

INVESTIGATION OF PHOTOACTIVE TiO₂ THIN FILMS OBTAINED BY MEPIIID STUDIM I FILMAVE TË HOLLË FOTOAKTIVË TË TiO₂ TË PËRFTUAR ME MEPIIID

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PERMBLEDHJE

Filmat e hollë të TiO₂ janë prodhuar nëpërmjet MePIIID (*Metal Plasma Immersion Ion Implantation and Deposition*) mbi substrate (100) Silicon-i në tensione pulsantë deri në 5 kV dhe cikël pune prej 9%. Temperatura e substratit ka varjuar nga temperatura e dhomës deri në 300 °C. Morfologjia e filmave është hulumtuar me SEM, ndërsa vrazhdësia e sipërfaqes është përcaktuar nga AFM. Duke krahasuar formimin favor për njejtën temperaturë të substrateve, rritja e bombardimit jonik gjithmonë rezulton në kristalite me strukturë kolonare të observuar përgjatë gjithë rangut të parametrevë. Përbërja fazore është analizuar me anë të XRD. Matjet e këndit të kontaktit janë përdorur për investigimin e vetive fotoaktive të kampionëve të TiO₂. Për bombardim jonik të ulët fotoaktiviteti zhduket. Fotoaktiviteti më i lartë është observuar për kampionët e prodhuar në mbi 100°C. Një kuadër i kufizuar lidhjeje ndërmjet temperaturës dhe bombardimit jonik, ngushtësisht i lidhur me përbërjen fazore, është observuar.

ABSTRACT

TiO₂ thin films are produced by metal plasma immersion ion implantation and deposition (MEPIIID) on (100) silicon substrates at varying pulse voltage up to 5 kV and a duty cycle of 9%. The film morphology was investigated with SEM, while the surface roughness was determined by AFM. Comparing the phase formation at identical substrate temperature, additional ion bombardment always leads to larger crystallites with a columnar structure observed across the whole parameter range. The phase composition was analyzed with XRD. Contact angle measurements were used to determine the photoactivity of TiO₂ samples. For lower ion bombardment, the photoactivity disappears. The highest photoactivity

was observed for samples produced beyond 100 °C. A limited process window of temperature and ion bombardment is found, strongly correlated with the phase composition.

Key words: TiO₂, MEPIIID, XRD, CAM, Photoactivity

INTRODUCTION

Neutralizing air pollutants is only one application field for photoactive thin films [9,17]. In addition to photocatalytic behavior [7,10] superhydrophilicity can be induced by UV irradiation, which leads to a reduction of the contact angle to values between 10° and 0° under illumination [19], thus allowing self-cleaning or anti-fogging applications.

Different preparation methods are reported in the literature for TiO₂, a widely used material either as a powder or as thin films, which include magnetron sputter deposition and metal arc deposition [11,6]. Anatase or anatase/rutile mixtures desired as photoactive phases, necessitates substrate temperature above 400 °C during thin film synthesis [4, 14], which is beyond the stability limit of most technologically interesting polymer foils.

Keeping an identical morphology is possible by increasing the average energy per incoming particle while reduce the substrate temperature is a well known technique in PVD processing. Furthermore, in the case of TiO₂, the phase composition can be adjusted in this way. According to the literature [12], particle energies around 30 eV corresponding to a substrate temperature of 800 °C will result in a pure rutile films in either case. However, a direct correlation between the phase composition and morphology does not exist as much higher ion energies are necessary to ascertain the phase formation than merely to establish a columnar structure. Furthermore, radiation damage

during the film deposition may lead to structural and electronic defects, which in turn could degrade the photoactivity [5].

In this experimental work, TiO₂ thin films have been produced by metal plasma immersion ion implantation and deposition (MEPIIID) [1] with additional substrate heating. A correlation between phase composition, morphology and photoactivity is attempted.

MATERIALS AND METHODS

In this work, the samples are produced on Silicon (100) substrates with variation of the high pulse voltage and substrate temperature up to 300 °C. A cathodic arc with a pure titanium (99.99%) cathode, running at 100 A was employed to generate Ti ions. An oxygen backfill of 55 sccm, which corresponds to approximately 3×10^{19} oxygen-molecules per second, was used to establish a working pressure of 0.36 Pa, which decreased during the process to about 0.1 – 0.2 Pa. 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 ion energy. Comparing the nominal Ti current from the cathode of about 10 A at an average charge state of 2.1 [2], a O/Ti ratio of roughly 3:1 is established in the gas phase with the available oxygen flow. The treatment time was 5 min. for each sample.

