIMS+ECWR) was used for the deposition of p-type CuFeO$_2$/CuO and n-type Fe$_2$O$_3$:Sn thin films. These p-type and n-type semiconducting oxides work as photocathode and photoanode for solar water splitting PEC cells, respectively. Two magnetron sources were used for the reactive co-sputtering. An additional plasma source based on special modification of inductively coupled plasma ECWR, was used for further enhancement of plasma density. A RF planar probe was used to investigate the time evolution of ion flux density during the pulsing cycle. A special modification of this planar RF probe made it possible to investigate the time evolution of both $T_e$ and of the ion concentration $n_i$. Generally, it was found that the obtained ion flux density and the $T_e$ were systematically higher in case of r-HiPIMS+ECWR plasma compared to pure r-HiPIMS during the active part of the discharge pulse. CuFeO$_2$/CuO thin films were deposited at different conditions and various crystal structures were achieved after annealing in air and in vacuum. Photocurrents in cathodic region for different crystal structures were observed by chopped light linear voltammetry and chronoamperometry. Fe$_2$O$_3$ films doped with Sn were investigated from the point of view of maximum achieved photocurrents in anodic region under illumination in dependence of crystal structure and Sn dopant concentration.

Keywords
plasma
HiPIMS
films
semiconductor
deposition
Chromium nitride deposition onto silicon pyramids for supercapacitor applications

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Transition metal nitrides are widely studied materials for electrochemical capacitors (ECs), due to their good electrochemical performance and good cycling life stability. In addition, they are easy to synthesize, especially by magnetron sputtering. However, the dense nature of the coating deposited by sputtering is one of the limiting factors to achieve high specific capacitance. One of the solutions to increase the capacitance lies in the increase of the specific surface either of the active material – as recently reported in the glancing angle deposition of CrN to obtain porous film – or of the substrate, prior to deposition. In this view, we report the use of silicon pyramids coated with chromium nitride for supercapacitor applications. The well-defined micrometer-sized silicon pyramids are synthesized by fast and low-cost chemical etching and are coated by reactive magnetron sputtering of chromium in argon and nitrogen. The resulting CrN@3D silicon Pyramids core-shell have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD), and electrochemical characterization. A high specific capacitance of 187.5 mF.cm⁻² is obtained on 0.5M H₂SO₄ electrolyte at scan rate of 2 mV.s⁻¹ (92.6 at current density of 0.6 mA.cm⁻²) with excellent stability over 10000 cycles. In addition, a solid-state symmetric device have been assembled with CrN@PySi electrodes and exhibits a high areal capacitance of 140.2 mF.cm⁻² at a scan rate of 2 mV.s⁻¹, with a high energy density of 8 µWh.cm⁻² at a power density of 240 µW.cm⁻² with long cycle life (10000 cycles). The combination of CrN coating and Si pyramids appears thus to be a potential solution for low-cost energy storage applications.

Keywords
CrN
transition metal nitride
electrochemical capacitor
Renewable Energy for Nitric Acid Production with Atmospheric Microwave Plasma

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Since electricity from renewable sources of energy is subject to fluctuations, energy consumption on demand plays a crucial role to create a reliable grid system. The annual nitric acid production is around 150 million tons worldwide. It is typically produced using the Ostwald process through the cathalytic oxidation of ammonia from the Haber-Bosch process. An undesirable by-product is emitted during the production of nitric acid: Nitrous oxide (N₂O) is a greenhouse gas that is 265 times more harmful to the climate than carbon dioxide.

In 1903 the Birkeland-Eyde process was invented using an arc for the production of nitrogen monoxide NO. NO is then oxidized to nitrogen dioxide NO₂ which reacts with water to form nitric acid HNO₃. But this type of production is only profitable when electricity prices are low.

A process for producing nitrogen dioxide from nitric acid for the production of nitric acid using atmospheric pressure microwave plasma process is presented. On the basis of technological requirements for a microwave plasma unit for NO₂ production a modular plasma torch, which enables a “self-ignition” and stable operation of an air plasma over a wide range of parameters, has been constructed. Due to the flexible operating mode, excess capacities of photovoltaics and wind can be used on demand. The air plasma has been investigated via optical emission spectroscopy and FT-IR absorption spectroscopy in order to determine the plasma parameters as well as the energy and conversion efficiency.

Keywords
atmospheric pressure microwave plasma
renewable energy
nitric acid production
climate protection
Gliding arc plasmatron- plasma chemical reactor for methane conversion

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A gliding arc plasmatron (GAP) is applied as part of plasma chemical reactor for methane conversion and synthesis of carbon containing materials without associated carbon dioxide production. This plasma source can be operated in two different modes, namely gliding arc channel with diameter of 0.2-0.3 mm in a vortex gas flow and “plasma plume” mode, with one (or several) hot and broad plasma object(s) with diameter 4-5mm incorporated into the gliding arc channel. Plasma conditions and efficiency of methane conversion in these two modes are very different. The first GAP mode is characterized by a gas temperature of 2000K-2500K, electron density of about $10^{14}$ cm$^{-3}$ and methane dissociation frequency of about $10$ s$^{-1}$. Under these plasma conditions manly formation of methyl radicals by methane dissociation is expected. Plasma of “plasma plume” is very hot – 5500K-6000K, electron density amounts to about $10^{15}$ cm$^{-3}$ and frequency of thermal methane dissociation is about $10^7$ s$^{-1}$. Under these plasma conditions methane will be completely dissociated. With optimized GAP geometry, gas flow rate and electric current (200-300 mA) plasma plume has contact to the plasma reactor surface only via thin GA channels. At that material of electrodes is not thermal overloaded and no metal lines are observed in emission spectrum of plasmatron. Switching between modes is possible by variation of plasma reactor geometry and gas flow rate.

Keywords
gliding arc
plasmatron
methane conversion
Microstructure, optical and electrical properties of p-type copper iodide thin films

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Copper iodide (CuI) is a p-type semiconducting compound that has turned out to be important in different material studies. The most interesting properties of copper iodide correspond to its high transmittance in the visible range combined with a high electrical conductivity that is close to that of ZnO:Al. Furthermore, CuI is suitable for applications in perovskite solar cells due to its ability to be bonded with many organic and inorganic ligands. Among the different structures of this material, the zinc blende like structure ($F4 \overline{3} m$) exhibits the best functional properties.

In this work thin films of CuI have been synthesized by the iodination of sputtered Cu thin layers with iodine vapor. We obtained transparent p-type semiconductors films and $\gamma$-phase of copper iodide ($\gamma$-CuI) with wide bandgap ($E_g \approx 3.1$ eV). The structural, electrical, and optical properties of CuI thin films deposited on glass and silicon substrates were studied by XRD, Hall effect, UV-VIS spectrometry, and photoluminescence. We observed that the growth of CuI on highly oriented copper leads to the formation of strongly textured along the [111] direction. As-prepared film shown a resistivity ($\rho$) of $12.8 \times 10^{-2} \Omega$ cm, hole density ($p$) of $1.8 \times 10^{20} \text{cm}^{-3}$, and mobility ($\mu$) of $35.6 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. As a result, specular transmittance of 48% was set at in averaged visible range. These findings would be used to assist studies in transparent electronics on applications of thin films $\gamma$-CuI. Thin-film morphology, examined by SEM, shows a variation of crystal size depending on the elaboration conditions. Crystallographic twin domain in CuI has been observed by using transmission electron microscopy (TEM) and selected area electron diffraction (SAED) through which we can understand the twin geometry and orientation, which are essential for further improving perovskite solar cells.

Keywords
Copper iodide, Sputtering, Semiconductor, Photovoltaic
Recent studies on II-IV-V$_2$ nitrides evidenced that this class of materials are potential candidates for photovoltaic applications due to their tunable band gap (1.4-3.2 eV). Furthermore, they are composed of earth-abundant and non-toxic elements for a low-cost industrialization. They may replace In$_x$Ga$_{1-x}$N alloys materials commonly used for optoelectronics devices because they present the same properties [1]. Few years ago, studies from Atwater’s group showed that a large composition of alloys can be grown without phase separation. Moreover, they exhibit a lower formation enthalpy than InGaN alloys [2]. Recently, few works investigate the disorder caused by unintentional oxygen incorporation, and the grains boundaries oxygen contamination in ZnSnN$_2$ thin films [3]. To reduce oxygen contamination and improve physico-chemical properties, a new approach is investigated by the use of bias during film growth. This work shows the results of ZnSnN$_2$ thin films grown by reactive co-sputtering using zinc, and tin metallic targets in a reactive nitrogen atmosphere in high vacuum chamber. The application of different bias power during the growth (from 0 to 30 W) modified the morphology, the texture and the properties of the thin films. The atomic content of oxygen can be significantly reduced by applying a bias power (from 6.3 to 2.4 at.%). The optical band gap has been deduced from UV-visible spectroscopy and electrical properties was investigated by four point probe method and hall effect measurements. The bias power decreases the experimental band gap energy until 1.42 eV by reducing the high electron carrier concentration responsible of the Burstein-Moss effect. Furthermore, applying a 30 W bias slightly enhances the activation energy and photoconductivity.


**Keywords**
photovoltaic, ZnSnN2, bias effect, thin films, magnetron co-sputtering
EU vision and initiatives on the Energy Transition

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Will follow soon.

Keywords
Energy Transition
Plasma activated electrochemical conversion for the electrification of the (chemical) industry

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Will follow soon.

Keywords
electrical conversion
plasma
ORD202

**Industrial equipment and coating solutions for the challenges of the energy-transition**

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Will follow soon.

**Keywords**

Keywords
Overview of developments of hydrogen technology

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Hydrogen technology is meanwhile recognized as key to enable decarbonisation and the use of large scale renewable energy for several industrial sectors. Zentrum für BrennstoffzellenTechnik GmbH (ZBT) is a development centre located in Duisburg Germany to support the industry with the development of hydrogen and fuel cell technology. This presentation will explain the main technologies and products that are being developed and general trends with a focus to the transportation sector including corresponding scaling and cost challenges for the industry. IHI Hauzer, one of the industrial partners of ZBT, is a coating equipment manufacturer for the automotive sector and is developing low cost coating technology for fuel cell bipolar plates. Coated steel is seen as the most promising material for bipolar plate manufacturing as this enables compact size, long fuel cell life time and low cost. Now that many coatings have been tested meanwhile by the automotive industry, the main challenge is to scale up while maintaining high quality. This presentation will show the coating test results and solutions for high volume manufacturing.

Keywords
Hydrogen technology
Fuel cell technology
Bipolar plate coating
High volume equipment
Proton Exchange Membrane (PEM) fuel cells and electrolyzers are in full development for automotive and industrial applications. Due to volume restrictions the classical graphite bipolar plate loses against a Titanium or Stainless Steel bipolar plate. Key is to keep a low Interface Contact Electrical Resistance and to avoid corrosion. The corrosion of metal in the PEM electrolytic environment of acidic character is one of the main challenges, since it decreases the efficiency and shortens the lifetime of the whole stack. The root causes are metal ions out-diffusion poisoning the catalyst and electrolyte, and non-conductive oxides formation increasing the electrical resistance. The problems outlined above are being overcome or minimized by applying corrosion-resistant and simultaneously electrically conductive coatings. This work extensively investigates the electrochemical and electrical properties of DOT™ and metal-doped ta-C coatings. The cornerstone of DOT™ coating is thermal spraying of noble metal droplets forming the electrical contact points and simultaneously the corrosion-resistant surface oxide layer of the base metal or metal interlayer. Both coatings meet the U.S. Department of Energy technical targets for PEM fuel cell and electrolyzer components by exhibiting very low values of interfacial contact resistances < 10 mΩ·cm² and corrosion currents < 1 µA/cm² in simulated PEM environment.

**Keywords**
Fuel Cells
Electrolyzers
PVD
Thermal Spraying
Energetic Tailoring of Magnetron Sputtering Deposition Processes for Defect-sensitive Materials: Transparent Conductive Oxides and other Semiconductors

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Since more than 40 years, magnetron sputtering is a widely used large-area, plasma-assisted deposition method for many industrial applications, especially used in fields like architectural and low emissivity glass coatings, mirrors and absorbers for solar concentrators, magnetic films for hard disks or hard coatings for tools, i.e., mainly for metals, oxides and nitrides. In the thin film photovoltaics industry, magnetron sputtering is the established technology for the deposition of metallic back contacts (Ag, Mo) and transparent, conductive window layers (ITO, ZnO) or for metallic precursor films. However, it is not yet applied on a technical scale for the absorber layers in thin film solar cells, i.e., for active semiconductors.

In this review, obstacles are outlined, which postpone the use of reactive magnetron sputter deposition for active semiconducting layers. The energies of species (sputtered atoms, positive and negative ions, energetic neutrals) are discussed and its influence on the film growth, especially of reflected neutral argon atoms (Ar$^0$) and negative ions (O$^-$, S$^-$, Se$^-$). Due to the low defect formation energies of semiconductors, tailoring of the discharge conditions (sufficiently low particle energies) is mandatory for the preparation of defect-poor semiconducting films of high electronic quality by reactive magnetron sputtering (RMS).

We present some highlighting results for the deposition of active chalcopyrite absorber films for efficient thin film solar cells (Cu(In,Ga)Se$_2$), as well as for transparent conducting oxides (ZnO) and discuss the challenges of epitaxial film growth for active nitride semiconductors (GaN etc.).

Keywords
reactive magnetron sputtering
defect generation
active semiconductors
energetic particles
In this work we present a plasma deposition technique that allows fast reactive deposition of various oxide layers with extremely high deposition rate. The new approach combines reactive sputtering by DC hollow cathode discharge with thermal evaporation from the hot surface of the hollow cathode. As an example of successful fast deposition, thin and thick layers of titanium dioxide (TiO$_2$) or cobalt oxide (Co$_3$O$_4$) were prepared using this technique. The uncooled titanium (or cobalt) nozzle served as a hot hollow cathode and simultaneously as an inert gas (Ar) inlet. The reactive gas (O$_2$) was introduced into the vacuum chamber through a separate inlet, which effectively prevents oxidation of the cathode material. During deposition, the temperature of the hollow cathode reached up to 1600 °C, depending on the discharge parameters. This made it possible to combine the ion sputtering of hot hollow cathode with its thermal surface evaporation, which significantly increased the deposition rate. The instantaneous value of deposition rate was measured by quartz crystal microbalance (QCM) technique. For titanium dioxide, the highest achieved deposition rate was 567 nm/min (34 μm/h), which (with respect to the geometry of this process) corresponds to the total volume of deposited TiO$_2$ material 1.2 mm$^3$/min per 1 kW of absorbed power. Despite extremely high thermal flux to the substrate, TiO$_2$ films were successfully deposited even on thermally-sensitive PET foil. However, the layers prepared by a single nozzle are considerably inhomogeneous. For the deposition of homogeneous films, a several plasma jets arranged side by side has to be used. In such configuration, we have prepared transparent TiO$_2$ layers with a high refractive index on micro-structured polymer substrates.

**Keywords**
Hollow cathode discharge
Sputtering
Thermal evaporation
Deposition rate
TiO$_2$
ORE102

**Reactive HiPIMS deposition of Ti-Al-N: Influence of the deposition parameters on the cubic to hexagonal phase transition**

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The introduction of enhanced ionization rates during reactive high-power impulse magnetron sputtering (R-HiPIMS) allows for additional pathways in tuning the structural and chemical evolution by surface-diffusion driven growth. Hence, especially depending upon the charge state and mass-ratio of the metal-ions incident on the growing film, metastable thin films are decisively influenced in their overall growth characteristics. Here, we review in detail the dependence of the phase-stability (*i.e.* \(x_{\text{max}}\)) on varying deposition parameters during R-HiPIMS of Ti-Al-N thin films using Ti\(_{1-x}\)Al\(_x\) composite targets. The influence of HiPIMS pulse parameters such as frequency, pulse length, or peak power density, but also of deposition parameters including \(N_2\) partial pressure, substrate bias voltage, or target compositions were investigated methodically. The so obtained coating structures were analysed with respect to phase-stability, thermo-mechanical properties, and morphology applying nanoindentation, X-ray diffraction combined with electron imaging techniques. The systematic studies revealed an Al solubility limit of \(x_{\text{max}} \sim 0.55\), obtained for a duty cycle of 3.75 % and a \(N_2\)-to-Ar flow-rate ratio of 0.3. Moreover, sufficient intermixing of the arriving film species controlled via bias potentials was observed as decisive for the deposition of high Al containing fcc-structured coatings. Based on time- and energy resolved mass-spectroscopy measurements it can be concluded that the ratio and energy of Ti\(^{n+}\)- and Al\(^{n+}\)-ions, arriving simultaneously at the substrate surface, are highly influential for stabilising the preferred cubic modification with respect to the prevailing deposition conditions.

