INVESTIGATION OF STRUCTURAL PROPERTIES OF TIO2 THIN FILMS BY MPIII&D

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Abstract

TiO_2 thin films were produced by metal plasma immersion ion implantation and deposition at room temperature, 200^0C and 300^0C with the voltage pulses, accelerating the ions towards the substrate, ranging from 0 kV to 5 kV and a duty cycle of 9%.

The Selected Area Electron Diffraction (SAED) diagrams of the samples deposited on silicon substrate clearly show the evolution from a pour crystallinity at room temperature (RT) up to an ordered structure at 200°C. At RT and 5 kV broader diffraction rings appear on the corresponding amorphous structure with crystallites showing a preferred orientation. The TEM dark-field view of the sample at RT shows a dense amorphous structure with rutile nanoclusters. In contrast, a columnar structure with anatase/rutile mixture for 200 °C and 300 °C samples is visible in dark field, column width decreases with temperature. However, with temperature-increase, the opposite effect is to be observed. The dark field image of the sample at 300°C shows a weaker contrast. In the SAED Diagrams of the samples at 200°C and 300°C, the increase of the azimutal tilting angle of particular lattice layers is visible.

Keywords: *TiO2, MPIII&D, SAED, TEM, DFTEM*

INTRODUCTION

Photoactive thin films have a large potential for neutralizing air pollutants [1, 2]. Photocatalytic behavior [3, 4] is a well-known process and is mostly employed to degrade or transform (into less harmful substances) organic and inorganic compounds and even microorganisms.

TiO_2 is widely used, either as a powder or as thin films, with different preparation methods reported in the literature, including magnetron sputter deposition and metal arc deposition [5, 6]. However, the photoactive anatase or anatase/rutile mixture necessitates substrate temperature above 400 °C during thin film synthesis [7, 8], which is beyond the stability limit of most technologically interesting polymer foils.

By increasing the average energy per incoming particle, it is possible to reduce the substrate temperature while keeping an identical morphology. In the case of TiO_2, additionally the phase composition can be adjusted in this way. According to the literature [9], particle energies around 30 eV correspond to a substrate temperature of 800 °C with pure rutile films obtained in both cases. However, a direct correlation between the phase composition and morphology does not exist, much higher ion energies are necessary to ascertain the phase formation than to establish a columnar structure. Furthermore, radiation damage during the film deposition may lead to structural and electronic defects, which in turn degrade the photoactivity [10].

In this report, TiO_2 thin films are formed by plasma based ion implantation and deposition (PBIID) [11] with additional substrate heating. A correlation between phase composition, morphology and photoactivity is established.

