Topic:

(3) Films and coatings – **Nano Films –** Nanostructures and nanoparticles

Title: **Silicon dioxide coating of titanium dioxide nanoparticles from dielectric barrier discharge in a gaseous mixture of silane and nitrogen**

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ABSTRACT

Titanium dioxide nanoparticles are used commonly in various applications due to their high catalytic activity. Many of these applications require subsequent treatments after the deposition of the TiO_2 particles. Some of these include thermal processing at high temperatures, e.g. roof tiles. For all of these applications, the crystal structures as well as the microscopic properties are essential. Thus, sintering severely affects the catalytic activity in most of the cases. During thermal processing, the nanoparticles transform from the catalytical highly active anatas structure to the substantially less active rutil structure. This structural change has been found to be significantly retarded when coating the TiO_2 nanoparticles with a closed film of SiO_2. During the thermal treatment, these films break open, revealing the underlying TiO_2 [i]. Thus, the film thickness has to be appropriate for the designated treatment subsequent to the nanoparticle deposition.

In this study, we present an approach of SiO_2 film deposition making use of silane gas. Pure silane gas is highly demanding on safety standards and technical installations, since it acts self-igniting and highly explosive when getting in contact with air or any oxygen containing gas. Thus, diluted process gases are used for most technical implementations, which contain just about 3% silane in 97% helium, neon, argon, hydrogen or nitrogen. While noble gases and hydrogen are used as dilution for a wide range of applications, the process gas consisting of nitrogen and silane is only implemented for silicon nitride deposition. Nevertheless, this gas should be the most suitable for many applications

regarding economics and handling. Closed films produced by dielectric barrier discharges in such mixtures of gases consist of mainly non-stoichiometric silicon nitride, while the other diluted process gases produce metallic silicon films. The deposition of silicon dioxide films is rather complicated, since the silane reacts instantaneously with every oxygen-rich gas. Thus, both gases must not get in contact until they have arrived in front the surface that is to be coated. Most of the existing work found in the literature focuses on the implementation of this condition, to merge the silane and the oxygen right at the surface being coated. Taking a quite different approach, we divided the film deposition into two steps: In the first step, a silicon nitride film was deposited from the process gas with the silane diluted in nitrogen employing a dielectric barrier discharge plasma. As a second step, the silicon nitride film has been tried to convert into silicon dioxide by means of a second plasma discharge using either oxygen for a process gas or even environmental air.

All studies have been carried out in an ultra high vacuum apparatus, while the plasma treatments have been carried out up to atmospheric pressure. During the investigations we employed Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS), as well as Atomic Force Microscopy (AFM). The microscopic measurements showed the deposited film to enclose the particles in a Frank van der Merwe – type growth mode. Film thicknesses determined by increased particle diameters in AFM were in good accordance to calculated film thicknesses from XPS peak intensity attenuation. Spectroscopic results show a formation of a silicon nitride film with substoichiometric nitrogen content, though free of oxynitrides. Surface impurities and adsorbates from the ex-situ preparation procedure were strongly removed and seemed to notably increase the growth rate. The second step gained a transformation of the film up to 98% silicon dioxide according to XPS. Remaining carbon impurities from the initially uncleaned surface were removed by both of the oxidizing plasmas. The transformation was found to be even more effective for the air plasma treatment than for the oxygen plasma treatment at a comparable oxygen partial pressure.

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[i] Qi F, Moiseev A, Deubener J, Weber A (2911) J. Nanopart. Res. 13:1325-1334.