**Keywords**
R-HiPIMS  
Mass-spectroscopy  
Phase Formation
Particles in coating technology are undesirable, but unfortunately, they can never be completely avoided. What are particles? - What size? - Where do they come from? - How can they be reduced? Every coating process is always faced with particles as disturbing variables. Particles impair or destroy the functions of the layers. They interrupt conductor tracks, create short circuits, make holes (diffusion paths for water or ions), prevent correct exposure in photolithography, create defects (display), scatter optical layers (laser mirrors), reduce the yield and much more. The list is long and the causes of particles are diverse. The lecture explains the relationships and causes of particle formation in sputtering. Topics like:

- System design, system cleanliness and surfaces
- Vacuum generation, pumping and venting
- Cathode-compartments, shielding, materials, expansion coefficients
- Cathodes-types, planar or rotary cathodes, design,
- Targets, structure, density, composition
- Power supplies, arc handling, bipolar sputtering
- Reactive processes
- And much more

are discussed. Particular attention is paid to the formation of particles in process technology as a whole and the role of Arc's in the process. For this purpose, some very interesting calculations are presented. Furthermore, the lecture gives recommendations and tips for reducing particles in everyday use.

**Keywords**
particles
layerdamage
pinholes
arcing
arc-energy
Mechanical properties and thermal stability of reactively sputtered multicomponent Hf-Ta-Ti-V-Zr nitrides

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High-entropy alloys (HEAs) and high-entropy ceramics (HECs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Within this work, we report on the thermal stability of high entropy nitrides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)N coatings were reactively sputtered from a single powder-metallurgically produced composite target and vacuum annealed between 600 and 1500 °C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, nanoindentation, transmission electron microscopy, thermogravimetric analysis, and atom probe tomography.

We observe a promising thermal stability of the single-phase face-centred cubic (fcc) coatings up to 1400 °C, whereas coatings annealed at 1500 °C indicate a slight decomposition into a nitrogen-depleted hexagonal phase next to the fcc matrix. As the XRD peak width remains relatively constant, we assume that the expected thermally-induced grain growth and/or decomposition takes place at significantly higher temperatures than compared to coatings like TiN and TiAlN. Our here presented results represent a promising basis for a further improvement in order to establish (HfTaTiVZr)N coatings as a candidate for (novel) high temperature applications.

Keywords
high-entropy alloys (HEAs)
high-entropy nitrides
magnetron sputtering
thermals stability
atom probe tomography
Enhancing the corrosion protection capability TiN and CrN PVD coated mild steels by addition of Mg-Rare Earth

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Today, innovative coatings must ensure wear protection and corrosion resistance for corrosive substrate materials, e.g. mild steel. Unfortunately, state of the art PVD coatings still lack in corrosion performance due to the low coating thickness and the presence of coating defects. An innovative solution to improve the corrosion properties is alloying TiN or CrN based PVD coatings with MgRE (RE = Rare Earth). The authors developed monolithic TiMgGdN coatings of 4-5 µm thickness using an industrial magnetron PVD, which exhibit a superior corrosion resistance of at least 800 h in the salt spray test without any macroscopic corrosion attack [1].

In the present work, the influence and the effect various rare earth metals (Gd, La, Ce) on the coating properties and the corrosion performance was investigated. The chemical composition was varied using segmented multi-component targets consisting of segments of the coating material metals Ti and Mg-RE.

As benchmark, conventional PVD coatings, DLC and electroplated Cr were included in the examination. 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.

It will be shown that both, the corrosion performance as well as the mechanical properties can be optimized by the choice of the Mg-RE constituent and the TiN or CrN matrix material.


Keywords
Magnetron PVD
Corrosion
Wear
Improving phase stability, hardness and oxidation resistance of reactive magnetron sputtered (Al, Cr, Nb, Ta, Ti)N thin films by Si-alloying

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High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance while also improving thermal and mechanical stability of the alloy.

(Al\textsubscript{v}Cr\textsubscript{w}Nb\textsubscript{x}Ta\textsubscript{y}Ti\textsubscript{z})N coatings were formed in a cubic solid solution in thin film form by reactive magnetron sputtering in N\textsubscript{2}-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at\% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm\textsuperscript{3} each) of Si on the cathode racetrack during deposition. The hardness and indentation modulus of the as-deposited samples were ~32.6 GPa and ~462 GPa without Si, and ~35.4 GPa and ~328 GPa with Si, respectively. X-Ray Diffraction (XRD) measurements of the samples after vacuum annealing to temperatures up to 1200 °C revealed that Si delays the decomposition from 1000 °C to 1200 °C. After vacuum annealing to 1100 °C we measured a hardness of ~30.3 GPa and ~38.1 GPa as well as an indentation modulus of ~445 GPa and ~430 GPa for the samples without and with Si, respectively.

We gauged the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30, and 100 h. After these durations we extracted the samples from the hot zone and analysed them with XRD, and Energy-Dispersive-X-Ray-Analysis (EDX). Without Si, the oxide scale was 2800 nm thick after 100 h, with Si-alloying the oxide was only 300 nm thick. Thus the oxidation resistance was improved significantly. Based on our results we can conclude that this type of high entropy nitride coatings, especially when alloyed with Si, provides excellent thermomechanical properties as well as oxidation resistance.

Keywords
High Entropy Ceramic
Hard Coating
Oxidation
Magnetron sputtering of Sn acetylacetonate coatings for sensor applications

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Sn acetylacetonate (SnAcAc) is an organic compound that is widely used as an active medium of chemical gas sensors for the detection of reductive gases like H\textsubscript{2}, CO, CH\textsubscript{4}. Its functionality is based on changing electrical resistance of the active layer in the presence of adsorbed gas. Thus the adsorption of reducing gas species control the conductivity of layer that strongly depends on surface morphology and structure of SnAcAc. In this work, we focus on the preparation of SnAcAc coatings by magnetron sputtering technology. This solution combines the sputtering target material with subsequent plasma polymerization of the sputtered molecules transported towards the substrate. This polymerization process takes place under suitable conditions of plasmatic discharge and working gas pressure. The SnAcAc coatings were prepared by means of RF magnetron sputtering from SnAcAc target in Ar gas. The sensitivity of the active medium can be enhanced by uniformly embedded SnO\textsubscript{2} nanoparticles in the SnAcAc matrix. Therefore, we prepared the target by mixing the SnAcAc with SnO\textsubscript{2} powder at different proportions, followed by a pressing and sintering process. The gas pressure was chosen between 2 and 10 Pa to tune the polymerization process. We prepared a number of samples of SnAcAc coatings on Si and fused silica substrates. The surface morphology of the prepared coatings was studied by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical bonding was studied using infrared and Raman spectroscopies. The electron-transport properties were evaluated by Van der Pauw method and Hall effect measurement. These layers were also deposited on special sensor substrates with interdigital Pt electrodes to test their sensitivity to the selected gases.

Keywords
Magnetron sputtering, acetylacetonate, gas sensors
Monitoring structure and physical features of NiTiO3 thin films grown by RF-magnetron sputtering

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Nickel titanate NiTiO₃ (NTO) is a transition metal oxide adopting three possible structures: Ilmenite structure (IL), which is the most stable, LiNbO₃-type structure (LN) and corundum-type structure (CR). NTO-IL is an n-type antiferromagnetic semiconductor used as gas sensors and as photocatalyst in the removal of organic pollutants from water. NTO-LN is predicted, by theoretical studies, to display a ferroelectric order in addition to its antiferromagnetic order. NTO-CN is a disordered structure usually stable at high temperatures (>1200°C).

While NTO-IL synthesis and physical properties have been reported in literature by several studies, few papers report on NTO-LN and NTO-CR compounds. Scarcity of reports is mainly due to its complicated synthesis conditions. Indeed, bulk material synthesis requires very high pressure and high temperature, and monocrystalline substrates with specific orientations for thin films growth. NTO-LN/CR synthesis has never been reported by magnetron sputtering despite the ability of this method to stabilize metastable structure by inducing residual and/or epitaxial stresses.

This work is focused on the preparation of NTO thin films by magnetron sputtering. NTO is sputtered from metallic targets (Ni and Ti) in convergent configuration on various substrates. Plasma parameters, substrate’s nature and deposition temperature are the main keys to monitor structure and preferred orientation of NTO. Chemical composition and morphological features of NTO thin films are investigated by Energy Dispersive X-ray spectroscopy and Scanning Electron Microscopy, respectively. The crystalline structure is examined by X-Ray diffraction, Raman spectroscopy and Transmission Electron Microscopy. Ferroelectric domain configuration and switching are investigated by Piezoelectric Force Microscopy. Thanks to the parameter optimization of magnetron RF-sputtering technique, control of NTO structure (IL, LN or CR) is achieved. Physical properties were related to the processing conditions of NTO films and their structural, morphological and physical features.

Keywords
NiTiO₃, multiferroic, sputtering
Are plasma nitriding treatments effective in changing wettability and evaporation of sessile water droplets on austenitic stainless steel surfaces?

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Wetting and evaporation of sessile droplets on engineered surfaces is now intensively studied. So, improving phase change heat transfer is important to meet the rising global energy demand in a sustainable manner in various industrial applications: thermal generation of electricity, electronics cooling, heat exchangers. Plasma nitriding is widely used to improve the surface properties of steels and is an attractive way to increase the durability of patterned steels. Strangely, the wettability of nitrided surfaces is poorly studied. The purpose of this communication is to study the ability of nitriding treatments in modifying the wetting and evaporation of sessile droplets on AISI 316L. The use of a multi-dipolar plasma coupled to substrate heating device for the nitriding treatment provides independent substrate biasing. It is thus possible to tailor the surface before and during the nitriding treatments. Wettability is extremely sensitive to the surface conditions, both from a chemical and topographical point of view. As it will be shown in this communication, a nitriding treatment can induce both types of modifications. Thus, for a 1 ml of pure water, the contact angle measured on a freshly polished surface of AISI 316L is 40°. If this surface is exposed to air for several days, it loses part of its hydrophilicity and the contact angle turns to 60° or even more. The cleaning treatment (Ar-H\(_2\) plasma), carried out before nitriding treatments, produces topographical modifications of the surface by selective sputtering of the grains. It is thus possible to reach contact angles between 80 and 90°. We obtain similar results when the nitriding treatments are carried out with a rather high bias (-200 V). For nitriding treatments carried out with lower bias (between 0 and -50V), surface contamination occurs and a discontinuous oxide layer is formed. The characterization by TEM of these oxides shows that they are amorphous and made up only of iron. The nanostructure formed by these oxides gives contact angles up to 120°. Finally, controlled polishing of the surface of the nitrided samples eliminates any physical contribution to wettability. Thus, an intrinsically hydrophylic chemical behaviour (contact angle 35°) of the nitrided layer is highlighted.

**Keywords**
wettability, nitriding, plasma cleaning, evaporation, stainless steel
ORE301

**Plasma surface interaction and modification on the nanoscale - Towards in situ TEM studies**

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Fabrication or modification of nanostructured materials and surfaces often requires plasma processes. The understanding of the interaction between plasma discharge and material itself is limited by state-of-the-art analysis only being available in an *ex situ* approach. Plasma treatment and material analysis via e.g. TEM, SEM or XPS are separated. To overcome this separation a microplasma chamber based on proof-of-principle experiments by Tai et. al [1] for *in situ* plasma treatment inside a TEM is in development. Thus, enabling the direct study of the plasma-surface interaction.

The effects of plasma treatment on highly porous, functional materials such as tetrapodal ZnO [2], Aerographene [3] and aero GaN [4] are investigated in an *ex situ* approach using TEM analysis. Plasma induced nitriding and, thus, functionalization of Aerographene was successfully achieved by treatment in a capacitively-coupled RF N\textsubscript{2} plasma. The effects of H\textsubscript{2} and H\textsubscript{2}/O\textsubscript{2} mixture plasma treatment on t-ZnO and the residual ZnO layer on the inside of aero GaN were investigated, too.

Furthermore, the plasma permeability of aero materials is investigated by using the surface activation of polymers and subsequent change in contact angle as marker for plasma penetration. Finally, we present an outlook for adapting the *ex situ* experiments to our *in situ* microplasma chamber as well as preliminary results.

REFERENCES:

**Keywords**
in situ techniques
microplasma
TEM
Newest developments in Plasma Diffusion Treatment

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Plasma diffusion treatment has been used in industry for more than forty years now. Many of the long-standing processes are still used daily. However, extensive new developments were necessary to keep plasma diffusion treatment competitive. Industrial use of plasma nitriding and plasma carburizing of ferritic steel started in the 70s and 80s. Surface hardness and wear resistance were the important technical features at this time. Nowadays, the requirements of surface treatment processes are much more versatile. As a matter of course the wear protection is still the reason for most of the plasma diffusion treatments, but properties like corrosion protection, electrical conductivity or surface morphology become more and more important. Therefore, over the years, plasma diffusion processes were optimized and tailored to operating conditions. Besides the desired technical properties of treated parts, the development of new steel alloys and the application of austenitic stainless steel required changes in the methods.

A brief introduction to the plasma diffusion treatment outlines the way to the current state of the technology. Then the contribution exemplifies the influence of high plasma voltage on the growth rate of the compound layer of alloyed steel. The high voltage is possible due to the modern arc-management system in the latest generation of plasma generators. After 2 h at 800 V the compound layer thickness is the same as after 16 h at 500 V. A second example of plasma diffusion is the boriding of tool steel without the formation of pores. PVD diffusion treatment, a B$_2$C coating with additional heat treatment, allows understanding the diffusion processes and the reason for the formation of pores.

The latest scientific research shows efforts focused on plasma diffusion treatment of steel, titanium, nickel-based alloy and aluminum.

Keywords
Plasma Diffusion Treatment
Nitriding
Boriding
Compound Layer Thickness
Wear Protection
Time-resolved Langmuir probe diagnostics of a bipolar high power impulse magnetron sputtering discharge.

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High power impulse magnetron sputtering (HiPIMS) of a cobalt cathode in argon gas was investigated by time-resolved electrical (Langmuir) probe diagnostics and by time-integrated energy-resolved mass spectrometry. The HiPIMS discharge was operated with a bipolar pulsed power supply providing a large negative voltage with a typical pulse width of 100 μs followed by a long positive pulse with a pulse width of about 310 μs. Time-resolved Langmuir probe results yield a small negative plasma potential in the negative pulse regime and a large positive floating potential and plasma potential in the positive pulse regime. Electron density is significantly reduced during the positive pulse regime. Probe results are supported by ion energy measurements.

Keywords
magnetron sputtering
HiPIMS
bipolar pulse
time-resolved Langmuir probe
energy-resolved ion mass spectrometry
Optimizing the deposition rate and ionized flux fraction by tuning the pulse length in high power impulse magnetron sputtering

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High power impulse magnetron sputtering (HiPIMS) is an ionized physical vapor deposition technique. While HiPIMS provides a high flux of metal ions to the substrate, the disadvantage is a reduced deposition rate compared to direct current magnetron sputtering (dcMS) at equal average power. This is mainly due to the high target back-attraction probability of the metal ions with typical values in the range 70 - 90 % during the pulse. In this work, we investigate how to reduce this effect by quantifying the contribution of ion fluxes after each HiPIMS pulse, a time also known as afterglow. Without a negative potential on the target at this stage of the HiPIMS process, the back-attracting electric field disappears allowing remaining ions to escape the ionization region. In order to analyze the fate of the film-forming ions, we extend the time-dependent Ionization Region Model (IRM) by adding consideration of an afterglow. This approach allows us to distinguish between fluxes from the ionization region during the pulse and during the afterglow. We show that by shortening the pulse length of a titanium HiPIMS discharge, the contribution to the outward flux of film-forming species from the afterglow increases significantly. The IRM predicts a gain in deposition rate of 46 % and 47 % for two discharges with different peak currents, when using 40 µs compared to 100 µs-long pulses at a constant average power. This is without compromising the ionized flux fraction that remains constant for the range of pulse lengths investigated here.

Keywords
HiPIMS
pulse length
ionized flux fraction
Effect of pulsed arc discharge energy on properties of doped ta-C films

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Hydrogenated Diamond Like Carbon (DLC) coatings are widely used as protective coatings in industry due to their high hardness, low friction and high wear resistance. However, their thermal stabilities at elevated temperature restrict many potential applications as high temperature lubricating coatings. Non-hydrogenated DLC is now in the focus of many industries due to its better temperature stability and higher hardness.

Extensive research has been done in the past whereby the effect of impact energy, angle of incidence, substrate temperature and deposition rate on properties of ta-C were studied. We have shown in earlier presentations that we can modulate the sp2-sp3 content in the film at nanoscale if the right conditions are chosen.

In the present paper we report about ta-C coatings prepared from pure and doped graphite targets by means of pulsed Arc evaporation. Two doping elements were chosen, Boron and Tungsten, with target dopant level varying between 0.5 and 8%. Majority of the work has been done on W doped, as W is clearly distinguishable from C in SEM and HRTEM.

The pulsed ARC discharge has been operated with a very steep rise rate of the ARC current, typical in 5 \( \mu \)s the ARC current reaches maximum peak currents, upon which the pulse discharge is switched off. Plasma densities in the ARC discharge are clearly higher than e.g. with HIPIMS. Manipulating the applied pulsed arc discharge energy influences the impact of the impinging carbon ions with the substrate and periodically applied deposition conditions. We have checked how the film properties are affected. The results from the two doping model investigation tests are described in detail.

Keywords

DLC
protective coating
doped ta-C
arc discharge
ORF103

Deposition of hard and dense nanocomposite Ti-Si-N films by DOMS without the need of energetic bombardment

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Nanocomposite Ti-Si-N thin films have been extensively studied for more than two decades mainly aiming at the production of super hard materials for applications such as cutting tools. In a previous work about the deposition of Ti-Si-N films by DOMS (Deep Oscillation Magnetron Sputtering), the authors have shown that, at low peak power, an optimal compromise of ionization fraction and the energy of the sputtered species can be achieved at low peak power. Recently, the authors have also shown that the use of low peak powers in DOMS of Cr coatings allows for control of the shadowing effect and to deposit dense films without the need of an energetic bombardment. The main objective of the present work is to further investigate the low peak power regime in the deposition of Ti-Si-N films by DOMS and to evaluate the role of the atomic shadowing effect in this regime.