A heating system with IR lamps from the backside of the substrates was installed in the vacuum chamber (Figure 1), and the temperature itself was varied between room temperature (RT) with lamps in the vacuum system, but no heating, 200° and 300 °C.

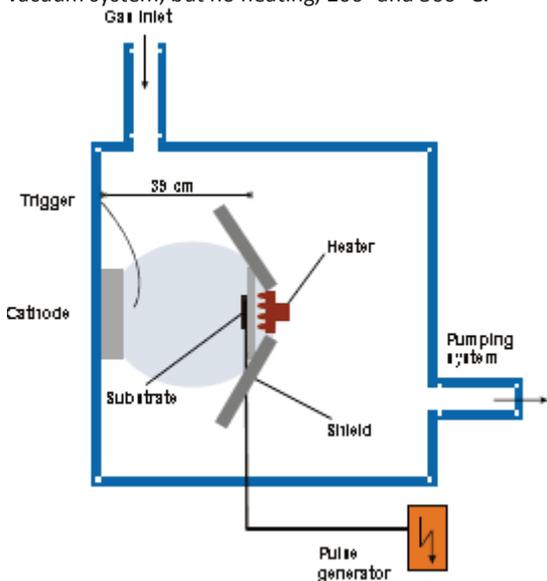


Figure 1: Schematic of MePIIID experimental setup.

Comparing the present experimental setup with previous experiments [18, 13], the heating system massively disturbs the supersonic plasma flow around the substrate [3]. Instead of kinetic energies in the range from 50 eV without pulse voltage up to 1.5 keV with 10 kV pulse voltage, much lower values can be expected for the present geometry. The mean surface temperature of the implanted layer doesn't depend on the pulse voltage although, at 5 kV, an increase of less than 50 °C occurs during the deposition.

The film morphology was investigated with scanning electron microscopy (SEM), while the surface roughness was determined by atomic force microscopy (AFM). X-ray diffraction measurements were performed in $\theta/2\theta$ geometry. The surface energy was derived from contact angle measurements employing water and ethylene glycol with the data analysis according to the Owens-Wendt method [16]. The photoactivity was examined by exposing the samples to UV-A light, generated from an actinic tube with a spectral range of 300 – 460 nm and the maximum at 365 nm, at an intensity of 1 mW/cm², for up to 3 hours.

RESULTS AND DISCUSSION

The films obtained by this procedure are slightly substoichiometric titania films with an O-Ti-ratio of 1.90 – 1.95 [15]. The film thickness was always close to 300 nm, indicating a growth rate of about 1 nm/s with no strong influence of the varying ion bombardment, respective sputtering, on the growth rate. Ion bombardment and substrate temperature strongly influence the phase formation. No phase formation was detectable 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.

For 200 °C and 300 °C substrate temperature qualitatively similar results were obtained, with the XRD spectra for samples treated at 200 °C depicted in Figure 2. Two peaks at 27.7° and 38.2°.

Comparing the results with previous experiments [8], the substrate influence on the phase formation can be neglected. The peak at 27.7° correlates very well with the (110) reflection of standard Rutile. The peak at 38.2° can be assigned to the (004) orientation of Anatase. The intensity of the 110 peak of Rutile grows monotonically with increasing pulse voltage from 1 kV to 5 kV at constant peak width. At the same time the 004 peak of Anatase, with the highest intensity observed at 3 kV, loses on intensity at 5 kV. The crystallite size, inferred by the Debye-Scherrer formula, increases from about 5 nm at 3 kV to 10 nm at 5 kV.

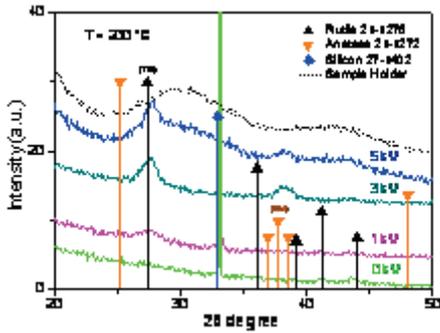


Figure 2: XRD spectra of samples produced at 200 °C with different ion bombardment on silicon substrates. The expected peak positions according to the powder diffraction files for anatase, rutile and silicon are indicated. The spectra are shifted vertically for clarity.