MATERIAL AND METHODS

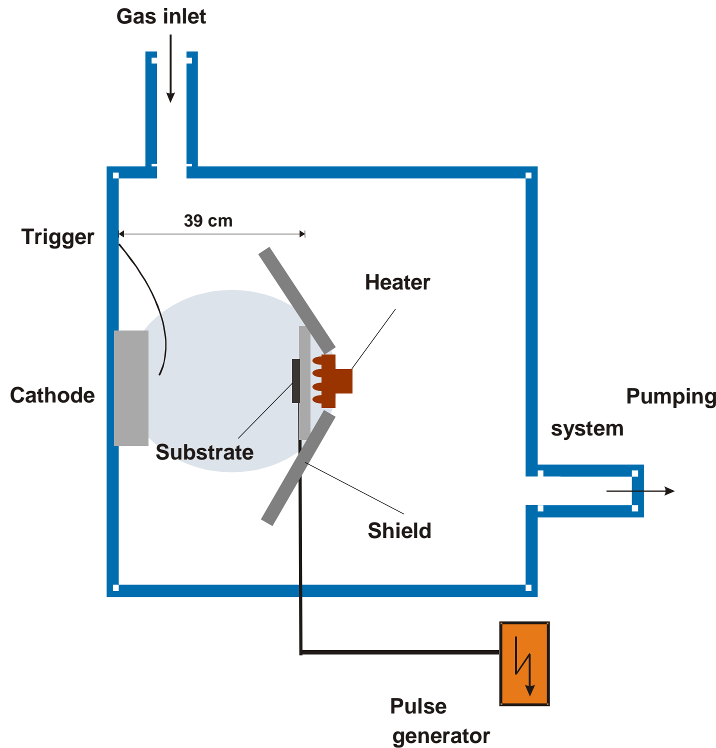

Figure 1: *Schematic of MePIIID deposition system.*

A cathodic arc with a pure titanium (99.99%) cathode, running at 100 A was employed to generate Ti ions. An oxygen backfill of 50 sccm was used to establish a working pressure of 0.36 Pa, which decreased during the process to about 0.1 – 0.2 Pa. Comparing the nominal Ti current from the cathode of about 10 A at an average charge state of 2.1 [12] with the oxygen flow, a O/Ti of roughly 3:1 is established in the gas phase.

Fused silica (SiO_2) coupons were used as substrate material, mounted at a distance of 39cm from the cathode. A heating system with IR lamps from the backside of the substrates was installed in the vacuum chamber (cf. Fig. 1), the temperature itself was varied between room temperature (RT) with lamps in the vacuum system, but no heating, and 300 °C. Comparing the present experimental setup with previous experiments [13,14], the heating system massively disturbs the supersonic plasma flow around the substrate [15]. Instead of kinetic energies of 10 – 50 eV, much lower values can be expected for the present geometry. Negative high voltage pulses between 1 and 5 kV with a length of 30 μs at repetition rate of 3 kHz (duty cycle 9%) were applied to increase the average energy.

The film morphology was investigated with scanning electron microscopy (SEM) and the surface roughness was determined by atomic force microscopy (AFM). Furthermore, layer morphology was investigated using TEM. X-ray diffraction measurements were performed in $\theta/2\theta$-geometry.

RESULTS AND DISCUSSION

The films obtained by this procedure are slightly substoichiometric titania films with an O-Ti-ratio of 1.90 – 1.95, as determined by elastic recoil detection analysis [16]. The film thickness was always close to 300 nm, indicating a growth rate of about 1 nm/s and no strong influence of the varying ion bombardment, especially the concomitant sputtering, on the growth rate.

However, ion bombardment and substrate temperature strongly influence the phase formation. No phase formation could be detected at RT for the pulse voltage range from 0 to 5 kV, indicating either an amorphous structure or nanocrystallites with a size of less than 5 nm. It has to be point out again that previous results showing rutile formation with similar pulse voltages [144] were performed with a completely different substrate setup.

For 200 and 300 °C substrate temperature, qualitatively similar results were obtained, with only the 300 °C data shown in Fig. 2. Without additional bias, no phases were observed with XRD, whereas highly textured rutile and anatase could be observed from 1 kV voltage onwards. For rutile, only the (110) reflection is visible near 27.45°, growing monotonically with increasing pulse voltage. For anatase, a preferred (004) orientation is visible with the highest intensity observed at 3 kV. The crystallite size, inferred by the Debye-Scherrer formula increases from about 5 nm at 3 kV to 10 nm at 5 kV.