All the Ti-Si-N deposited in this work have a fine compact columnar morphology with V-shaped columns, as shown by both SEM and Bright-field TEM. The Ti-Si-N films deposited in the low peak power regime have much sharper and thinner column boundaries (1 nm wide). EELS analysis shows that Si is preferentially segregated to the column boundaries, constituting a SiNx tissue phase, while the columns have a heterogeneous Ti/Si elemental ratio. The films have a high quality mosaic structure, consisting of grains only slightly misoriented with respect to each other, as confirm by TEM and XRD. The bi-axial compressive stresses increase strongly at low peak power, while only moderate increases of the lattice parameter and the hardness are registered. The results show that, in the low peak power deposition regime, the atomic shadowing effect is prevented rather than counteracted by an energetic bombardment. Thus, the low energy of the bombarding species is sufficient to promote the mobility of the film forming species without inducing subplantation.

Keywords
Ti-Si-N
HiPIMS
DOMS
Recently, it has been demonstrated that the addition of a positive voltage pulse adjacent to the negative HiPIMS sputtering pulse allows the increase of film ion assistance and thus, the improvement of coating properties on both biased and insulating substrates. This study presents results of experiments conducted to further deepen the understanding how the shape of the positive pulse, such as delay, amplitude and length of the pulse, affects the deposition rate and film density, and in consequence, the resulting film properties. Some examples will be presented for different applications such as:

- Hard metal nitrides for cutting tools, molds and dies. The properties of AlTiN-based nitrides where the spinodal decomposition at higher Al contents is prevented.
- Trench filling for wafer packaging. Filling of deep trenches with metallic conductive layers is improved with the addition of positive pulses. Experiments were performed with 15:1 aspect ratio trenches.
- Increase on sp³ contents in hydrogen-free diamond-like carbon coatings. Hardness up to 40GPa are achieved.
- Improved barrier properties of AlSiOx oxide layers on PET substrates for high-end transparent barrier applications. Tests were performed on an industrial web coater using rotatable magnetrons and reactive sputtering. Water vapour permeation tests were measured using the Mocon W-700 instrument.

Avino et al., Plasma Sources Sci. Technol. 28 (2019) 01LT03.
Eichenhofer, I Fernandez-Martinez et al., UJPA 11(3), (2017) 73

Keywords
HiPIMS
Positive Pulse
Ionized deposition
Increasing demand in smart, efficient and green Nanotechnology implies continuous progresses in the synthesis of always more complex Nanomaterials. Tremendous progress in the synthesis of complex Nanoparticles (core-shell, Janus etc...) has been achieved within the last decade so that shape and composition of Nanoparticles (NPs) can be tailored in an always more accurate way. However conventional chemical routes enable only the synthesis of stable compounds. Metastable NPs is large and relatively unexplored library of NPs that is not reachable by conventional routes. High-density energy processes in liquids (plasmas, lasers, ultrasounds etc...) provide strongly non-equilibrium that enable the formation of metastable compounds. For example, dielectric discharges in liquids may locally generate high temperature (up to 3300K) and high pressure (30 bars) with high gradients ($10^5 - 10^6$ K.s$^{-1}$). Within these conditions, a new metastable crystallographic phase of lead oxide PbO$_2$ has been discovered by Hamdan et al. The present communication will focus on the formation of metastable alloys, and to a larger extent to the microstructure control of NPs. The combination of a plasma and a laser treatment, both conducted in liquids is shown to be beneficial high rate synthesis of metastable NPs, thanks to high cooling rates. The relationship between the microstructure, and mechanical properties has been well studies even at nanoscale. However, this relationship is less obvious for sub-wavelength light matter interaction. In this contribution we investigate, with a model system (Cu-Ag), the influence of different microstructure on the scattering of Nanoparticles. The microstructure of nanoparticles, in terms of phase composition, grain size within the sub-wavelength NPs is shown to be a potential way to reshape plasmon resonances.

**Keywords**
Nanoparticles
Discharges in liquids
Laser process
A microwave plasma torch for CO2 conversion

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Mankind nowadays is strongly affected by the ongoing climate change which is caused mainly by the increasing emission of carbon dioxide (CO2) from e.g. traffic, coal power plants and industry. An inherent problem of the energy production by renewable sources such as photovoltaics and wind mills is the often observed discrepancy between actual energy "production" and energy demand, due to their discontinuous availability. The so-called "excess" energy can be used to operate a microwave plasma torch at atmospheric pressure. The CO2 plasma leads to the formation of carbon monoxide (CO) and oxygen radicals (O\textsuperscript{•}). To avoid the thermodynamically forced recombination of both back to CO\textsubscript{2}, when leaving the plasma state an effective separation process is required. The separation is achieved by ceramic hollow fibers. Firstly, preliminary test with single fibers consisting of different chemical compositions are tested for their oxygen permeation and thermal behavior in the plasma as well as for the brittleness of ceramics by temperature loads. To increase the amount of the separated oxygen several fibers are collected in arrays. The remaining CO in the afterglow can be used as an important chemical C\textsubscript{1} -building block, which can be further employed for creating molecules with a higher commercial value.

This work is focused on the conversion and energy efficiency of the CO2 plasma by different process parameters like microwave power, gas flow and distance from inside the plasma to the afterglow. The efficiencies are determined via FT-IR and mass spectrometry.

Keywords
Atmospheric plasma torch
CO2 conversion- and energy efficiency
Mass spectrometry
FT-IR
Oxygen separation
Development of an AP-DBD plasma assisted CVD process with submillimetre resolution: Experimental and Simulation approach

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Additive Manufacturing patterning technique is beneficial for a wide range of applications such as manufacturing of memory device, sensors and lab-on chip devices. Inkjet printing has emerged as a major patterning process in additive manufacturing. Whereas it has some limitations in terms of homogeneity and printing resolution because of coffee ring effect and its dependence on surface energy of substrate. Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) has been a promising technique in printing as it is a solvent free technique and it is driven by cold plasma. In this work, we focus on how we can obtain the micro-resolution plasma polymer coatings by using AP-PECVD.

The developed deposition process relies on a co-axial AP-DBD plasma torch. The precursor is injected through a hollow inner capillary, whose diameter defines the plasma polymerised dot resolution, in the plasma post-discharge region. Methyl methacrylate (MMA) and Vinyltrimethylsilane (VTMS) are used as model precursors. X-ray Photoelectron Spectroscopy (XPS), Fourier transform Infrared Spectroscopy (FTIR) and Mass Spectroscopy (MS) analysis were achieved to characterize the atomic and molecular composition of the microdot coatings. A series of micro-plasma polymerised MMA coatings ranging from 200 (+- 10\%) μm to 1 mm in diameter has been obtained with the precursor injector nozzle of 500 μm. In addition, thanks to the low substrate temperature increase (<40°C), plasma-polymerised microdots can be deposited on a wide range of substrates like polymer and paper.

Through a comprehensive study combining experimental and computational approaches, the mechanisms controlling the deposition are explored. In particular, correlation in between the diameter of precursor injector nozzle and thus coated plasma polymer has been studied. Hence, the nozzle diameter, gas flow ratios and the distance between the nozzle and substrate has been experimentally verified to be of vital important. A fluid dynamic plus mass transport simulation approach has been taken in account to understand correlation of gas dynamics, geometrical design of the reactor and coating resolution.

\textbf{Keywords}
Plasma Printing
ORF203

A scalable linear PECVD microwave source for transparent films

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Microwave induced plasma has many benefits, low ion energies with high plasma densities among others, but distributing the microwave emission uniformly for large area coatings (LAC) can be problematic. This talk demonstrates a source concept for LAC that uses an array of independent microwave emitters to build a scalable linear plasma source. Among other benefits the independent control of every emitter allows to achieve high uniformity and even locally compensate for non-uniform gas distribution by adjusting the emission power of every single emitter in the array. The design of those microwave emitters allows easy cleaning and operation in the same pressure range as typical magnetron sputter processes, allowing operation in hybrid process systems.

Keywords
PECVD
Microwave
SiO2
Linear Source
**Power-to-X Applications Performed by Atmospheric Microwave Plasma Torches**

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“Power-to-X” is a general term summarizing technologies for conversion of surplus energy from renewable sources into matter that either can be stored and reconverted when required, or that will serve as basic materials for the production of e.g. more complex substances in chemical industry or synthetic fuels replacing fossil fuels in the transport sector. Carbon dioxide (CO₂) conversion is a promising approach for storing surplus renewable energy. The concept of CO₂ conversion is based on splitting CO₂ into oxygen (O) and carbon monoxide (CO) radicals in an atmospheric pressure plasma process. Highly energetic atmospheric microwave plasma torches, using excess electrical energy from regenerative sources, were applied for efficient CO₂ dissociation. By separation of the oxygen from the gas mixture via a perovskite membrane, the purity of the remaining CO gas is sufficient for conversion into syngas or higher hydrocarbons. The combination of methane (CH₄) and CO₂ conversion is an efficient means for the production of syngas, too. The H₂/CO mole ratio of the syngas is relatively easy to control by adjusting the ratio of CO₂/CH₄ during the feeding process, while additional application of a suitable catalyst can significantly enhance the process efficiency. The same atmospheric microwave plasma torches were used for decomposition of alcohols like methanol and ethanol to hydrogen in a water vapour plasma discharge. In fact, nearly 100% decomposition of methanol can be achieved in an atmospheric microwave plasma process. The steam reforming reaction C₂H₅OH + H₂O → 2CO + 4H₂ is the most likely source of H₂ production in this case, which is confirmed by the fact that no formation of solid carbon was observed. H₂ produced by this kind of atmospheric microwave plasma processes is a practical means for storing electrical energy from renewable sources.

**Keywords**

Atmospheric Microwave Plasma
Power-to-X
In the early days of polymer surface activation flames were used to produce oxidizing gases for increasing the surface free energy and to enable printing and adhesive joining. Soon the flame treatments were replaced by electrical discharge plasmas. Today it is mostly polypropylene and its copolymers, which are treated with flames. For example, PP films are treated with flames on a large industrial scale. But there are other interesting applications of the thermal plasmas, too. One of them we will demonstrate here.

Using capillaries for feeding the burning gas small flames can be produced, which are useful for the locally confined treatment of polymer surfaces. The time required for activation is small and the time of exposure has to be small if the thermal input has to be minimized.

Moving the flame over the surface is one approach to meet this demand. Pulsing the flame is another one. With a single flame pulse up to 26 at% of oxygen (XPS) can be found at the surface of a polyethylene film. The distribution of the surface oxygen concentration is rather narrow with a FWHM of some mm and a lowest value of 2.8 mm for a 0.5 mm capillary. Pulse repetition rates of 1 pulse per second can be produced easily.

Acetylene, ethene, and butane were used as burning gases in mixture with oxygen. The surface treatment results were very similar for all the gases with respect to the level of oxygen concentration and the distribution of the oxygen concentration at the surface. Of course, all the gases require different gas to oxygen ratios for obtaining optimum treatment results. The oxidation of the surface was found to be rather stable and did not change after storage of two weeks. This is in line with literature results for flame treated polymer surfaces. The flame temperature is highest for acetylene and lowest for butane. The heating of the sample turned out not to be an issue in our investigations. On the other hand, the heating of the surface can be useful for example in the case of treating 3D printed polymer objects. The partial melting results in a smoother surface.

**Keywords**
- activation
- flame treatment
- structured treatment
- polyethylene
Highly productive pretreatment of metallic substrates

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Substrate pretreatment is the first step in the quality chain of coating technologies. A sputter etching process for metal substrates based on hollow-cathode arc discharge plasma sources has been developed for this purpose. The main advantage is the realized high etching speed. This represents the precondition for highly productive and cost-effective lines. Technically, this is caused by the high plasma density generated by an arc discharge source. Ion currents with a density of up to 50 mA/cm$^2$ could be extracted from the plasma zone to the substrate. Etching rates of 40 nm/s were achieved on copper substrates. Nearly defect-free surfaces could be obtained after pretreatment by implementing a mid-frequency bias power source in combination with fast arc detection and suppression.

The plasma source was completed with a solenoid in a separate equipment. The magnetic field can elongate the plasma plume nearly to the meter range. The collected spatial ion current distributions reflect different regimes. They depend from the gas flow through the hollow cathode and the adapted background pressure and scale with the discharge current. The different characterizations will be presented in detail.

A process version was realized where the bias voltage is applied to the plasma source. Consequently, the substrates can remain on ground potential during the sputter etching pretreatment. This presents an advantageous simplification for the equipment design, for example for the pretreatment in strip coating lines. Furthermore, the method was adapted for the highly productive pretreatment of parts.

Keywords
highly productive pretreatment
vacuum surface cleaning
sputter etching
hollow cathode arc discharge
Treatment of soft-PVC with dielectric barrier discharge to reduce the migration of plasticizers

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Polyvinyl chloride (PVC) is a frequently used, cost-effective and very durable polymer. For many of its applications (e.g. blood bags, medical tubes, flooring laminate, electrical insulation) a high flexibility of the material is required. Therefore, considerable amounts of plasticizers (in the order of 40% by weight) are added to produce so-called soft-PVC. As these plasticizers are not chemically bound to the PVC, migration may occur. This leads to a shortened service life of these PVC products due to embrittlement or migration of plasticizers into the surrounding material. The latter is particularly critical for applications in the medical sector, as the plasticizers used here are often harmful phthalates that accumulate in the human body as a result. We have found that by treating soft-PVC surfaces in a dielectric barrier discharge under atmospheric pressure in argon gas, the migration of plasticizer molecules from the plastic can be almost completely reduced within treatment times of only 1 minute. To analyze the migration, we exposed the treated surfaces to well-defined amounts of n-decane and measured the dissolved plasticizer amount by ATR-FTIR spectrometry. Since there are no layer-forming precursors, the effect can only be attributed to structural changes of the polymer surface itself. The migration barriers created by this treatment are stable at room temperature for more than 4 months and can withstand short-term heating to 80 °C or storage in aqueous media. In our work we have also investigated the influence of different process conditions (process gas composition, power, treatment time, design of the plasma source) on the migration barrier efficiency for different plasticizers. Especially contamination of the argon gas with more than 1% oxygen or hydrogen led to a significant reduction of the barrier efficiency. Furthermore, the influence of short-wave UV radiation generated in the plasma was studied as well.

Keywords
PVC
plasma treatment
plasticizer
migration barrier
Structuring surfaces from thin film metallic glasses: bottom-up and top-down approaches

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Obtaining new nanostructured surfaces is of crucial importance in the development of modern industry. Metallic glasses (MGs) have emerged as a new class of materials with remarkable properties compared with their crystalline counterpart. Meanwhile, phase separation phenomenon is widely observed in thin films and has been thoroughly studied in order to manipulate the resulting functional properties. Here, we explore two routes for surface structuring supported on the separation of amorphous and crystalline phases of initially grown thin film metallic glasses. First, we developed a novel and simple bottom-up approach, applicable to a broad range of alloys, for the design of adjustable multifunctional surfaces. We demonstrate that the composition-driven transition to the crystalline state occurring in thin film metallic glasses offers an excellent scenario for the fabrication of two-phase crystalline-amorphous nanostructures. The resulting surface topography can be controlled by thickness and composition, consequently, surface-related properties such as optical reflectance and wettability are manipulated to a large extent. Second, a top-down approach is developed based on laser irradiation of thin film metallic glasses, allowing the generation of ripples known as laser-induced periodic surface structures (LIPSS). We report on the laser-induced structural changes occurring at the surface and near-surface in thin film metallic glasses. Sputter-deposited Zr-Cu thin films, largely known for their good glass forming ability, were used as a model system. Transmission electron microscopy has been used to study the evolution of the film structure, microstructure and composition after laser irradiation, shedding new light on the laser-amorphous material interaction process. Our results delve into the control of surface topography and related functional properties in thin films, opening new avenues for future applications.

Keywords
Thin film metallic glass
Zr-based alloys
sputtering
phase separation
LIPSS
Comparison of four atmospheric pressure plasma jets applied for treatment of polypropylene

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Non-thermal atmospheric pressure plasma discharges are one of the most promising technologies for low-cost modification of adhesive properties of polymer surfaces. As working conditions of various types of discharges can differ by, for e.g., working gas, gas temperature and species’ excitation path; the way how they affect polymer surfaces can also differ significantly. In this work, we compare effects of four different atmospheric pressure plasma jets on polypropylene (PP) slips.

The three industrial jets (PlasmaTreat rotating plasma jet, AFS plasma torch and SurfaceTreat gliding arc) utilize air as their working gas. The home-built RF plasma slit jet, developed by the Plasma technologies group of CEITEC, Masaryk University uses Ar. The gas chemistry was studied mainly using optical emission spectroscopy. While spectra of all discharges contained OH, N2 optical bands of different intensities, pronounced O and N atomic lines were observed only in the spectra of PlasmaTreat and SurfaceTreat jets. A distinct continuous emission observed in AFS plasma torch spectrum is assigned to NO2+ molecule whose formation was later confirmed by mass spectrometry measurements. In addition to the species identification, the rotational gas temperatures were determined by modelling the OH (A–X) 0-0 and N2 (C–B) 0-0(0-1) bands.

