DECOLORIZATION OF METHYLENE BLUE FROM TIO$_2$ THIN FILMS PRODUCED BY METAL PLASMA IMMERSION ION IMPLANTATION AND DEPOSITION

Altin Gjevori[*]

[*]*Polytechnic University of Tirana, Department of Physics Engineering, Boulevard "Dëshmorët e Kombit", Square "Mother Teresa", 4. 1000 Tirana, Albania*
Corresponding Author: altingjevori@yahoo.com

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, ranging from 0 kV to 5 kV and a duty cycle of 9%. The photocatalytic activity of the samples was investigated by the decolorization of Methylene blue. The nanocrystalline 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.

Key-words: *TiO$_2$, MEPIIID, XRD, SEM, Photoactivity*

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.
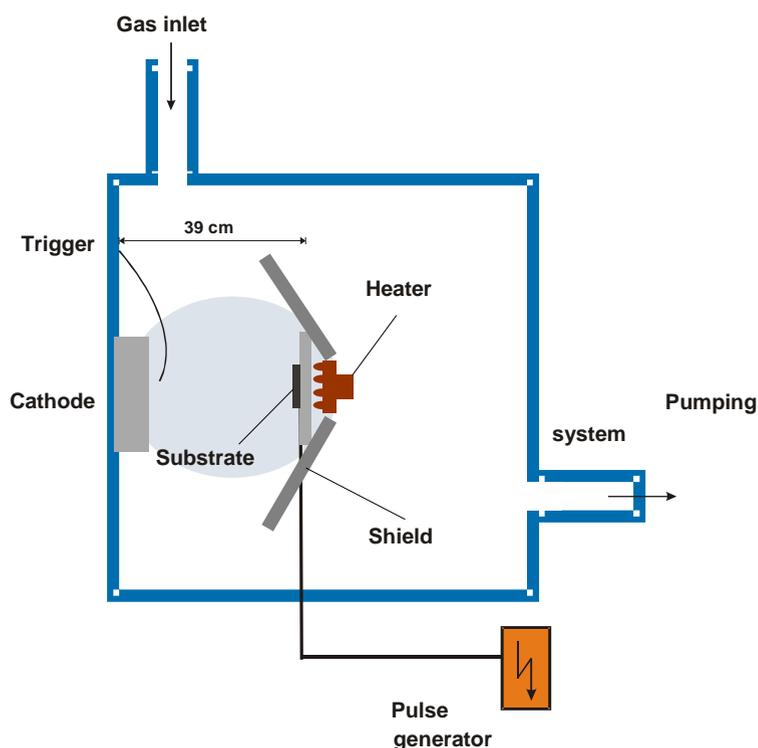
MATERIAL AND METHODS

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). X-ray diffraction measurements were performed in θ/2θ-geometry. The absorption spectroscopy measurements on TiO_2 samples were performed using a spectrometer SHIMADZU UV-2101PC. In the experiment, a methylene blue solution with an initial concentration of 0.007 mmol l^{-1} was tested. Volumes of 20 ± 2 ml of this solution together with the samples were irradiated for 1-3 hours time intervals (power density in air 1 mW cm^{-2}). As reference, a solution without TiO_2 sample inside under the same parameters was irradiated. The respective maximum absorption was determined by the spectrophotometry with a split-width of the spectrometer of 1.0 nm, a

resolution of 0.1 nm and a scanning interval of 0.2 nm.

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.
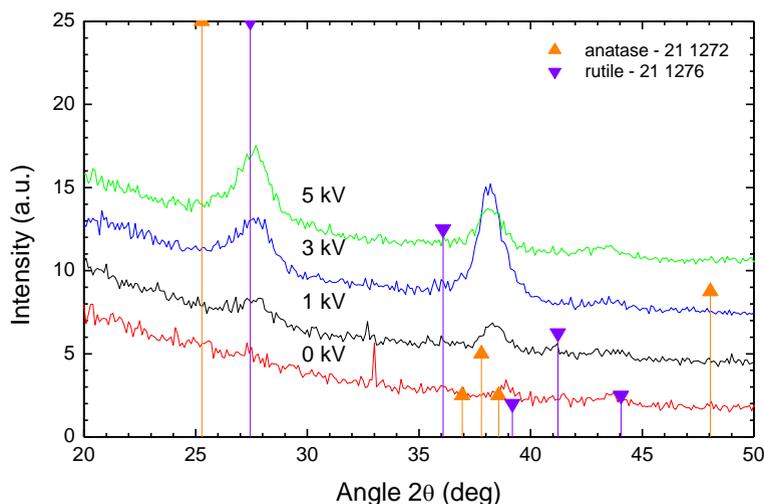

Figure 2: XRD spectra of samples produced at 300 °C with different ion bombardment. The expected peak positions according to the powder diffraction files for anatase, rutile and silicon are indicated. The spectra are shifted vertically for clarity.

