Photocatalytically Active TiO_2 formed by Plasma Based Ion Implantation & Deposition

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Titania ceramics are highly versatile materials. The outstanding tissue compatibility and haemocompatibility of the rutile polymorph result in several applications as an artificial biomaterial. At the same time, TiO_2 powder is known as one of the most effective photocatalysts for neutralising aqueous organic compounds or air pollutions. Over the last several years a large number of applications have been examined here. While the anatase powders are well known and widely used materials with large surface areas there are fewer investigations on the photocatalytic activity of TiO_2-based thin films, which also possess self cleaning, antifogging and antibacterial properties.

In this study, metal plasma immersion ion implantation and deposition was employed for formation of TiO_2 films on either Si, SiO_2/Si or fused silica substrates. Titanium ions were delivered from a Ti cathodic arc with an initial energy around 40 - 100 eV. Backfill with oxygen gas was used to supply either oxygen molecules (adsorbing on the reactive TiO_x surface) or oxygen ions (from charge exchange collisions with Ti ions). Additionally, negative high voltage pulses of up to 10 kV were applied to the substrate, thus increasing the average energy per particle. The results are discussed with respect to the influence of the particle energy on the phase formation and the photocatalytic properties of the films.

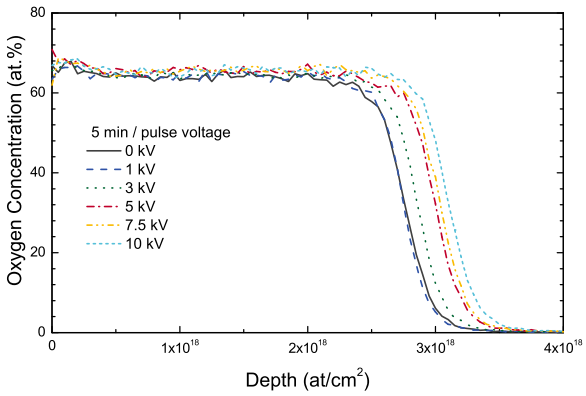

Fig. 1: Oxygen concentration as a function of depth, measured with ERDA for TiO_2 films deposited on Si at different pulse bias. The signals for Ti and the Si substrate are omitted for clarity.

The results from ERDA measurements of TiO_2 films deposited for 5 minutes are presented in Fig.1 and show slightly substoichiometric TiO_2 films with a constant oxygen to titanium ratio of 1.84. No influence of the high pulse voltage on the Ti/O ratio or the depth distribution was found. The slight increase in film thickness with higher pulse voltages results from the competition between two different effects: increased deposition rate due to a farther expanding dynamic plasma sheath collecting more ions at higher pulse voltages and an increase in the total sputter loss. Analysis of phase formation with X-ray diffraction (XRD) and Raman spectroscopy show a strong dependence on the ion energy and the substrate material. Amorphous films are found below 3 kV pulse voltages, for all substrates. Rutile dominates above 3 kV, independent of the substrate. However, a mixture of anatase and rutile is observed depending on voltage and substrate. For Si and SiO_2/Si substrates anatase starts forming at 5 kV, while for fused silica is only visible for 10 kV. Compared to the published phase diagram depending on the temperature and ion energy, an additional effect of the fast deposition rate is present. At the same time, XRD is more sensitive to the long-range order while Raman spectroscopy detects the local chemical composition. The photo-induced hydrophilicity was investigated by contact angle measurements before and after UV irradiation, while the photocatalytic activity was estimated from degradation of methylene blue dye by means of SIMS analysis.

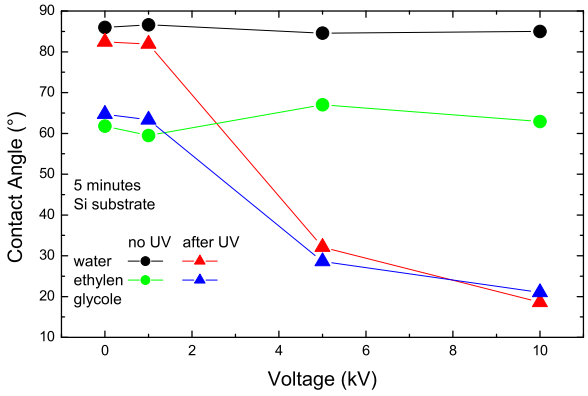

Fig. 2: Contact angle for water and ethylene glycol for TiO_2 films deposited on Si before and after UV irradiation as a function of pulse bias.

Fig.2 depicts the contact angle for two different liquids as a function of applied pulse bias for the films deposited on Si substrate before and after 3 hours of UV-A irradiation at 1 mW/cm. A similar contact angle is measured without UV irradiation for all samples. No effect of UV light was found for pulse voltages up to 3 kV, whereas a strong reduction of the contact angle with increasing of pulse voltage at 5 kV and above was observed after illumination. In addition, SIMS analysis indicates a strong correlation of the photo-induced hydrophilicity with the decomposition of methylene blue. The increase of these two photo-activities with higher energy per deposited particle, indicating a higher activity for a higher rutile content should be taken with precaution. As the deposition temperature was around room temperature without bias voltage and less than 100 °C for 10 kV bias, an additional reduction of the defect density, either by ion bombardment induced surface mobility or thermal annealing could be the main cause for the observed effects.