The chemistry of PP surfaces was assessed mainly by water contact angle and X-ray photoelectron spectroscopy (XPS). As revealed by XPS, both oxygen and nitrogen containing functional groups can be attached onto the surface when air plasma is used. Ar plasma promotes only attachment of oxygen containing functional groups. Tensile strength measurements suggest that the presence of nitrogen containing groups might be beneficial for a stronger bond between PP and the epoxy adhesive (DP190, M3). Surface morphology was observed using a combination of scanning electron and atomic force microscopy. Smoother PP surfaces were obtained after treatment with higher gas temperatures.

Keywords
atmospheric pressure plasma jet
plasma treatment
polypropylene
Chlorine-based plasma etching of Fe-Cr alloys for the development of steel patterning: modeling, plasma diagnostics and etching rate measurements

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Surface structuring is highly developed in microelectronics through plasma etching processes. The patterning of metallic materials is currently arousing great interest by its numerous applications on various fields including wettability, adhesion, self-cleaning, drag reduction, friction (lubricated or not), biotechnologies, etc. However, there are very few studies devoted to the etching of austenitic or ferritic steels. The approach developed in this study consists in using both modeling and experimental approaches to understand more about the Fe-Cr alloys etching under an ICP chlorine plasma. Experiments have been carried out in an ICP/RIE SENTECH device delivering a 800W RF power with a chlorine plasma operated at 5 mTorr pressure with a substrate temperature up to 220 °C and -150 V DC bias on pure iron and five Fe-Cr alloys with up to 12 wt% of Cr. The etching rate is higher for pure iron (around 270 nm.min\textsuperscript{-1}) and decreases to 70 nm.min\textsuperscript{-1} as the chromium content increases in the alloy. Optical emission spectroscopy measurements show that the introduction of Fe or Cr samples in the plasma reactor, even in small quantities, strongly affects the plasma. The etching simulator developed in this study is based on the multiscale approach, which allows us to follow the steel etch profile evolution as a function of the operating conditions such as pressure, RF power, gas flow rate and DC bias. Cellular Monte-Carlo approach is used to quantify the etching kinetics of steel through the mask. The output parameters in terms of positive ions and reactive neutral fluxes as well as the Ion Angular Energy Distributions Functions IAEDFs calculated from the plasma and sheath models are introduced as input parameters in the surface model. Experiments show a strong decrease of etching rate of Fe-Cr allows with Cr percentage. To obtain such a strong decrease, the model consider that Fe or Cr sites, if they are surrounded by Cr or Fe sites respectively, are harder to etch in this case.

**Keywords**

steel etching; plasma diagnostics; modeling; chlorine plasma; Fe-Cr alloys
Heterogeneous nanoparticles (NPs) combine the advantages of the two different materials. Different NPs like Janus, dumbbell, satellite and many others have already been reported. The main attention has been paid to the investigation of core@shell NPs because their optical, electrical, chemical and catalytic properties can be tuned by combining specific core and shell materials.

Titania (TiO2) in a form of anatase is well known for its photocatalytic properties and silver exhibits strong plasmon resonance. In case of Ag@TiO2 NPs those two effects can be combined in a way that the photocatalytic properties of the titania are enhanced due to the SPR-mediated electron transfer from the Ag core to the titania shell.

In the most cases wet chemical methods are used, however, in this study Ag@TiO2 NPs were produced using a fully plasma-based strategy. The Ag NPs as cores, were fabricated in the gas aggregation source (GAS) of Haberland type. These NPs were subsequently in-flight coated by a thin Ti shell in a modification chamber with the two DC magnetrons facing each other with an axis perpendicular to the beam of NPs. Closed and opposing magnetic fields arrangements were tested. Changes in the magnetron current, distance between magnetrons or magnetic field configuration allowed to tune the thickness of the Ti shell. The XPS, EDX, (S)TEM and SAXS analysis confirmed the expected core@shell structure with the shell thickness up to 3.5 nm. According to XPS the Ti shell is fully oxidized and the TiOx oxide is amorphous as witnessed by XRD. The possibility to convert TiOx amorphous shell in the TiO2 anatase will be discussed.

Acknowledgements
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Keywords
In-flight
Core@shell
Ag@TiO2
Magnesium and its alloys are the most electrochemically-active metals amongst engineering alloys. Surface preparation by plasma electrolytic oxidation (PEO) process prior to the application of organic layers on the surface of Mg alloys leads to the desired electrochemical properties. The oxide layer formed by the PEO process due to the in-situ growth mechanism has high adhesion strength to the surface and, owing to the process mechanism, consists of two dense inner and outer porous layers. Micro-pores and micro-cracks in its structure can act as suitable sites for mechanical interlocking to enhance the adhesion strength of organic layers to Mg substrates. Furthermore, a variety of corrosion inhibitors such as rare-earth (RE) elements (such as Ce, La, ...) were used as an additive in its structure to provide active corrosion protection properties. Another solution involves chemical optimization of the surface by introducing coupling agents to improve the chemical bond between the coating and the substrate. Coupling agents (such as silanes) act as a molecular bridge between the substrate and the coating and are capable of establishing covalent bonding or physical interaction or both, thereby enhancing adhesion. The performance of the silane layers can be further enhanced with the addition of components with corrosion-inhibiting properties. The effects of adding RE salts as dopants, as well as nanoparticles with inhibitory properties in silane solution, to produce a film with active corrosion protection and self-healing properties, have been investigated in our group. This paper introduces new milestone for surface treatment of Mg using PEO/Silane coatings with active corrosion protection and investigate their effects on the anticorrosion properties and adhesion strength of epoxy layer on Mg-based substrates. PEO process shows itself a suitable method for pretreatment of Mg-based alloys to design and fabricate suitable coating systems with superior corrosion resistance.

Keywords
Plasma Electrolytic Oxidation
Corrosion
Magnesium
Pretreatment
Conversion Coating
ORH101

**High-temperature performance of quaternary system (Ti, Al, Cr) N deposited by HiPIMS**

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c-TiAlN coatings have been widely used in advanced machining due to their excellent outstanding mechanical, thermal and tribological properties. To withstand oxidation \(\geq 950\, ^\circ\text{C}\), we studied the influence of Cr additions on the structure, mechanical properties and oxidation resistance, including the oxide scale characterization, of different nitride TixAlyCr1-x-yN coatings deposited on WC-Co and Si wafer by High-power impulse magnetron sputtering. The properties of c-Al0.62Ti0.38N were studied as a reference. The film at 850°C was oxidized and formed a bi-layered oxide scale with dense Al2O3 outer-layer and porous TiO2 sub-layer then at 950°C because of the fast Ti ions diffusion to the surface, the formation of the continuous and protective Al oxide layer was impeded. TGA measurements showed that Cr rich coatings showed different oxidation kinetics depending on their chemical composition. The surface hardness of the coatings was obtained by a nano-indentation test and it has shown that the Cr content can stabilize the hardness and the Young modulus independently the Al/Ti ratio. The structural evolution during annealing of TixAlyCr1-x-yN coating by XRD diffraction at different temperatures revealed that all coatings kept the B1 structure until 950°C. Cross-section observations by TEM of the oxidized coatings have shown that the addition of Cr promoted the formation of a TiO2 layer over a gradient Cr(Al)2O3 layer. Thanks, to-depth profile analysis by SIMS after oxidation at 950°C under an alternative atmosphere containing \(^{16}\text{O}\) and \(^{18}\text{O}\), it has been possible to give information on the different mechanisms controlling each oxide scales. The growth of the oxide layer appears at three levels: a rutile TiO2 on the external surface was formed followed with intermediate Al-rich gradient Cr(Al)2O3 layer then a Cr2O3 layer at the interface with the coated nitride layer.

**Keywords**

TiAlCrN HiPIMS coatings
Oxidation resistance
Elimination of Crazing Defects in Large Area Sputter Coating of Glass

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In large area coating of architectural glass, one cause for yield loss is the so-called crazing. This refers to the formation of dendritic traces on the glass surface due to electric break-down within the coated layer stack during sputter deposition. The occurrence of these defects is, like their appearance of erratic nature and hence the root cause analysis and mitigation pose a significant challenge.

Recently, methods to minimize or avoid crazing has increasingly moved into the focus of glass manufacturers, due to two reasons: the increased density of sputter magnetrons in coaters and the increasing use of Bipolar power supplies. The underlying mechanism leading to crazing is related to the difference between plasma potential and the ground potential. For MF or sine wave power supplies, one way to minimize crazing is to use rather low output frequencies of about 20 kHz. The Bipolar power supplies allow appropriate selection of not only the output frequency but also of the operation mode and thus, the output signal shape.

In this contribution, we first investigate the electrical signals used in dual magnetron sputtering. We compare their nature and characteristics when a sine wave (MF) and a modified square wave (Bipolar) is used and make an assessment of their influence on the crazing likelihood. Finally, the configurability of Bipolar operation mode and frequency combined with proper means to evaluate the plasma potential with respect to ground and the application of a self-learning algorithm for fine-tuning of plasma discharge parameters will be demonstrated as an effective method to eliminate crazing defects.

Keywords
Crazing
Surface defects
Bipolar power supply
Dual magnetron sputtering
Large Area Coating
Laser structural patterning for accelerating the self-adaption mechanism in low friction W-S-C coatings

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One of the main problems of low friction TMD-based coatings (transition metal dichalcogenides), is the need to supply enough energy for promoting the self-adaption mechanism which allows the re-orientation / crystallization of TMD crystals. If such a transformation occurs, the alignment of the (001) planes parallel to the sliding direction can give rise to very low friction forces. Then, high shear stresses and/or long running-in periods are needed to achieve this interesting tribological performance. However, in many applications (e.g. in contact with rubber) the low contact stresses impede this self-adaption phenomenon, particularly when TMD-based coatings have high mechanical strength. Only for pure soft TMD coatings the realignment of the planes is possible. In this presentation, we are proposing to partial laser treat a hard self-lubricating coating of W-S-C system in order to optimize its frictional performance from the very first moments of the sliding contact. W-S-C films were deposited by closed field unbalanced magnetron sputtering. The coatings were treated using two types of lasers, with peak emissions in the UV and IR, under different laser power conditions and patterning. The structure, mechanical and tribological properties of the treated coatings were analysed using X-ray diffraction (XRD), Raman spectroscopy, nanoindentation and reciprocating ball-on-disk tribometry. Although XRD diffractograms illustrated an overall amorphous structure in all as-deposited and treated samples, their Raman spectra confirmed the presence of WS₂ crystalline phase in some of the treated areas. Furthermore, in the samples where WS₂ Raman peaks were detected, the friction coefficient was in the initial part of the test lower than that of untreated coating.

Keywords
Self-adaption
Low friction
TMD
Laser patterning
W-S-C
Thermal stability of nanostructured TiAlN-based coatings deposited by HiPIMS with positive pulses

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In recent years, due to the advancement of high-speed machining (HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance, anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured TiAlN and TiAlBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The influence of the multilayer structure on the films was also tested by varying thicknesses to further improve the mechanical properties at high temperature. The formation of nanocrystalline grains (TiAlN) embedded in an amorphous phase provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splitting were used to evaluate toughness and thermal resistance of the coatings.


Keywords
Hard Coatings
High Temperature
Fracture Toughness
Multilayer
Positive Pulse
Bimetallic clusters incorporated on a:C matrix for antimicrobial applications

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The propose of this work is the development of Ag/a:C and Ag-Au/a:C coatings for biomedical devices, to provide them with antimicrobial characteristics. Silver was selected due to the well-known antibacterial properties, while gold was included to assess its capacity to accelerate the silver ion release forming a galvanic couple between Au and Ag. Thus, the metallic (Ag) and bimetallic clusters (Ag/Au) were produced by three different configurations: i) unbalanced magnetron sputtering (conventional sputtering), (ii) plasma gas condensation process and by (iii) a combination between both previous approaches.

Coatings with Ag/Au bimetallic clusters were characterized by transmission electrons microscopy (TEM) in order to study the arrangement (alloy, core-shell and galvanic couple) of these particles in the carbon matrix. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to quantify the Ag ions released through artificial urine from the different coatings deposited on thermoplastic polyurethane (TPU) tape (one of the materials used in the ureteral stent manufacture). Then, the antibacterial and cytotoxicity properties of Ag and Ag-Au/a:C coatings were evaluated.

TEM shows that a biphasic structure was not detected, thus not allowing to anticipate the establishment of a galvanic couple. The ICP-OES results demonstrate that the silver ionization is mainly function of the amount of silver incorporated in the a:C matrix, and the bimetallic alloy clusters has a detrimental effect on the silver ions release. The antibacterial activity was regulated by the silver ionization mechanisms, since the coatings with higher Ag release had a higher antibacterial activity.

Keywords
sputtering
plasma gas condensation process
antibacterial
Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), the technique connected with Nobel Prize, has become an important analytical tool capable to detect various molecules including peptides or whole proteins. However, conventional MALDI-MS using organic matrix has two intrinsic limitations: (i) it provides mostly qualitative results and (ii) organic matrix spectra often interfere with low-mass biomolecules. Therefore, a lot of measurements are usually needed to find so-called “sweet spots” from which mass spectra with sufficient quality are obtained. The presence of “sweet spots” is pointing to the sample inhomogeneity, here caused by matrix distribution in a sample. This brought us to two fundamental questions: Is it possible to make all spots “sweet”? Is it possible to detect small molecules without matrix interference? Both questions may be answered yes if the organic matrix is substituted by inorganic plasmonic nanoparticles (NPs) as will be presented. First, the drops containing low-mass analyte are dried into concentrated spots on conductive plates with tailor-made wetting properties. Then the dried analyte is homogeneously overcoated by the silver NPs synthesized in a gas aggregation source, which as low-pressure plasma based technique ensures high purity of produced NPs and allows tailoring their size, morphology, etc. This, in turn, enables to match NPs plasmonic absorption with the wavelength of the used Nd:YAG laser (355 nm). We prove that the biomolecule peaks intensity is strongly linked with the amount of deposited Ag NPs showing maxima for the highest surface density $3\times10^3$ NPs/μm$^2$ at which the NPs still do not form an interconnected metallic network. The biomolecules signal intensity is then comparable to MALDI-MS organic matrix measurements acquired at the “sweet spots” with the detection limit of $3\times10^{-8}$ g/L and excellent spectra reproducibility (SD 10 %) and therefore presented technique is applicable for advanced mass imaging. (Support by TACR Gama TP01010019 is acknowledged)

**Keywords**

nanoparticles
Study of the local segregation of multi-component powders during a plasma spray process for biological applications

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Atmospheric plasma spraying is a versatile coating process, which can be utilized for biomedical applications. The use of powder mixtures consisting of different materials allows the fine-tuning of specific coating properties. For instance, by addition of a small amount of Cu to TiO$_2$ powder, antimicrobial coatings on implant surfaces can be generated. However, the achieved functionality depends heavily on the particular coating structure.

Our investigations show that the different components in the powder mixture can segregate during the plasma spray process on the way from the injection to the substrate. The segregation can be ascribed to different particle sizes (a few tens microns in diameter) and relevant material properties (e.g. density and melting) of the constituents. The segregation causes gradients in the chemical composition of the coating. Coating depositions with a mixture of TiO$_2$ and 3\% Cu revealed a lateral deviation of the resulting elemental profiles of up to 2 cm as verified by XPS analysis. Depth profiles were prepared and analyzed by SEM. Actively utilizing the effect of material segregation, different coatings (maximum of Cu at the top and close to the substrate) could be produced demonstrating that the deposition of coatings with controlled material gradients is feasible. This opens prospects for films with tailored local properties for biomedical applications. According to our analysis, the gradient coatings display different dynamics of copper release over time.

The results show the components in powder mixtures employed for plasma spraying need to be selected carefully. Particle sizes and the material properties have to be considered for spatially homogeneous coatings. However, the segregation can also be used for the deposition of coatings with controlled material gradients.

Keywords
plasma spraying
atmospheric pressure
gradient coating
medical
technical
ORI103

**First insights of a novel antibacterial and cytocompatible porous Ta2O5 surface doped with zinc oxide nanoparticles**

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This work is focused on the development of a novel surface with graded functional treatments that will give a solution for the main problems of dental implants used nowadays: poor bioactivity that delays osseointegration and periimplantitis, an inflammatory disease caused by bacterial infection. In a first step, it was developed a porous tantalum oxide (Ta\(_2\)O\(_5\)) surface with incorporation of osteoconductive agents, calcium (Ca) and phosphorous (P) by plasma electrolytic oxidation (PEO). The anodizing parameters were optimized in order to achieve a Ca/P ratio near to 1.67 (theoretical value of hydroxyapatite) and thus mimic the bone morphology and chemistry enhancing the surface bioactivity. As second step, Zn nanoparticles (NPs) were deposited onto the bioactive surfaces by DC magnetron sputtering in order provide the surface of antibacterial activity. Moreover, an additional thin carbon (C) layer covered the Zn NPs in order to control the NPs release. The morphologic analysis by SEM reveled the formation of a micro/nano-porous structure on the oxide layer with a non-uniform and non-homogeneous porosity. The deposition of Zn NPs did not affect the surface morphology and the NPs were around and inside the pores increasing consequently the surface roughness. The additional presence of the C layer slightly covered the nano-pores and reduced the roughness. Additionally, BF-STEM was performed to characterize the samples with the Zn NPs, and the morphology indicates that the nanoparticles had irregular shapes and a core-shell structure with two crystalline phases: HCP Zn and ZnO. *In vitro* results demonstrated that after a maximum of 4h leaching the surfaces, an initial osteoblasts adhesion was ensured with a significant proliferation on the surface with Zn NPs. The surfaces with Zn NPs substantially reduced the planktonic bacterial with a greater sessile bacteria inhibition on the surfaces. Thereby, these findings are promising for biomedical applications.