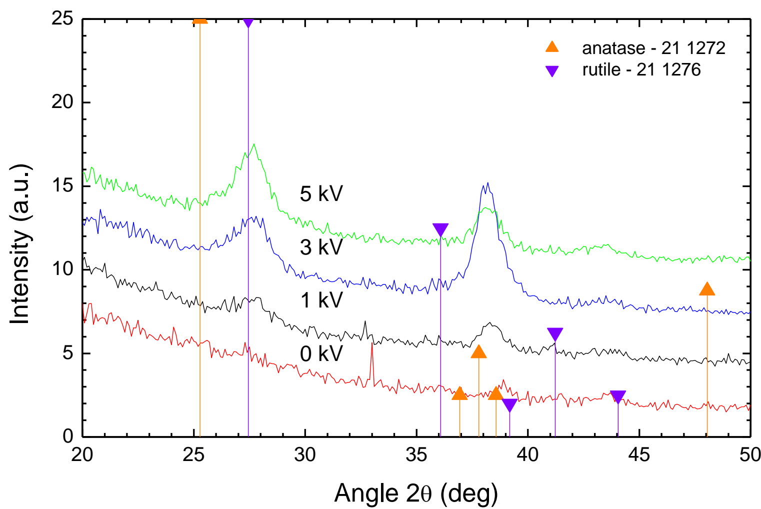

Figure 2: XRD spectra of samples produced at 300 °C with different ion bombardment. The expected peak positions according to the powder diffraction files for anatase, rutile and silicon are indicated. The spectra are shifted vertically for clarity.

Similar results are obtained for the film morphology when investigating thin film cross-sections with SEM. As can be seen in Fig. 3, no contrast is visible for a film deposited at room temperature with 5 kV pulse voltage.

However, grain boundaries are visible for films formed at 200 and 300 °C. The column width decreases from 65 – 75 nm at 200 °C to about 50 nm at 300 °C. Nevertheless, dense and pore-free TiO_2 films were observed for all process conditions.

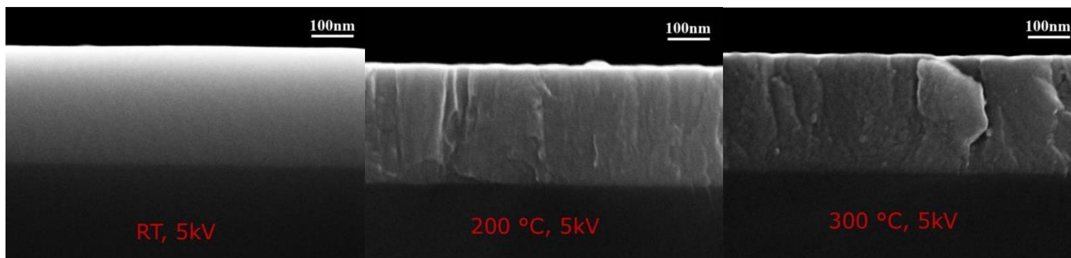

Figure 3: SEM cross-section

viewgraphs of three different samples, deposited at 5 kV pulse voltage at room temperature, 200 °C and 300 °C

The Selected Area Electron Diffraction (SAED) diagrams of the samples deposited on silicon substrate clearly show the evolution from a pour crystallinity at room temperature (RT) up to an ordered structure at 200°C (figure 4). At RT and 5 kV broader diffraction rings appear on the corresponding amorphous structure with crystallites showing a preferred orientation. The influence of the ion energy is not taken for the moment into account.

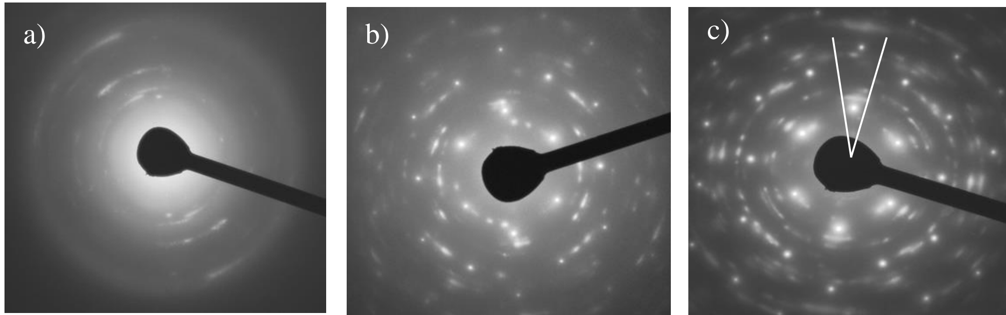

Figure 4: SAED-Diagram of TiO_2 on (100) Silicon with beam direction parallel to [110] Si (200 keV acceleration voltage) a) 5 kV, RT b) 5 kV, 200°C (inverted) c) 5 kV, 300°C. The angle area of the azimutal grain tilt is marked.