A similar tendency with temperature and voltage was obtained for the film morphology, when investigating thin film cross-sections with SEM. As can be seen in Figure 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 TiO₂ films were observed for all process conditions.

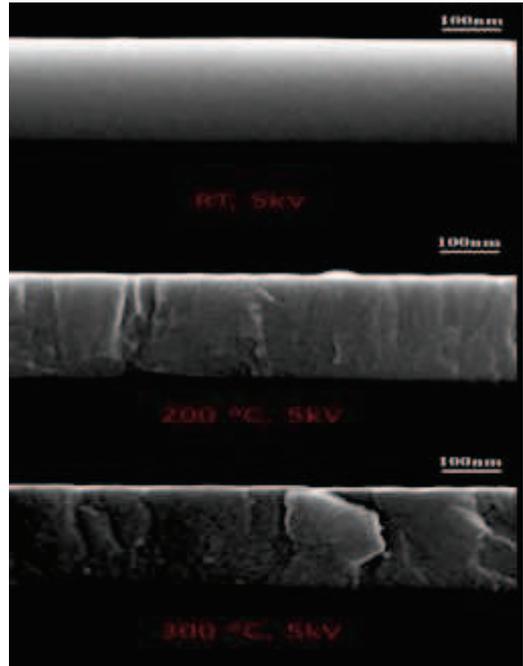


Figure 3: SEM cross-section viewgraphs of three different samples, deposited at 5 kV pulse voltage at room temperature, 200 °C and 300 °C

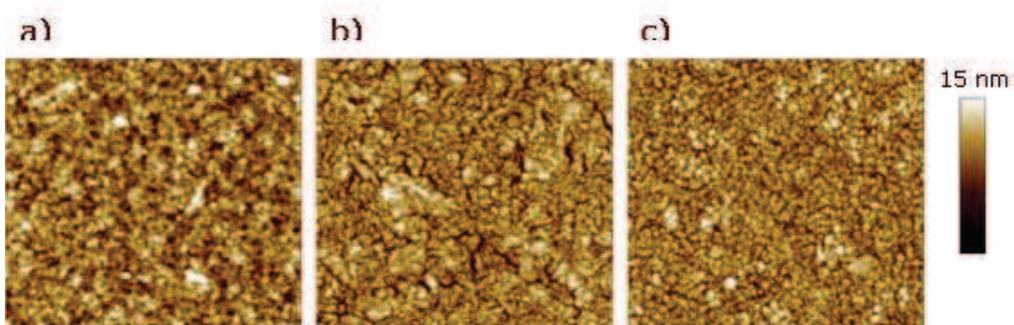


Figure 4: AFM viewgraphs of three samples, deposited at (a) 200 °C, 1 kV, (b) 200 °C, 5 kV and (c) 300 °C, 5 kV. The corresponding roughness values Rrms are (a) 1.7 nm, (b) 2.0 nm and (c) 1.5 nm.

AFM results, depicted in Figure 4, agree with the SEM results on the morphology. Minor droplet contaminations from arc deposition process are visible in some panels. A columnar structure visible for all samples with slightly higher elevation between the

grains and the grain boundaries for higher pulse voltages, indicating a preferential sputtering of grain boundaries. With increasing temperature, the surfaces become smoother as an increased surface mobility counteracts the localized sputter processes. At the

same time, the surface roughness R_{rms} , decreases from 6.4 nm at RT to 1.5 nm at 300 °C.

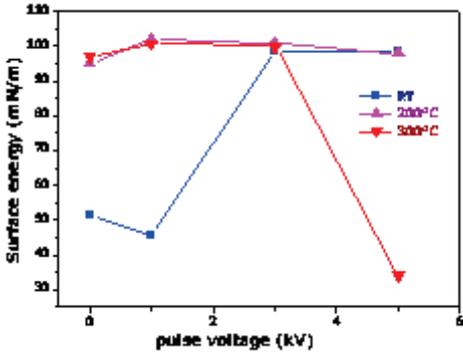


Figure 5: Surface energy of titanium oxide layers deposited on silicon substrates after 3 hours of UV illumination as a function of substrate temperature and substrate bias.