**Keywords**
tantalum oxide
zinc oxide nanoparticles
plasma electrolytic oxidation
magnetron sputtering
antibacterial activity and cytocompatibility
**POB004**

**Hot Filament CVD Diamond Coating Technology for Cutting Tool Applications**

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In addition to a variety of DLC-based coatings for machining applications and other tribological applications, pure polycrystalline diamond has been established as an excellent coating material in the industrial cutting market for hard to machine materials such as carbon fiber reinforced plastics (CFRP), zirconium oxides, cemented carbide, aluminum silicon alloy and graphite. Modern industrial machining operations often require complex tool geometries that present major challenges for tool coaters. The well-established filament assisted CVD diamond coating technology offers a solution to this challenge while combining complex geometries with extreme mechanical thin film properties. This presentation shall give an insight into the basic principle of Hot Filament CVD diamond deposition for cutting tools on an industrial scale. Furthermore, results of case studies regarding exemplary cutting application on hard to machine materials will be shown. These case studies include applications in CFRP systems for the aerospace industry, zirconium oxide systems for dental applications, direct milling of cemented carbides and milling operations in graphite for the 3C industry (Computer, Communication and consumer electronics).

**Keywords**

CVD diamond  
Hot Filament CVD  
Machining  
Coating technology
Diamond like carbon (DLC) films are one of current most promising solution for the automotive industry to reduce friction in piston’s rings of internal combustion engines. In a previous work, the authors have shown that adding Ne to the discharge gas in Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS, allowed for a significant improvement of the tribological and mechanical properties of DLC films. DLC films with a significantly lower specific wear rate than standard state of the art CrN films (4x10-17 against » 1.1x10-16 m3/Nm for CrN) and much lower friction coefficient (0.15 against 0.75 for CrN). However, the thermal stability under operation at elevated temperatures is a fundamental requirement for piston’s ring thin films. In this work, the tribological properties of DLC films deposited by DOMS with and without Ne in the plasma were investigated as a function of temperature.

The DLC films were tested using a pin-on-disk tribometers with increasing temperature up to 300 ºC. All the tests were carried out in ambient atmosphere using AISI52100 counterparts. At each temperature, the wear tracks, ball-wear scars and wear debris were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) and micro-Raman spectroscopy. The specific wear rate was calculated using interferometric optical microscope. The specific wear rate of the DLC films increases with increasing temperature for both the films deposited width and without Ne in the discharge gas. The DLC film deposited without Ne is completely worn at 300 ºC, while those deposited with Ne still show relatively low specific wear rates (between 4.5 x10-15 and 4x10-15 m3/Nm). The increase in the specific wear rate by more than one order of magnitude from room temperature to 300 º C was attributed to the transformation of sp3 sites to sp2 sites and subsequent loss of hardness. Although adding Ne to discharge gas significantly improves the DLC films performance, additional development of the deposition process has to be carried out in order to increase their temperature stability.

**Keywords**
DLC
HiPIMS
Tribology
Controlling structure and morphology of WC based thin films

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Tungsten carbide coatings are used in various tribological applications such as interlayers for DLC based films or as abrasive protection coatings. The morphology of transition metal carbide based thin films synthesized via PVD methods ranges from crystalline to nanocomposite coatings as well as nano-clustered structures in amorphous films. In addition, for WC based coatings two competing phases, hex-W\textsubscript{2}C and fcc-WC\textsubscript{x}, strongly disturb a purely crystalline growth.

Therefore, this study aims for an understanding of the deposition parameters and hence obtained morphology and phases applying diverse target materials in reactive (C\textsubscript{2}H\textsubscript{2}+Ar) and non-reactive sputter processes. We compare a wide range of target types: metallic W, WC ceramic including a conventional cobalt binder, as well as binder-free WC ceramic targets (with or without graphitic carbon additions). We applied XRD, XPS, TEM, SEM and nanoindentation to investigate structure, composition, morphology, carbon bonding nature and mechanical properties. For an in depth understanding on the phase formation, we also applied atomistic modelling using DFT (Density Functional Theory). The addition of acetylene strongly triggers the formation of amorphous structures, but highly sensitive for each individual target type. Carbon concentration within the target as well as within the reactive atmospheres affects the carbon bonding nature observed by EELS and XPS. Furthermore, in non-reactive processes (using Ceramic targets) the phase formation and morphology can be adjusted by bias potential. This study therefore gives new insights and perspectives for this well-known thin film material.

Keywords
Tungsten Carbide
Reactive Sputtering
Ceramic Targets
DFT
Graphite Addition
Analysis of CVD diamond coatings on tungsten carbide tools and their ability to machine ceramic materials

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Milling tools made of tungsten carbides are coated with diamond to find maximum fields of application for protective films and used to machine ceramic materials. Such hard and brittle materials are difficult to machine. Grinding is the mainly used cutting process to finish the geometry of ceramic components. The application of milling tools with defined cutting geometry is highly advantageous because of the larger removal rate which reduces the processing time and hence also the machining costs.

In this project milling tools with a geometry normally used for high speed cutting (HSC) are chosen. Such tools are commercially available and have a relative huge wedge angle which stabilises the cutting edge. These tools were coated with diamond films by chemical vapour deposition (CVD) in a modified hot filament process developed by CarbonCompetence. The diamond coatings are characterised by scanning electron microscopy (SEM) and Raman spectroscopy at different positions on the tool to obtain information about the morphology and the bonding structure of the diamond coating and the interface material. Local dependent X-ray diffraction (XRD) gives direct evidence for diamond in the coatings and allows the estimation of microstructure in the films.

As ceramic material, a carbon fibre reinforced ceramic with SiC matrix is used. During the machining process the forces on the work piece are recorded. After different lengths of application, the diamond coated tools were examined by using optical microscopy and SEM concerning wear.

It was found that machining of fibre reinforced ceramics with diamond coated tungsten carbide tools with defined cutting geometry is in principle possible. The influence of morphology and the composition of the diamond film on the tool life time will be discussed.

Keywords
diamond coating
XRD
Raman spectroscopy
Boosting the corrosion properties of PVD-TiMgGdN coated mild steels using sophisticated powder metallurgical TiMgGd targets

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PVD-TiMgGdN coatings were successfully developed by the authors in an industrial DC-magnetron PVD unit, which reveal an excellent corrosion protection capability for mild steel substrates for at least 800 h in the salt spray test [1]. The MgGd was implemented in the coating by using segmented multi-component targets, consisting of segments of pure Ti and a Mg-30 wt.% Gd alloy. The drawback of the segmented target was an increased defect density due to droplets forming at the gaps between the segments. In consequence, the wear performance was unsatisfactory. To overcome this problem, a TiMgGd target with a specific Ti:Mg:Gd ratio was manufactured by powder metallurgical technology processing pure metal powders.

In the present work, DC-PVD-TiMgGdN were synthesized with the new powder metallurgical TiMgGd targets by variation of the deposition parameters (power, BIAS, pressure, reactive gas portion). The influence of the deposition parameters on the resulting coating properties as well as the corrosion performance and the wear behavior were 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. Furthermore, ball on disk wear tests were conducted by reciprocal dry sling tests by using a SRV 3 tribometer. It is shown that the excellent corrosion performance, which was already observed for the segmented targets, could be boosted by application of the powder metallurgical TiMgGd sputter targets. Besides that, the wear performance is in the common range of typical nitride based PVD hard coatings deposited with the powder metallurgical targets. It was found that the deposition parameters show a minor influence on the mechanical coating properties but a major influence on the resulting microstructure, which directly correlates with the corrosion and wear performance.


Keywords
Magnetron PVD
Corrosion
Wear
The Corrosion resistance of Ag and Ag-Au/a-C nanocomposite coatings deposited by dc magnetron sputtering

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Ag-doped DLC nanocomposite thin films were found to be promising coatings for biological applications owing to their great capability for antibacterial activity. However, the practical clinical purposes of the DLC coatings doped with Ag-nanoparticles require to tackle with two main concerns: bacterial colonization and also to corrosion under an aggressive biological environment. Furthermore, the bimetallic Ag-Au nanocomposites showed a higher antibacterial efficiency due to an improved activity of Ag atoms surrounded on the Au nanoparticle surface. In this research, we deposit the Ag-DLC and (Ag-Au)-DLC coatings onto the stainless steel (SS) by means of DCMS. To mimic the biological conditions, the coatings are exposed to the simulated urine solution. The ICP-OES analysis demonstrated a higher Ag release in the Ag-DLC coating. The surface morphology of the coatings was carried out before and after 14d immersion into artificial urine. The corrosion resistance of the coatings under immersion condition was characterized by the EIS technique. An appropriate equivalent circuit based on the two-layer model consisting of the inner intact barrier layer together with a thinner porous surface layer was proposed to simulate the electrochemical features. Furthermore, the results demonstrated that the inner intact layer resistance of (Ag-Au)-DLC coating is bigger than in Ag-DLC coating expressing higher corrosive resistance against the aggressive solution over Ag-DLC coating. A higher protective feature of Ag-Au doped DLC coating can be due to changes in the corrosion potential of the Ag-Au alloy with respect to pure Ag, and therefore, the alloy in contact with the carbon matrix will oxidize less when compared to Ag-DLC coating. Eventually, the galvanic coupling between Ag and carbon matrix is also constrained when Au is added.

Keywords
DCMS
Ag and Ag-Au nanocomposite coating
Corrosion resistance
EIS
Ag release
In almost all industrial sectors, the request for specifically adjustable surface characteristics is being voiced. However, often the desired characteristics cannot be reached by the basic material. For example, the solid body is made out of economical plastic material, but the final product is supposed to be resistant to scratches and chemicals. Besides the financial perspective, environmentally-friendly aspects are becoming more and more prominent. Therefore, the surface coating by means of plasma technologies plays an increasingly important role. Multitudes of the deployed basic materials are sensitive to temperature damage and therefore cannot be treated with the common coating methods. A possible solution to this is provided by plasma-enhanced chemical vapour deposition (PECVD) technology. General operating temperatures of distinctly below 200 °C make treatments of almost all common basic materials possible. The focus of this research are different silicon based hard coatings like Silicon nitride ($\text{Si}_3\text{N}_4$) and Silicon carbide ($\text{SiC}$) as well as oxide ceramic coatings like Aluminum oxide ($\text{Al}_2\text{O}_3$) and Zirconium dioxide ($\text{ZrO}_2$). In the context of testing methods, the coatings are mainly tested on mechanical stability. They are fundamentally tested on coating adhesion as well as wear resistance in dependence on the basic material and its pretreatment. Since there are many applications of the named coatings, additional testing methods have to be employed. Furthermore, scratch resistance and stability to temperature fluctuations are tested. Besides the contact with other solid counter bodies, often the contact with liquids occurs. On this account, more characteristics like wetting properties towards different substances and media resistance is tested. This research points out fundamental possibilities and applications of different coatings. It is carried out in close cooperation between the Fraunhofer IGB and the IGVP of the University of Stuttgart.

Keywords
PECVD
hard coating
ceramic coating
scratch resistance
POB012

Determination of durability and optical properties for Low-E coating
ZnTiAlO / Ag / ZnTiAlO

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Low-emissivity glasses (Low-E) allow to reflect middle infrared (IR) produced by heated object or human body while letting visible sun light in. This is a major goal for energy saving and, in the actual climate context, it is a very interesting technology. This particular optical property can be easily achieved by a thin noble metal as silver, gold or copper. Among them, silver show the lowest absorbance in visible range [1]. However, the silver layer is easily ripped off if it is not protected by surrounding layer(s). In this way, a seed layer promotes the growth of silver layer and a barrier layer protect the silver layer to avoid the ripping off of the silver [2,3].

Several compounds have been used as seed and growth layers such as Bi$_2$O$_3$, In$_2$O$_3$, SnO$_2$, TiO$_2$, ZnO and ZnS. Among them, ZnO is interesting due to its large gap, its low cost and its abundance. Utilization of dopants in ZnO enables to increase the chemical stability and to reduce the stress of the Low-E stack [4]. However, limited work show results for co-doped ZnO on the durability. In this way, we propose to study a periodic table IV type element (Ti) and Al to increase the electronic density of the layer, and so to improve the durability of the Low-E stack.

Moreover, for industrial applications, the use of metallic targets in reactive DC mode may be advantageous because it allows to the control the stoichiometry of deposited films with regulation. Thus, Ti and Al co-doped ZnO (ZTAO) films are deposited by reactive co-sputtering between ZnAl and Ti targets. Low-E film durability and optical properties related to the composition of ZTAO films are investigated in this work.


Keywords
Low-E
doped ZnO
ZnTiAlO
Optical
Durability
Thin Film Sensors for Additively manufactured components

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Additive Manufacturing (AM) offers a whole new spectrum of design and fabrication potentials. Components of complex structures can be realized and a significant decrease in weight of the workpiece can be achieved. To further increase the applicability of AM components integrated thin-film sensors like, e.g., resistance strain gauges or thermometers are of great value. This work evaluates the requirements of integrating thin-film sensors in the fabrication process of AM parts. We concentrate on workpieces fabricated by Selective Laser Sintering (SLS) and using powdered polyamide (PA12) as a non-conductive material to abstain from using one or rather two additional insulating layers during process development and evaluation.

Fabrication of thin-film sensors requires a smooth and defect free surface. As additive manufactured parts are known to incorporate a certain quantity of bulk and surface defect, caused by process parameters as variations of powder size or distribution or application of unideal design parameters, a thorough study of the actual defect rate is necessary. Based on this statistical parameter the probability of a working thin-film sensor with respect to its length, depth, and width can be determined and, hence, the minimal sensor size.

Inter- or post AM surface treatment is investigated to increase the probability of obtaining a working sensor. Furthermore, to integrate a thin-film sensor into an AM fabricated workpiece, the printing process has to be interrupted and resumed at the exact position. To achieve this, one must know both, the position of the reinserted workpiece with an uncertainty of a few micrometers at the most (powder size and, hence, layer height being 20 – 40 µm), and the machining tools, i.e. scraper, roller, laser focus point, as well.

Keywords
Thin Film
Sensors
SLS
Polyamide
Surface Quality
Fracture toughness of TiAlN hard coatings with soft metal inclusions

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Fracture toughness and adherence are crucial for the performance of hard ceramic coatings in multiple applications such as punching, stamping, forming or printing application. Of course, due to the wear in these applications, the coating should also be hard. In the present work we developed a tough TiAlN coating by adding a metallic phase during the sputtering process. The mechanical properties of the coating were evaluated quantitatively based on the H/E ratio the scratch resistance and during the Rockwell C adhesion evaluation. A qualitative evaluation of the coating hardness was done based on the cracking patterns during scratch test and Rockwell C impression.

The PVD Coating was done in an industrial MS 1400 sexta, a 6-magnetron coating machine from Inorcoat using the patented Magnetron Sputtering cathodes. The machine allows an asymmetric nitrogen distribution in the coating chamber, allowing the simultaneous deposition of the ceramic TiAlN and metallic Cu. The metallic Cu was deposited in the form of nano-inclusions in the ceramic matrix and in the form of intermediate layers, giving the coating architecture a sandwich like structure.

TiAlN can be deposited in the Inorcoat machine as a well adherent (critical load > 90 N during scratchtest), hard (HV₀.₀₀₅ = 3 300) coating on Ni substrates. The inclusion of Cu reduces, obviously, the hardness, but increases the H/E ratio. The cracking pattern during scratch test and Rockwell C indentation changes, the cracks become shorter with an increased spacing.

Keywords
Ceramic coatings
Fracture toughness
Adherence
TiAlN(Cu)
Metallic inclusion
POC001

**Low pressure BCl3 gas boriding of hot working materials**

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Because of high temperatures in the contact zone of up to 1,000 °C, tools for the hot extrusion molding of copper and brass require surfaces with high thermal stability. In addition, the high pressure used for plastic deformation in this hot forming process increases the demand for hard and wear resistant surfaces, while the hot and very reactive copper or brass tend to stick at the surface and cause adhesive wear. Often-used hot forming tool materials, like hot working steel AISI H11 and DIN ISO 1.2367, Alloy 718 DIN ISO 2.4668, and Stellite Alloy 1, are known for low service lifetimes in this application. However, these materials, thermochemically treated by boriding, are developing hard and thermally stable layers, and possibly increase the wear resistance in this harsh environment. The boriding process is carried out at low pressure of p = 3 - 7 mbar and temperatures ranging from T = 720°C to 900°C. Under these conditions, the thermal energy is sufficient to decompose BCl\(_3\) and form MeB\(_x\) metalborides at the surface in the case of hot working steels or Alloy 718 with layer thicknesses of 8 - 10 and 10 - 15 µm, respectively. Stellite Alloy 1 needs additional energy from DC-pulsed plasma to form a comparable, but thinner (ca. 2 µm) MeB\(_x\) layer at T = 730°C. The boride layers show high hardness (2,000 - 2,500 HV\(_{0.05}\)), an increase in thermal stability and oxidation resistance, and strong adhesion to the substrate. The strong adhesion of the formed thin layer may be due to thermochemical diffusion processes. This is different to ceramic coatings, which create a sharp interface between the dissimilar metal substrate und ceramic coating. The thermochemical treatment during boriding converts the metallic phases of the edge layer into MeB\(_x\) phases with a strong adherence to the substrate.