The dark-field view of the sample at RT shows a dense amorphous structure with rutile nanoclusters (figure 5). In contrast, a columnar structure with anatase/rutile mixture for 200 °C and 300 °C samples is visible in dark field (figure 5), column width decreases with temperature. Numerous Crystallites are visible in the dark field view, at higher temperature close to the layer surface, with correlating azimuthal orientation. The crystal formation is not very strong restricted by the azimuthal tilt of the diffracting lattice layers, because the hole aperture selects a limited area of the diffraction image.

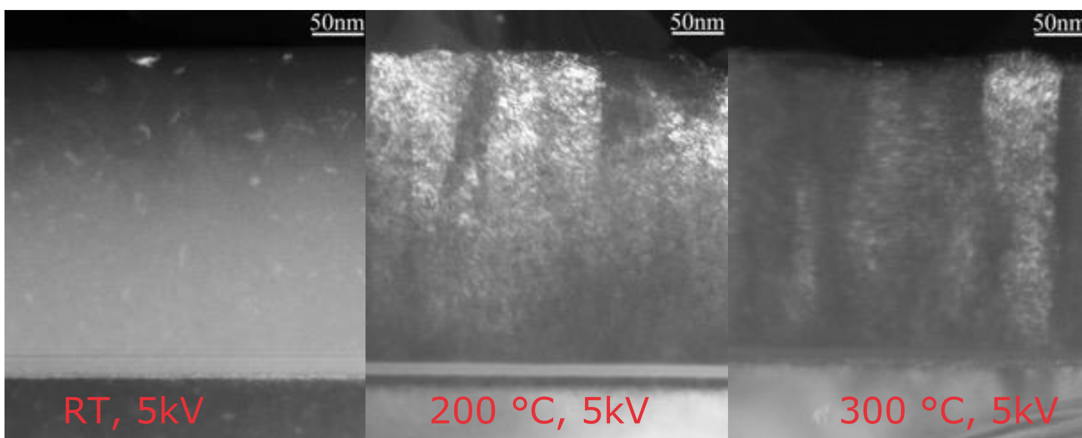

Figure 5: Dark field images of layers deposited on silicon substrate at a pulse voltage of 5 kV at RT, 200°C and 300°C.

Beside the titanium oxide layer and silicon, there is also an amorphous inter-layer, with 25 nm thickness, visible due to the chemical mixing with the silicon substrate. The thickness of the

amorphous inter-layer increases with increasing bias voltage and with a sufficiently high relationship from implantation to deposition. Additionally, the temperature has an influence on the diffusion. At the additional oxygen implantation of titanium on silicon at temperatures above 350 °C, the oxygen diffusion from the titanium layer in silicon was proved. Also, by simultaneous deposition of Ti and O, at room temperature, an amorphous layer created due to ion beam mixing is verified. The comparison of the three texture structures shows that already at 200 °C nanosized crystallites grow on 50 nm broad columns orthogonal to the substrate, in which a correlated orientation pre-exists. The columns are aligned along ion beam direction. On high resolution images one can recognized that the amorphous areas between the crystallites, that are still present at 200°C, disappear completely at 300°C. At the same time a strong texture of the crystallites is visible. The texture development can be explained due to the ion bombardment. The investigation of the crystal growth with the MePIIID in dependence of the pulse voltage shows that with increasing pulse voltage from 5 kV to 10 kV the grain tilt goes over to a higher ordering of the crystals.

However, with temperature-increase, the opposite effect is to be observed. The dark field image of the sample at 300°C shows a weaker contrast. In the SAED Diagrams of the samples at 200°C and 300°C, the increase of the azimutal tilting angle of particular lattice layers is visible. The angle-area marked in the figure 5 increases from 2.5° at 200 °C to 5° at 300 °C. In the high-resolution image of the sample at 300 °C a random coalescence of crystallites in the azimuthal layer is visible.

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