The surface energy before and after illumination with UV-A was derived from the contact angle measurements. No systematic differences were found before illumination, however a strong effect was found after illumination. These results are presented in Figure 5 as a function of pulse voltage and deposition temperature. For 200 °C deposition temperature, all samples showed a value of 100 mN/m or more for the surface energy, whereas low pulse voltage at 300 °C and high pulse voltages at room temperature were necessary to obtain these values.

Comparing the contact angle for water and ethylene glycol, the relative fraction of the disperse and the polar part of the surface energy could be obtained. As shown in Figure 6, the dispersive part dominates over the polar part before illumination for samples deposited at 200 °C, whereas after irradiation with UV light the disperse part is tending towards zero with increasing irradiation time and the surface energy is close to the polar part.

The area of higher surface-energy corresponds to the mean parameter-region with higher ion energy (3.kV - 10 kV) and lower temperature (RT - 200°C) or lower ion energy (1 - 3 kV) and higher temperature (300°C). The area of high energy and high temperature as well as low energy and room temperature lie outside the area the photo-activity.

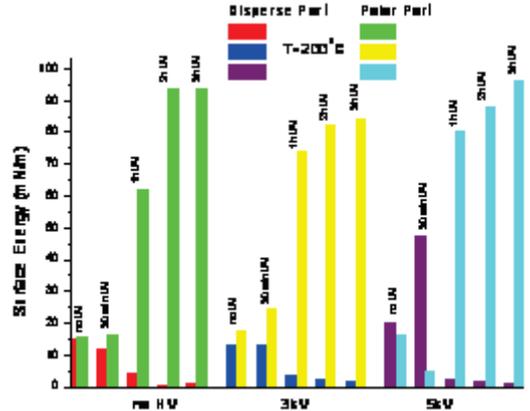


Figure 6: Deconvolution of the surface energy into a disperse and a polar fraction as a function of pulse voltage for the samples deposited on silicon substrate at 200 °C.

Summarizing these results and comparing them with the published phase formation [12] tendencies lead to the presentation in Figure 7.

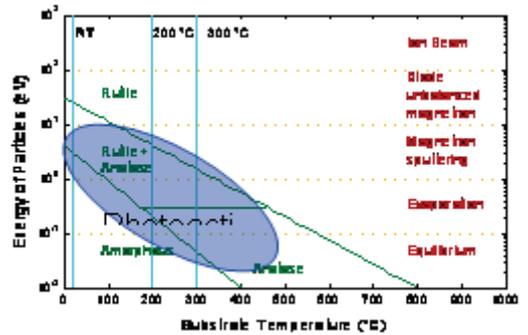


Figure 7: Identification of process window to obtain photoactive thin films using the correlation between phase composition and temperature/energy.

A good agreement between the photoactive thin films and a phase composition of anatase or an anatase/rutile mixture is observed. When interpreting these data, two points have to be considered. First, the absolute quantification of the particle energies in the present MePIIID experiments is still unfinished. Plasma density measurements and energy flux measurements reported earlier for an experimental setup without additional substrate heating [18] are not valid for the present experiment due to the completely different plasma flow in the new setup. A reduction of the energy of the Ti ions arriving at the surface from 50 eV towards 1 – 3 eV is very likely, which would also

explain the variation in the microstructure found for nominally identical pulse voltages without heating in Ref. 3 and here. Second, the published model [12] is purely empirical and summarizes the experimental observations.

Thus, the phase composition is more important than the microstructure for the photoactivity. The nanocrystalline or amorphous film obtained at 5 kV and RT is photoactive, similar to the columnar structured film at 5 kV and 200 °C. In contrast, the film deposited with 5 kV pulse voltage at 300 °C, which is structurally nearly identical except for slightly smaller grains, is not photoactive at all. At the same time, temperature is counteracting ion bombardment as additional defects are produced by the impinging ions, which can only anneal at higher temperatures.

As the conclusion, the replacement of substrate heating with ion energy is possible in a restricted process window, thus enabling the formation of photoactive TiO₂ thin films on temperature sensitive substrates. However, no exact correlation between microstructure or phase composition with the photoactivity was found.

Further work is necessary to quantify the energy flux impinging on the substrate, which is much more complicated for MePIID processes than for conventional ion beam assisted deposition. At the same time detailed investigations of the electronic properties and their changes under different process conditions is necessary to explain and optimize the present findings.

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