**Keywords**

boriding  
hot forming  
wear resistant
XPS, ATR-FTIR and friction studies on modifications of polydimethylsiloxane after exposure to argon-oxygen plasma and UV radiation at 172 nm, 185 nm and 245 nm

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The biocompatibility of polydimethylsiloxane (PDMS) makes this polymer a valuable material for various medical applications. To modify the surface properties of PDMS plasma or UV radiation are frequently used. While there are several studies investigating the physicochemical changes after surface treatments [1-3], currently there are no studies comparing the treatments or documenting the tribological properties. In this study the modifications of PDMS by an atmospheric pressure argon-oxygen plasma and UV radiation at 172 nm, 185 nm and 245 nm have been compared. The surface has been analysed with X-ray photoelectron and ATR-FTIR spectroscopy. Friction tests have been conducted to evaluate the differences in the tribological properties after the treatment. It was observed that UV treatment with 172 nm and 185 nm radiation for time periods above 5 min produced SiO$_x$ films reaching to greater depths and with a higher proportion of hydroxyl groups than with a plasma treatment. On the other hand, a plasma treatment produced films with a stoichiometry closer to SiO$_2$. Furthermore it was noted that UV radiation at 254 nm had little effect on the chemical structure of the material. The friction coefficient decreased significantly after exposing the specimens to 172 nm radiation and noticeably for 185 nm. After plasma or 245 nm radiation exposure, the friction coefficient exhibited a comparably small decrease. Exposures to UV radiation at 172 nm and 185 nm for a time period of 1 min produced surfaces with an increased friction coefficient compared to reference measurements.

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References

Keywords
UV
polydimethylsiloxane
dielectric barrier discharge
Influence of the deposition parameters on the structural evolution and thermo-mechanical properties of HiPIMS sputtered Transition metal carbides coatings

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Transition metal carbides are well known for their outstanding thermal stability, high melting temperature, and excellent mechanical properties. Hence, these so-called ultra-high-temperature ceramics (UHTC) are successfully applied in the aviation and space industry. Depending on the transition metal, the compositional range of the most preferred cubic NaCl structure ranges from TM-C\textsubscript{0.6} to TM-C\textsubscript{1.1} or higher. With these variations in elemental composition, also the properties of these materials are modified. Our recent work indicates similar properties and dependencies for magnetron sputtered thin films (TaC\textsubscript{y} and HfC\textsubscript{y}) \cite{1}.

As the deposition of carbon-containing coatings is challenging with respect to chemical and structural evolution, high power impulse magnetron sputtering (HiPIMS) is an interesting approach due to high ionization degrees and hence enhanced surface mobility of arriving species. Within this work, we successfully deposited Transition metal carbides hard coatings using a pulsed DC, as well as a HiPIMS powered target, in a lab-scaled magnetron sputtering system. We examined them for structural characteristics using x-ray diffraction, studied their mechanical properties, and determined the elemental composition – especially, with respect to the off-stoichiometry. We performed these investigations with regard to a wide variation in deposition parameters such as deposition pressure, duty cycle, as well as peak power density. Furthermore, the thermal stability and oxidation resistance of selected coatings were investigated by a set of high-resolution characterization (HR-TEM, APT, and DSC) techniques.


**Keywords**

Transition metal carbides
Ultra-high-temperature ceramics
High power impulse magnetron sputtering
Magnetron Sputtering of suitable sensitive materials for Hall sensors

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The all commonly used Hall sensors in industry are based on semiconductors which are inconvenient for devices operating in a hard environment with radiation and high temperatures. In such environment the ceramic-metal Hall sensors with high temperature and radiation resistance have to be used. The metal Hall sensors consist of a thin film of suitable metal deposited on a ceramic substrate. The DC magnetron sputtering was used for the preparation of series of thin film sensors based on various metals. During depositions there was a necessity to find proper combination of parameters such as the power of DC source, i.e. deposition rate, substrate temperature, deposition time, which corresponds to the thickness of thin film, and an appropriate positioning of substrates in the deposition chamber. All these parameters have significant influence on final properties of the thin film Hall sensor. The research was focused on the optimization of deposition parameters and determination of production processes leading to improve sensor functionality. The research and development of thin sensitive layers made from bismuth resulted in the implementation of a new magnetic diagnostics for the international fusion reactor ITER. The outer vessel steady-state magnetic field sensors based on bismuth thin films will perform an absolute measurements of the ITER magnetic field. The Hall sensors with bismuth thin film were deposited on ceramic aluminum nitride AlN substrates at the deposition temperature of 200°C. The steady-state magnetic sensors will also be an important part of diagnostics for the future fusion power reactors starting with the DEMO device. The higher ambient temperature at some sensor locations in DEMO compared to ITER limits the applicability of bismuth sensors and, therefore, several candidate materials like antimony, molybdenum, tantalum, and niobium, offering higher operational temperatures compared to bismuth are the subject of the present research.

Keywords
magnetron sputtering
thin film
hall sensor
NEW REACTIVE SPUTTERING PROCESSES WITH BIPOLAR-PULSE-SYSTEMS

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In terms of sputtering, high-resistance or insulating sputter-layers are very demanding. Reliability, long-term stability and reproducibility are still a challenge. The layers have important functions and become more and more interesting; electrical, optical, decorative, wear and diffusion inhibiting properties that are of great importance to the user. Reaction materials such as Oxides (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ...), Nitrides (Si\textsubscript{3}N\textsubscript{4}, AlN, TiN, ...), Borides and others are in focus. New bipolar pulse-systems offer the solution. Bipolar pulse-systems can deliver absolutely constant voltage pulses. Every pulse energy can be regulated exactly, there are no critical overshoots and the ratio "on-off" can be adapted to the process. In particular, fast arc shutdown with the lowest arc energy continues to be a very important factor. Excellent and best reproducible layers are the result. If there are still many reactive layers with a sine wave frequency today, the use of bipolar pulse-systems increases significantly due to their advantages. The lecture reports on the use of bipolar pulse-systems with their clear advantages in reactive sputter deposition for best layer performances.

Keywords
Bipolar-Sputtering
Reactive-Sputtering
Pulse-Energy
Pulse-Advantages
Pulse-System-Solution
Sputtering of TiAl-Monolayers for Highly Planar Micro-Mirror Arrays - Stress Adjustment over Target Lifetime

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Amorphous Titanium-Aluminium (TiAl) is used as mirror core material for the fabrication of microelectromechanical systems (MEMS) based micro-mirror arrays (MMA). This presentation challenges the planarity optimization of such micro-mirrors with pixel sizes ranging from 10 to 100µm processed on 200mm wafers. We present an approach for mirrors consisting of a TiAl core of 2...3µm total thickness. Using this approach, we aim at low surface RMS values close to zero after deposition and patterning as well as at a good long-term stability. We present the deposition and subsequent characterization of 250 to 2000nm thick TiAl-monolayers. To achieve a high thickness uniformity, the target substrate distance is adapted over a full TiAl-sputter target lifecycle. Pressures during deposition between 0.15 and 0.50Pa are used to set the individual layer stress. The results match well with the Thornton model of film growth and are described within a model for subsequent stress prediction. We present a model for the deposition rate depending on pressure, aimed thickness, target lifetime and target substrate distance. Additionally, we give an impression of the stability of the sputter process of the monolayers over a full TiAl-sputter target lifecycle.

Keywords
TiAl
sputtering
micro-mirrors
Growth of nanocolumnar thin films on patterned substrates at oblique angles

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Nanocolumnar porous thin films deposited at oblique geometries are nowadays receiving much attention due to their unique morphological features and remarkable properties. From an experimental point of view, porous nanocolumnar thin films have been classically grown by evaporating a given material in vacuum and promoting the glancing incidence of gaseous deposition species onto a tilted substrate, in a so-called Glancing Angle Deposition. The magnetron sputtering technique operated at oblique angles (MS-OAD), has emerged as one of the most interesting procedures in terms of efficiency, reliability, reproducibility, and potential industrial scalability. The variety of typical porous morphologies that can be achieved by the magnetron sputtering technique operating at oblique angles (MS-OAD) is rich, allowing the customization of film nanostructures with optimum performance for numerous functional applications. However, to our knowledge, there are important unexplored conditions that require further study and that might widen the possibilities of the method even more. In this work we have analyzed the influence of substrate patterns on the nanocolumnar development of thin films grown by magnetron sputtering at oblique angles. A critical thickness has been defined, below which the columnar growth is modulated by the substrate topography, while for thicknesses above this value, the impact of substrate features is progressively lost in two stages; first columns grown on taller features take over neighbouring ones, and later the film morphology evolves independently of substrate features. These results have been experimentally tested by analysing the nanocolumnar growth of SiO₂ thin films on ion-induced patterned substrates.

Keywords
magnetron sputtering
nanostructures
oblique angle deposition
patterned substrate
thin films
V doped-TiO$_2$ anatase thin films deposited by Plasma Enhanced Chemical Vapour Deposition at low substrate temperature for photocatalytic applications

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Anatase TiO$_2$ thin films are of major interest due to their valuable properties. However, anatase band gap (3.2 eV) limits the photocatalytic reaction under visible light irradiation. Thus, one of nowadays’ burning topic in photocatalysts is the redshift of photocatalytic reaction. Among various approaches, transition metal doped TiO$_2$ layers appears to be a very promising one. In this work, we investigate the possibility of synthesizing V doped anatase TiO$_2$ layer by a low-substrate temperature pulsed Electron Cyclotron Wave Resonance (ECWR) PECVD process, using Vanadyl (V) triisoproxopoxide (VTOP) and Titanium (IV) isopropoxide (TTIP) as precursors. The influence of several experimental parameters such as the RF power, the pressure, and the plasma gas mixture are explored. We mainly focus on the V doping concentration, which can be tuned by varying the TTIP/VTOP ratio injected in the plasma. The cristallinity, morphology and composition of these V-doped titania layers are characterized by means of Scanning Electron Microscopy, Raman Spectroscopy, X-Ray Diffraction analysis. V position in the TiO$_2$ lattice is also monitored by XRD and Raman. UV/Visible absorption spectroscopy and ellipsometry were used in order to monitor the impact of the dopant concentration on the optical properties, i.e. their band gap, to evaluate their ability to absorb visible light. Finally, the photocatalytic performances of the V-TiO$_2$ layers are evaluated by measuring their ability to decompose stearic acid under 365 nm UV-light and solar spectrum simulator.

**Keywords**
Pulsed-PECVD
V-TiO$_2$
Low-temperature
Photocatalysis
Solar simulator
Study of non-thermal tetravinylsilane plasma by mass spectrometry

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Organosilicon films are an important part of many mechanical, optical, electronic and medical devices and are also necessary to optimize the surface properties of any type of material with respect to its application. By using low pressure PECVD, the non-thermal tetravinylsilane (TVS) plasma allows the deposition of organosilicon films with variable chemical and physical properties controlled by the input power. The power dependence of plasma species is investigated by mass spectrometry (Process Gas Analyzer HPR-30, Hiden Analytical, UK) and mass spectra are interpreted using the fragmentation patterns of the TVS molecule predicted by ACD/MS Fragmenter (Advanced Chemistry Development, Canada). Plasma species (TVS fragments, intermediates, by-products) are found to be products of electron impact dissociation in the plasma and chemical reactions at the surface of a growing film. Mass spectra contain many tens of fragments of different reactivity (non-radicals, monoradicals, biradicals, and higher-degree radicals or atoms, e.g., carbon) and their analysis leads to the selection of dominant species responsible for film growth. Power dependence varies for carbon species, silicon-containing species, and by-products such as hydrogen or methane molecules. The deposition rate evaluated by in situ spectroscopic ellipsometry correlates with the flux of plasma species hitting the film surface, including the probability of species binding. Thus, it is expected that the plasma species may be related to the elemental composition and chemical structure of the deposited material. The C/Si flux ratio in different plasma (different power) is related to the C/Si ratio in the deposited films characterized by Rutherford Backscattering Spectrometry (RBS). Also, the flux of vinyl-containing species in different plasma is related to the concentration of vinyl groups incorporated in deposited films characterized by infrared spectroscopy. Thus, some relationships between plasma chemistry and film chemistry are confirmed.

Keywords
thin film
PECVD
mass spectrometry
TVS fragmentation
The Systematics of Reactive Ion Beam Sputter Deposition of SiO2 and TiO2 Thin Films

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Ion beam sputter deposition (IBSD) is a physical vapour deposition (PVD) technique, which uses a low-energy ion beam for sputtering a target. In contrast to other PVD techniques, for instance, magnetron sputtering or evaporation techniques, IBSD offers more degrees of freedom for tailoring the properties of the secondary, film-forming particles and, hence, thin film properties [1].

This paper focuses on systematic investigations of the IBSD process of oxide thin films, namely, SiO₂ [2,3] and TiO₂ [4-6], using O₂ [3,6], Ar or Xe ions [2,4,5] with an ion energy between 0.5 keV and 2.0 keV. Additionally, the ion incidence angle and polar emission angle were systematically varied. The films were characterized with respect to crystal structure, composition, surface roughness, mass density and optical properties. Systematic correlations of between process parameters and thin film properties were found, which can be assigned to properties of sputtered target and scattered primary particles, especially, to the energy of these particles. The most crucial process parameters were identified to be the scattering angle and the ion species, or, to be more precise, the mass of the primary ions in relation to the mass of the target particles. The systematics are similar for SiO₂ and TiO₂ films. However, the variations in absolute numbers can differ considerably.


Keywords
Ion beam sputter deposition, film properties, scattering geometry, SiO₂, TiO₂
POC020

**Multifunctional coatings with antibiofouling properties**

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*Biofouling is “the accumulation of microorganisms, plants, algae, or small animals on wetted surfaces that have a mechanical function, causing structural or other functional deficiencies”.* Biofouling process has enjoyed a special attention for its affectation to a big number of different pieces from different applications: offshore platforms, vessels, biomedical devices, architectural pieces, decorative pieces... All aforementioned applications have a common need, achieve a multifunctionality in order to accomplish its main function, avoiding biofouling formation. Focusing in this issue, doped metallic oxynitrides are a plausible solution, bringing to the board an interesting viewpoint of multifunctionality in surfaces: aesthetics and antibacterial. The present study developed Ti(O)N and Zr(O)N films doped with two different biocides agents, silver and copper. Reactive direct current magnetron sputtering with reactive gas pulsed process was used in order to obtain the aforementioned films over metallic samples. Physical, chemical and morphology characteristics were assessed, as well as functional properties like colour variation, wettability, roughness and antibacterial resistance. Comparing the colour palette, Zr(O)N got a wider variation than Ti(O)N system. Blue, rose-gold, golden, purple and black tones were obtained. Antibacterial and antifouling tests proved that the biocidal agents inhibited *S. epidermidis* and microalgae growth. The coatings developed by the present study can be easily tunable to the desirable decorative purposes with antibacterial and antifouling.

**Keywords**
Multifunctional
Antibiofouling
Aesthetic
Oxynitride
Oxide semiconductors and related devices produced by high power impulse magnetron sputtering and selective area atomic layer deposition methods

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Zinc oxide (ZnO) and Al-doped ZnO (AZO) are widely used as n-type semiconductors and transparent electrodes due to the abundance and low cost of Zn and Al in addition to their high optical and electrical properties. An important technique for depositing (AZO) films is the High Impulse Magnetron Sputtering (HiPIMS) method that allows us to deposit highly conductive and transparent films on large surfaces and at low temperatures [1]. Another important technique is the Atomic Layer Deposition (ALD) which is used for depositing high-quality films with excellent surface coverage on high aspect ratio structures; this method enables us to combine metallic Cu films with semiconductor oxides (ZnO, Cu$_2$O, or both) leading to many applications in different fields related with optoelectronics, catalysis, gas sensing and photovoltaics [2]. Cuprous oxide (Cu$_2$O) is a direct-gap semiconductor also used as an absorber in solar cells. The fabrication of segmented p-Cu$_2$O/n-ZnO nano-junctions is facilitated by selected area atomic layer deposition (SA-ALD).

In this presentation, we report on the optimization of AZO layers synthesized by reactive HiPIMS [1], on the fabrication of devices based on p-Cu$_2$O/n-ZnO nano-junctions by a combination of HiPIMS and a SA-ALD method we have developed [2] and on the strategy we are developing, towards the fabrication of segmented textured solar cells based on such junctions.


Keywords
Solar cells, HiPIMS, ALD, Texturing, Semiconductors
Multiscale simulation of multicathode reactive magnetron sputtering processes at industrial scale

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This contribution presents a novel approach to predictive simulation of DC reactive magnetron sputtering with multiple cathodes and multiple sputtered elements. It enables a prediction of reactive gas distribution, reactive gas depletion and target poisoning for each cathode separately. This model can therefore be used for optimizing coating uniformity and stoichiometry, as well as position of the reactive gas inlet(s). The presented model overcomes the “multiscale” nature of reactive magnetron sputtering, which poses a problem for efficient simulation of this process. This is achieved by segregating the plasma dynamics timescales, metal vapor transport timescales and reactive gas timescales - ultimately arriving at computation times of approximately one day for a fully loaded industrial chamber in 3D.

Keywords
reactive DC magnetron sputtering
plasma model
simulation and optimization
uniformity and stoichiometry prediction
target poisoning
Gas flow simulations of a DBD plasma for deposition processes in pipes

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Dielectric barrier discharges (DBD) at atmospheric pressure are known to be able to create thin layers by means of plasma enhanced chemical vapor deposition (PECVD). Such processes can also be employed to directly deposit thin coatings on the inner sides of pipes and ducts. To this purpose, a DBD electrode for PECVD coatings has been developed.

The experimental setup consists of an inner glass-covered electrode and the metal pipe wall acting as counter electrode. The carrier gas (air) admixed with the film precursor hexamethyldisiloxane (HMDSO) is injected into the gap between the electrodes, where the discharge is located and chemical reactions take place. The inner electrode is moved continuously and steadily through the pipe to achieve a thin and uniform layer along the whole pipe length.

In the current work, a model of the DBD reactor has been replicated by means of an FEM-based model with the aim to investigate the gas flow injected in the reactor: in order to ensure a homogeneous deposition both in thickness and in chemical composition, the monomer-based reactive species must be homogeneously distributed in the plasma phase along the whole deposition volume, with a long enough residence time to attain a higher deposition efficiency. Backflow and stark pressure gradients must also be avoided in order to prevent the formation of dust directly in the plasma phase or in the immediate after-glow. The inner electrode shape, size and conformation have been thus accordingly tuned and optimized.

Subsequently, the simulation model has been refined by taking into account the effects of the heat caused by the plasma itself, the deposition process and the compression/expansion of gas along the pipe. For this purpose, optical emission spectroscopy in the ultraviolet range and thermo-camera analyses have been employed as experimental reference for the FEM-model.

Keywords
Dielectric barrier discharge
Simulation and modeling
Gas flow
Plasma enhanced chemical vapor deposition
Diagnostic of Magnetron Sputtering by using a Passive Thermal Probe

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Plasma surface processes (e.g. magnetron sputtering) have enabled the production of different thin films and devices, leading this way to new technologies for research and industry. A strong correlation between the film properties and process parameters is proven, which makes the diagnostic of the process plasma necessary in order to understand and manipulate the deposited films.

Recently, we have been able to study the plasma parameters during the production of memristive devices [1]. Memristive devices are valued for their non-volatile electronic property, which allows them to store their resistance even after the power supply is switched off. According to this, they can be applied in image processing algorithms or even neuromorphological circuits in order to build brain-like chips. Since the investigated films are deposited by magnetron sputtering, it is important to understand the physics of the discharge through plasma diagnostic. Therefore, we used a passive thermal probe, which can be operated simultaneously as a calorimetric probe for energy flux measurement, and as a planar Langmuir probe for measuring the floating and plasma potentials as well as the electron temperature [2].

The passive thermal probe has also been used during many other coating processes such as sputtering of magnetoresistive films [3]. Through their ability of matching the electric resistance to the applied magnetic field, they received importance in contactless position and angle measurements. With the plasma diagnostic method radial measurements across the substrate region and for the operation of one or more targets can be performed. Based on the results we can explain possible radial variations along the films and conclude for dominating factors affecting the films electric or magnetic properties, respectively.


Keywords
passive thermal probe
Energy flux measurements on atmospheric pressure plasma spray torches with passive thermal probes

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Plasma spraying is an established coating process for the deposition of metallic and ceramic layers onto various substrate surfaces [1]. The control and optimisation of the whole process is of great interest in research and industry. Nevertheless, since the energy density in the plasma is much higher than in other experimental plasma sources the choice of diagnostics is very limited. The energy flux from the plasma to the surface is an important parameter to understand film growth and plasma surface interaction in general [2]. To measure the energy flux of plasma spray torches with and without the involvement of coating materials [3], efforts were made to adopt existing calorimetric probes. In order to withstand the harsh environment and temperatures, some changes of the probe design and evaluation were necessary and show promising results. The presented measurements showcase the applicability of a thermal probe for diagnostics of a plasma spray torch. Two different plasma spraying devices were investigated with regard to spatial resolution, input parameter as e.g. input energy and coating powders. The energy flux is among others dependent on the amount of impacting material, its temperature and degree of melting. When correlated with coating properties this method could provide a versatile control tool for the complex coating process. [1] Vardelle, A., et al. "A perspective on plasma spray technology." Plasma Chemistry and Plasma Processing 35.3 (2015): 491-509. [2] Gauter, S., et al. "Calorimetric investigations in a gas aggregation source." Journal of Applied Physics 124.7 (2018): 073301. [3] Kewitz, T., et al. "Investigation of a commercial atmospheric pressure plasma jet by a newly designed calorimetric probe." IEEE Transactions on Plasma Science 43.5 (2015): 1769-1773.

Keywords
atmospheric pressure plasma
ergy flux
plasma spraying
Directionally Resolved Characterization of Sputter Processes with Force Probes and Quartz Crystal Microbalances

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In today's technology, sputtering is a well-established method to etch semiconductors or to deposit thin films. The optimization of the sputter and coating process requires a detailed understanding of the physical phenomena. The particles released by sputtering a target do not distribute uniformly in all possible directions. Deposition rates can be measured by quartz crystal microbalances, while charged particles in the sputter plume can be characterized by Faraday cups or retarding field analyzers. The diagnostic of the neutral particles requires more complex diagnostics, such as optical emission fluorescence, laser-induced fluorescence [1], or mass spectrometry [2]. Interferometric force probes allow for a more direct measurement of all particles in the sputter plume by measuring their momentum transferred onto the probe surface. Previously, these probes have been used to determine the thrust of ion engines, forces exerted by a low-temperature plasma onto a solid boundary [3], or the recoil of reflected and sputtered particles at a sputter target [4]. In this study, force measurements were combined with measurements of deposition rates. Sputter plumes are generated by an ion beam directed onto a rotatable copper or aluminum target, respectively. A directionally resolved momentum profile and the deposition rate are obtained by circling a force probe and a quartz crystal microbalance about the target at a fixed distance. The profiles are compared with numerical simulations using SRIM [5]. Measurements and simulations are carried out for different angles of incidence, ion energies, gases and target materials.


**Keywords**
sputtering
force probe
QCM
Predicting coating uniformity on substrates with planetary rotation in 2D and 3D

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Recent advancements in the fundamental knowledge of PVD and PECVD mechanisms enabled high-fidelity simulation of numerous processes powered by vapor deposition. Together with the advancements in physics solvers and the ever-improving access to high-performance computing, it has become possible to utilize numerical simulation for predicting the coating uniformity and, to some extent, coating properties. All this can be done on realistic 3D substrates or even industrial chambers with realistic loading. This contribution discusses the challenges of pre-processing and post-processing of 3D simulation data. It also illustrates, on several examples, what kind of additional insight can be obtained from 2D and 3D coating simulation on realistic substrates.

\textbf{Keywords}

vapor deposition  
numerical simulation  
coating prediction  
3D simulation  
coating properties
Self-consistent modelling of a linear microwave plasma source

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Microwave plasmas have a wide range of technical applications such as thin film deposition, etching, surface activation or gas conversion. The Duo-Plasmaline, a linearly extended low pressure microwave plasma source, is particularly suitable for such purposes because it can be extended to several meters in length and can produce large volume, high density plasmas.

In this work, the Duo-Plasmaline is investigated for the application in a conceptual recycling system of unburnt fuel (deuterium and tritium) in future fusion devices. Here, the exhaust gas is dissociated by the plasma source so that the atomic and ionic hydrogen isotopes can be separated from other gas species by a metal foil pump via superpermeation.

A self-consistent numerical model of hydrogen plasma from the Duo-Plasmaline was set up to gain insight into the spatial and temporal evolution of the plasma properties and production rates of hydrogen atoms and ions under different operating conditions. An FEM-based fluid approximation for the plasma is used and coupled with the wave equation for the microwave field. A reduced set of reactions, including electron impact collisions, heavy particle reactions and wall reactions, is considered for the plasma chemistry. The distribution of important plasma quantities, such as electron density and temperature, as well as the densities of ionized, excited, and neutral species are studied in terms of gas pressure and microwave power. The simulation results are compared with experimental data.

Keywords
microwave plasma
Duo-Plasmaline
plasma modelling
Characterization of Surface Topometry and Determination of Layer Thickness by Scanning White Light Interference Microscopy

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3D coherence scanning interferometry (CSI) is an optical, non-contact and rapide measurement technique using a defined bandwidth of white light at normal incidence. Based on this operational principle, white light interference microscopy (WLIM) provides three-dimensional surface topometry data up to a resolution of 0.4 μm lateral and 0.1 nm vertical. Three operating modi, i.e. surface, films and advanced films, enable measurements of step heights, roughness, wear volume, cone angle, surface pattern and layer thickness of transparent coatings.

The determination of layer thickness by WLIM requires the knowledge of optical constants, i.e. the refractive index n and the extinction coefficient k. For technical surfaces, data base values - if available at all - have to be determined or validated by spectroscopic ellipsometry (SE). From this oblique incidence technique both optical constants and layer thickness can be derived based on a model for at least semi-transparent coatings. For different layer thicknesses, a comparison is made between WLIM and SE. Measurement uncertainty is discussed for both topometric features and layer thickness for different use cases.

Traceability to SI system is ensured by certified standards (PTB/NIST) within a DAkkS DIN EN ISO/IEC 17025:2018 accredited lab.

Keywords
roughness and step heights
lateral surface pattern
layer thickness of transparent coatings
scanning white light interferometry
spectroscopic ellipsometry
An automated evaluation for the Rockwell indentation test

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Coating adhesion is one of the most important parameters for evaluating the quality and functional reliability of thin-films for tribological purposes. The Rockwell indentation test, standardized in ISO 26443 and DIN 4856, is an established test method in industry and research for determining coating adhesion. A hardness indentation according to Rockwell C is performed on the coated component. Any damage to the coating around the indent is qualitatively assessed and classified into adhesion classes according to the visual impression. For this purpose, comparative images are used which schematically show typical crack and spalling patterns in various forms. The evaluation can only be carried out by experienced personnel, but nevertheless, evaluation differences occur with different persons. The documentation is complex and there is no possibility for automation. This procedure no longer meets the current requirements of quality assurance. Therefore, there is an urgent need to be able to carry out an automated quality check of the layer adhesion.

In a project, funded by the Federal Ministry for Economic Affairs and Energy, (PtJ_03TNH023A) the basics for an automated coating adhesion test are developed. The overall objective of the project is to move the Rockwell indentation test for evaluating the adhesion of hard coatings from a subjective assessment to an objective measurement and to prepare the results for standardization.

The Poster will show the automatic Rockwell indentation device, the technical innovation of the software and fields of application.

Keywords
Coating adhesion
ceramic coatings
Rockwell indentation test
Evaluation of impedance spectroscopy for the characterization of dielectric thin films

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The overall thickness characterization of thin films coated on complex 3D geometries (e.g. drills) is in many cases very time-consuming or expensive. For dielectric coatings impedance spectroscopy can be an option to determine the thickness from impedance measurements. The impedance of a capacitor is directly connected with the layer thickness of the dielectric coating and the permittivity. In order to evaluate the method simple flat samples coated with Al$_2$O$_3$ and TiO$_2$ have been produced by reactive RF sputtering and ALD. The thicknesses measured by X-ray reflectometry and ellipsometry have been compared with the results obtained by impedance spectroscopy. Finally, impedance spectroscopy has been applied to the overall thickness characterization of Al$_2$O$_3$ thin films conformally coated on drills with 0.3 and 3 mm diameter.

Keywords
layer thickness
permittivity
thin film
defects
Oxidation resistance of Ta doped WB2-z coatings

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Future tasks in many different fields of academia and industry are directed towards environmental sustainability, asking also for new advances in the field of protective coating materials. Especially, transition metal diboride based thin films exhibit a great potential to be applied in various applications, due to their extreme refractory character as well as interesting electrical properties. Latest studies on various diborides emphasized their strong and weak points being on the one hand high hardness and phase stability in a wide range but on the other, the limited oxidation resistance. Alloying concepts involving transition metals (TM) such as W, Ta, or Zr forming ternary diborides (TM₁₋ₓTMIIₓB₂₋z) suggest to be a proper solution to overcome these restrictions.

Hence, the oxidation behaviour of WTaB₂ thin films was experimentally investigated up to 700 °C and annealing times from 1 to 1000 minutes. Decreasing oxide scales and a change from linear to paralinear or parabolic oxide growth mode have been attested for coatings with increasing amount of Ta. Thus, adding Ta to α-structured WB₂₋z does positively influence the oxidation resistance. Due to resolution limits regarding boron detection with EDS technology, we additionally conducted TOF-ERDA. Especially, tungsten rich coatings revealed nearly boron free oxide scales, indicating a clearly volatile character of boron containing oxides during heat treatment. Moreover, a distinct increase in oxide scale density with increasing Ta content could be detected, also underlined by detailed TEM investigations.

Keywords
Ternary Borides
Protective Coatings
Oxidation Resistance
Scale Formation
Influence of the sputtering mode on thermochromic properties of LaCoO₃ selective layers for thermal solar collectors

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Thermochromic rare-earth perovskite LaCoO₃ is a promising functional material for a new generation of selective layers for passive regulation in thermal solar collectors. An efficient absorber coating of a thermal solar collector should possess both high solar absorption within the visible and near infrared wavelength range (>90%) and low infrared emissivity (<10%) within the wavelength range of 6 to 10μm. However, when the solar panel is exposed to strong solar radiation while hot water demand is poor or if the system is off, the temperature inside the collector may reach 200°C (stagnation conditions) resulting in heat-transport fluid degradation. A possible solution is to use thermochromic materials capable to reversibly switch their emissivity. Nevertheless, due to structural and chemical complexity, the design of this material is challenging and requires a deep understanding of crystallization mechanisms. In this work, we investigate the influence of in-situ (i.e. during deposition) oxidation of LaCo metallic films on perovskite formation conditions and eventual optical properties of the material. All films were deposited on aluminium substrates by magnetron sputtering in elemental (ESM) and compound (CSM) modes using a semi-industrial reactor with back-and-forth scrolling of the substrate. The samples were annealed in air for 2, 5 and 10 minutes at temperatures in the range between 500 and 600°C and characterized using XRD, FTIR, TEM and IR camera. TEM cross-sectional evaluations reveal that the structure of as-deposited films issued from the semi-industrial reactor corresponds to La/Co multilayers. It was found that preoxidizing fosters perovskite formation allowing to significantly decrease the annealing temperature. Obtained emissivity change (Δε) results confirm the great prospect of LaCoO₃ for the considered application.

Keywords
thermal solar collector
perovskite
thermochromism
thermal regulation
thin film
Securing in-line layer thickness measurements by using spectroscopic plasma monitoring for real-time control and adjustment of refractive indices in production processes

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While specifications in thin film industry are getting more and more demanding, high production yields and cost effective production becomes a major factor in this competitive market. Quality control of the final product does ensure the specifications of the shipped product but is of limited use for real-time process control due to the indirect feedback loop. Smart and combined in-line or even in-situ control techniques will fill this gap in production lines by monitoring process and product simultaneously with real-time production feedback. Spectroscopic measurements of the reflectivity and/or transmissivity of the deposited layer is a well-known technique to determine the thicknesses of the individual layers of a coating. The underlying calculation depends critically on the knowledge of the refractive indices of the coated layer, which in general are fixed input parameters. It is also known that these material parameters depend on conditions of the coating process, i.e. the plasma parameters. However, plasma parameters will change over production time, e.g. due to parasitic coating of the vacuum vessel in PECVD applications or due target erosion in sputtering applications, and thus the refractive indices must be adjusted for reliable layer thickness calculation. By measuring continuously the plasma parameters, especially the relative content of certain plasma species, via spectroscopic plasma monitoring changes in the refractive indices can be deducted and provided as input parameters for the layer thickness calculation in real time. This combined measurement technique results in more reliable thickness values of the coated layer.

Setups for in-line and in-situ applications are presented and results from PECVD process producing e.g. silicon nitride and a-C:H layers as well as from sputtered Al₂O₃ layers are discussed.

Keywords
spectroscopic plasma monitoring
thickness measurement
real-time control
In-situ plasma monitoring during pulsed laser deposition of Cu2O thin films and comparison with HiPIMS

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Copper oxide Cu$_2$O is an important and well known p-type transition metal oxide semiconductor material which has the advantages of direct band gap 2.1 eV and high absorption coefficient in the visible spectral range. In our work we prepared the thin film by means of Pulsed Laser Deposition (PLD) and we compare with those fabricated and reported by means of HiPIMS in literature. The aim of the study was to carried out the Optical emission spectrometry (OES) and generates spatial maps of the main elements of the transient plasmas generated laser ablation. In situ plasma monitoring of the laser produced plasma plays an important role as a feedback and control mechanism in order to adjust the technological processes. OES is the best candidate for plasma monitoring as it is a non-invasive technique and has abilities for quantitative and qualitative analyses. PLD of the a ceramic CuO and metal Cu targets was performed on a wide range of O$_2$ pressures (from 10$^{-3}$ up to 20 Pa) in order to achieve stoichiometric transfer and tailor the properties of the thin films. During the deposition process, the optical emission of the plasma was recorded using a 10 linear bundle full range optical fibre connected to high resolution spectrometer. The fibre was positioned at various distances with respect to the target in order to extract the spatial distribution of the species within then plasma volume. Using a specialized database, we identified emission lines for both Cu atoms and ions and only O ions. Using the Boltzmann approach from we determined the global excitation temperature, the electron density was also estimated using the stark broadening approach. The results are compared with the properties of the deposited thin films determined by surface analysis techniques like, AFM, SEM, XPS, Raman Spectroscopy or XRD.

Keywords
Optical emission spectroscopy
Cu2O
thin films
laser plasma
The Multipole Resonance probe as a real-time in-situ plasma diagnostic for process monitoring and control

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Based on the concept of active plasma resonance spectroscopy (APRS) the Multipole Resonance Probe (MRP) has been introduced as a diagnostic tool for electron density measurements. It takes advantage of the fact that electrons can resonate near the electron plasma frequency. In recent years efforts in modeling, simulation, and experiments lead to advances in understanding and design of the MRP.

In this contribution, the probe is applied to industrially relevant processes such as sputtering. Due to the ceramic tube surrounding the probe, the MRP is insensitive against dielectric coatings and can be adapted as a highly functional and fast diagnostic system for such deposition processes, where other diagnostics, e. g. Langmuir probes, fail. It can be used for real-time electron density monitoring and has been tested in control loops to stabilize deposition processes, e.g. reactive sputtering. This process suffers with surface dependent instabilities. The appearance of ambiguous working points can be controlled by use of the MRP and the introduction of a special precontroller unit.

Additionally, a new electronic concept is introduced to deal with the real-time requests of control applications to balance plasma parameters. The MRP is a realization of the vision to build up process controls based on plasma diagnostic.

Keywords
MRP
plasma diagnostic
plasma monitoring
control
sputtering
A robust method for in-situ gas monitoring of CVD processes using optical emission spectroscopy of a pulsed remote plasma

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Effective and robust monitoring of individual gas concentrations during CVD processes offer a unique insight into the condition of the process. In particular, CVD processes that utilize large organic molecules as precursors, such as Atomic Layer Deposition (ALD), can present challenges due to contamination of sensors and subsequent stability issues.

Conventional quadrupole residual gas analysers have difficulty monitoring CVD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many CVD precursors. For these reasons, monitoring of precursor gas concentrations during the CVD process is not often undertaken.

An alternative gas sensing technique, built around the principle of remote plasma emission monitoring, can operate directly at pressures up to 1 mbar. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the vacuum system. Importantly, this plasma, generated inside the sensor, has a sole function as an optical emission spectroscopy (OES) based gas detector and does not affect the process itself.

This work will demonstrate that the sensing method is robust when exposed to two examples of CVD process; ALD and HMDSO based SiOx CVD. Previous work has demonstrated the usefulness of this technique with PVD processes. However, contamination and instability developed in the plasma generator when exposed to large organic precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. The results show that the pulsed power technique is effective in preventing contamination of the sensor’s electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products through increased molecular disassociation. Also, a method of regenerating the condition of the sensor electrodes using a pulsed oxygen purge and an MF plasma will be discussed and demonstrated with monitoring HMDSO for SiOx process.

Keywords
ALD
In-situ
OES
Coating development focussed for decades on the film’s composition in an endless endeavour for increasing the hardness of the coating. On the other hand it was taken for granted that the thickness of tool coatings is limited to 3-4 µm. More than 6 µm is for traditional technologies not a viable option due to excessive intrinsic stress. No real improvement are the usual workarounds such as bond coats and multilayers with soft intermediate layers. The process gets slower and more prone to failures. There was no technology available to deposit the extra thick coatings for heavy-duty metal cutting applications. This paper will shine a light on a new direction for protective coatings: managing intrinsic stress and a dense morphology of the film.

HiPIMS is a good candidate since it is known for a dense structure without any droplets resulting in toughness and hardness at the same time. The real innovative leap is stress management by synchronising the HiPIMS pulses on the cathodes with the substrate bias. This paper will introduce the concept of selective ion biasing. Plasma analytics reveal that the flux arriving at the substrate per HiPIMS pulse is composed of the wanted metal ions coming from the target and other ion portions which highly influence the intrinsic stress of the growing film. Selective ion biasing is a fully new tool and allows to precisely select certain ion portions out of the pulse while suppressing unwanted species. Now the coating developer can actively tune the intrinsic stress of the film by setting the synchronisation parameters.

Full control on the process, the morphology and the intrinsic stress growing film - that’s the quantum leap of selective ion biasing. And this for different HiPIMS frequencies and pulse data for each and every cathode - tailored for the respective target material.

A case study of FerroCon®Quadro as a 12 µm PVD coating illustrates how HiPIMS moves the frontiers of the possible in tool coatings. Applications such as the milling of crank shafts, railway tracks and heavy duty turning show the enormous performance benefit of very thick PVD coatings for cutting tools. 12 µm PVD work, in HiPIMS.

**Keywords**

- HiPIMS
- thick
- stress management
- dense
Anisotropic mechanical performance of TiO₂ coatings produced by magnetron sputtering at oblique incidence

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TiO₂ coatings are of great interests for optical application due to the porosity control achieved by glancing angle deposition techniques. In order to investigate the dependence of the deposition incidence direction on the mechanical integrity of the coatings, nanoscratch analyses were performed on samples produced at an incidence angle of 75º. The scratch direction on the sample surface was also investigated and its response analysed according to the atoms’ arrival direction on the Si substrate. The plastic deformation produced was examined by Scanning Probe Microscopy (SPM) prior and subsequent to each test. Additionally, the specimens’ cross section was studied by Scanning Electron Microscopy (SEM) in order to correlate the film structure to its mechanical behaviour. For constant scratch depths of 25, 50 and 100 nm and scratch lengths of 5 μm, normal and lateral friction forces were measured during the tests. A notable dependence between the nanocolumns inclination direction on the mechanical response of the coating has been determined.

Keywords
Anisotropic mechanical behaviour
Magnetron sputtering
Oblique angle
Nanoscratch
Plastic deformation
Ready for the next step in tool performance!

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In our continuous search for improvement we have taken the step for industrial units with HiPIMS capability, discovering new properties, different material behaviour compared to conventional ARC coatings and better performance in cutting and forming applications. As many investigations were done on small-scale units, bringing this technology to industrial scale, larger units and also process upscaling was needed.

Today real production of coated parts require not only good coating properties also production related topics like reliability, easy maintenance, cost per part and flexibility of the coating unit itself plays an important role.

In this regard different HiPIMS coatings from AlCrN-based and AlTiN-based systems were deposited on industrial scale units for tool applications. The applied coatings were investigated concerning mechanical film properties like hardness, Young´s Modulus, chemical properties like composition and phase formation.

To verify the performance of the coating machine and the deposited coatings, industrial tests are carried out. The obtained results shown, that the HiPIMS technology is ready for serial production in a modern production environment.

**Keywords**

HIPIMS
ALCRN
ALTIN
Tool
Utilization of a Cold Plasma Source for the Metal Foil Pump of a Fusion Reactor

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In the last decades, a lot of research has been carried out to advance the technology towards a nuclear fusion power station. The current programme is in the pre-conceptual design phase of a demonstrational fusion power plant with 2 GW fusion power. Due to the unprecedented scale of the facility, it faces its individual challenges. One of these is a most efficient recycling technology of unburnt fuel (an equimolar mixture of the two hydrogen isotopes deuterium and tritium), which has to be extracted from the exhaust gas of the fusion reactor.

The most promising technology concept to achieve the fuel separation at the low densities close to the divertor is superpermeation. This phenomenon describes the permeation process of energized particles across a metal foil with an inlet surface barrier. KIT is currently developing a design for a metal foil pump (MFP), the technical realization of this process. On the metal foil, a naturally forming monolayer of impurities raises the energy barrier for dissolution of hydrogen into the metal, prohibiting the absorption of ground-state hydrogen to a large extent. A cold plasma source is used to energize hydrogen which enables it to overcome this monolayer and be absorbed into the metal bulk in atomic form. Subsequently, it can recombine to a molecule on the downstream surface, yielding an effective pumping which follows an energy-gradient.

KIT has set up a facility to investigate the Duo-Plasmaline manufactured by Muegge GmbH and developed at IGVP Stuttgart for the purpose of suprathermal hydrogen production. It is experimentally tested for its performance and reliability with varying operation parameters in view of application for fusion. Next to experimental findings and results linked to the above named varying operation parameters, the experimental facility of KIT and its diagnostics is presented. An outlook is given to future experimental activities at KIT.

Keywords
Fusion
Direct Internal Recycling
Metal Foil Pump
Superpermeation
Investigations on the two step process of plasma electrolytic based etching

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Plasma electrolytic polishing allows modifying material surfaces by etching. Depending on the starting surface roughness it can be decreased down to several nm. This process works under atmospheric pressure in an electrolytic bath. The conductive substrate which shall be etched is on positive potential (anode) and the box with the electrolytic bath on mass potential (cathode). The potential difference is in the range of 100 to 400 V, approximately. Due to strong heating induced by high current the electrolyte around the substrate evaporates leading to the formation of a thin gaseous layer in which the plasma is formed containing a lot of different species. The etching process consists of two steps which are not well understood, yet. During the first one the elements (principally not all) of the substrate material (e.g. stainless steel) are reacting with the negative ions, formed in the plasma, at the surface. That leads to a formation of one or more reaction products still staying at the material surface. In the second process step the reaction products are removed by further plasma chemical processes. Especially the last step is remarkably influenced by the conductivity of the electrolyte as well as the voltage applied at the substrate. In this talk results will be presented and discussed related to investigations on the etching of iron based material. Surface analytics provide information about the effect of applied voltage, conductivity of the electrolytic bath and the correlation of both focusing on understanding the two step etching process.

Keywords
plasma electrolytic polishing
etching
liquid
Controllable growth of graphene layer on dielectric substrate in microwave plasma torch at atmospheric pressure

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The initial stage of graphene layer deposition on silicon oxide substrate (Si/SiO₂) by ethanol decomposition in dual-channel microwave plasma torch at atmospheric pressure was studied in dependence on precursor flow rate and delivered microwave power. Prepared layers were analysed by scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The microwave plasma diagnostics was carried out using optical emission spectroscopy (OES). The sample analysis by SEM showed increasing density and lateral dimensions of horizontally aligned carbon nanosheets with increasing ethanol flow rate and their delamination and transition into vertically aligned graphene sheets with increasing substrate temperature. The Raman spectroscopy analysis of layers showed presence of D (1345 cm⁻¹), G (1585 cm⁻¹) and 2D (2685 cm⁻¹) peaks with 2D/G ratio corresponding to few layer graphene structure. At higher microwave power, above 400 W, mixture of amorphous carbon particles and graphene sheets was deposited on the substrate. In this case deposition, the D* peak at 1210 cm⁻¹ and D** at 1500 cm⁻¹ was observed in Raman spectra and C1s XPS spectra of carbon contained 20.4 at% of sp³ carbon phase in comparison to 8.3 at% in case of graphene nanosheets layer. The ability to controllably grow wide range of carbon-based layers directly on dielectric substrate using simple precursor at atmospheric pressure plasma system represents unique opportunity for future applications such as transparent conductive layers, sensors and carbon functional coatings.

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Keywords
graphene
plasma
torch
nanosheet
ethanol
POF013

Energy balance of a diffuse coplanar surface barrier discharge (DCSBD)

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For many industrial applications atmospheric pressure plasmas are of great interest as they can be easily integrated into existing processes and allow the treatment of surfaces without vacuum equipment [1-2]. In particular, Dielectric barrier discharges (DBDs) and diffuse coplanar surface barrier discharges are suited for numerous types of surface treatment including cleaning, oxidation and surface activation [3-5]. While efforts have been made to characterize such a setup with various diagnostics [6-7] it is not fully understood yet. For this purpose combined measurements of energy flux, current and voltage signals of the discharge, as well as the temperature of the oil cooling were carried out. These diagnostics were complemented by optical emission spectroscopy (OES). For the energy flux a passive thermal probe (PTP) described in [8] was used and the gas temperatures were confirmed by OES. By measuring the temperature at inlet and outlet of the cooling system the power absorbed in the oil could be estimated. Thus, the power delivered to a substrate and the power dissipated in the cooling system could be compared with the electrical input power. By performing the measurements simultaneously, the energy balance of a DCSBD could be obtained.

References

Keywords
DCSBD
DBD
energy flux
thermal probe
Argon-water DBD pretreatment and vapor-phase silanization of silica - Plasma-chemical model and experimental data

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A dielectric-barrier discharge (DBD) in an Ar/H\textsubscript{2}O mixture is an efficient tool to generate simultaneously H atoms and strongly oxidizing OH radicals, species which are able to remove organic contaminants from the surface (OH) and to catalyze the gas-phase rehydroxylation of high-temperature annealed silica (H). DBD pretreatment with 0.3 \% water vapor, combined with an immediately subsequent vapor-phase silanization in a flowing gas stream of Ar, saturated with (3-aminopropyl)trimethoxysilane at 80 °C, was applied for the amino-silanization of U-bent silica fiber optic sensors. In an immunoassay-based comparison, virtually the same results are achieved with the new vapor-phase procedure on the one hand, and the wet-chemical method on the other, although about 30 \% less reactive amino groups were still generated on the surface by the dry procedure. More important for biochemical applications appears to be, instead of the maximum reactive amino group density, its standard deviation, which is found to be three times smaller than for wet-chemical silanization. In a study of the impact of a reduced water fraction on the attainable density of amino groups it was found that the density could be increased by a factor of 1.4 at 0.075 \% water vapor. This observation is in qualitative agreement with results from a chemical-kinetic model of the gas-phase reactions in an Ar/H\textsubscript{2}O DBD, based on the simplifying assumption that the dissociation of water (and of molecular reaction products) in the DBD is only due to energy transfer from excited argon species (Ar\textsuperscript{*} + H\textsubscript{2}O → Ar + OH + H) where Ar\textsuperscript{*} represents, as a “lumped species”, the four excited Ar 1s states as well as an excimer Ar\textsubscript{2}\textsuperscript{*}. Aside from better reproducibility the new procedure has the advantage, compared with the wet-chemical procedure, that no hazardous chemical wastes are generated.

Keywords
dielectric-barrier discharges
plasma pretreatment
argon-water
silanization
OPTICAL EMISSION SPECTROSCOPY OF A LINEAR GAS-FLOW SPUTTER SOURCE FOR NANOPARTICLE GAS-AGGREGATION

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In this work, we present the optical diagnostic of a gas aggregation source for deposition of nanocomposite coatings using a combination of gas phase condensation (GPC) and standard PECVD processes. This experimental setup has various applications such as advanced TiO₂ photocatalytic thin films, conductive polymer composites for sensors, plasmonic coatings, and structured surfaces for condensation and heat transfer.

Ag Metal nanoparticles are synthesized by inert gas phase condensation (GPC) of sputtered atomic vapor, transferred into the gas flow by a hollow cathode Gas Flow Sputtering (GFS) source. Both pressure in the aggregation zone and discharge power strongly affect Nanoparticles Size distribution and plasma characteristics.

The optical diagnostic of the gas-flow sputter source was carried out in the research of oscillations due to dusty plasma phenomena. Despite the lack of regular oscillation, transitory and oscillatory phenomena were recorded and a tentative interpretation of the observed phenomenon and of their dependence on experimental parameters such as gas flow, pressure, and power are proposed.

**Keywords**
Ag nanoparticles gas flow sputtering OES gas aggregation
Aim of this work was to achieve an improved dispersibility of hydrophobic dry lubricants in aqueous media through plasma activation. As a result, the use of wet chemical and environmentally questionable substances, e.g. certain surfactants, to ensure the dispersibility of such particles, can be avoided. Those plasma-activated particles can be embedded in electroless nickel coatings to improve their wear resistance.

Therefore, hydrophobic polymeric powders like polyimide and polyetheretherketone as well as ceramic powders based on hexagonal boron nitride were treated with atmospheric pressure plasma in a diffuse coplanar DBD-system. The generation of polar chemical bonds on the powder surface lead to an improved dispersibility of the powders in aqueous media and therefore in the electrolyte medium used for nickel electroless plating. As a result a higher deposit volume of the particles in the nickel dispersion coatings could be observed. The modified bonding conditions at the powder surfaces were analysed by infrared and x-ray photoelectron spectroscopy. Optical microscopic and SEM investigations of the nickel coatings in cross sectional view showed the distribution of embedded powder particles in the growing film matrix. Furthermore, the coating’s wear resistance was investigated by taber-abraser test.

The plasma activation lead to surface modifications namely a linkage of polar groups at the powder surfaces and therefore to an improved dispersibility. The embedding of these plasma-functionalised particles in electroless nickel coatings was possible with all three investigated materials, correspondingly the wear resistance of such dispersion coatings was improved compared to pure nickel coatings.

Keywords
powder
dry lubricants
atmospheric pressure plasma
dispersion coatings
electroless metal deposition