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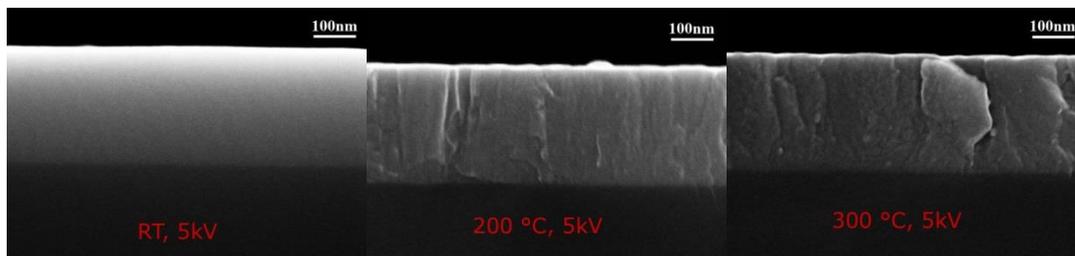
Figure 3: SEM cross-section viewgraphs of three different samples, deposited at 5 kV pulse voltage at room temperature, 200 °C and 300 °C

The photocatallytic activity was examined by exposing the samples to UV light, generated from an actinic tube with a spectral range of 300 nm – 460 nm with the maximum at 365 nm, at an intensity of 1 mW/cm^2, for up to 3 hours.

The photocatalytic activity of the samples was investigated by the decolorization of Methylene blue, that is used as standard substance also in the literature. In this case, can be assumed that the superhydrophilic activity is strongly correlated with the photocatalytic activity [17]. The superhydrophilic property as like as the photocatalytic activity of titanium dioxide is based on the generation of electron-hole pairs by activation with photon-energies in the range of the band-gap energy.

Initially, the adsorption and dissociation of water takes place at the surface of titanium dioxide. The water binds at oxygen-atoms at the surface, that are coordinated by fivefold titanium atoms. The role of the titanium coordination of the oxygen is essential. The reduced oxygen then becomes transferred in the Thiazinring (NC4S) of the Methylene blue under formation of a Sulfoxids and reduction of the nitrogen through hydrogen on the Thiazinring. The Sulfoxid is colorless since the aromatic system of the Methylene blue was changed. The kinetics of the catalytic demineralization from Methylene blue to Carbon dioxide and nitrate - ammonium and sulphate ions through titanium oxide in form of Nanoparticle dispersion is already described [18].

The linear area of the absorption of Methylene blue near 664 nm is depicted in Figure 4. With increasing irradiation time, the spectrum of a product that forms as an intermediate, overlapped with the absorption spectrum of Methylene blue. After 27 hours of UV Irradiation, only the spectrum of the product remained. Under the assumption, that the concentration of the product at this time corresponds to the exit-concentration of Methylene blue, the sum absorption spectrum can be separated into two shares. Afterwards, the concentration c of Methylene blue at a time t could be expressed using the following formula:

$$c\Delta\varepsilon = I - c_{t=0}\varepsilon^{'}$$

$$\Delta\varepsilon = \varepsilon - \varepsilon^{'}$$

with the absorption I, the extinction coefficient of Methylene blue ε (79,51 lmmol^{-1}) and the extinction coefficient of the product ε' is calculated.
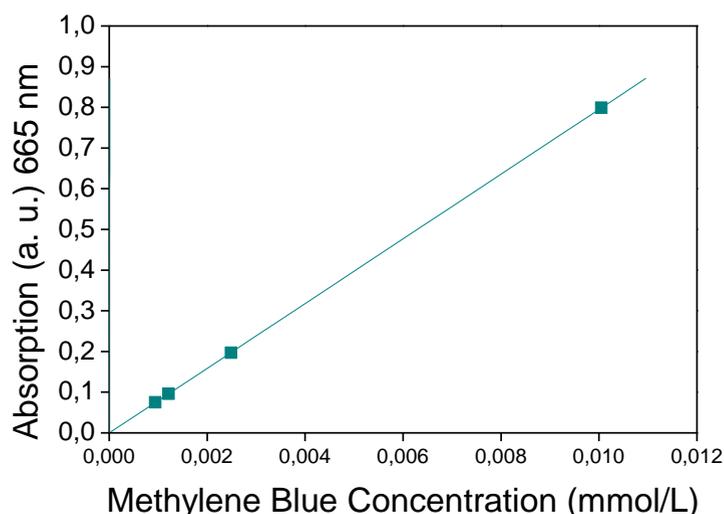
Figure 4: Absorption of different concentrations of Methylene Blue solution

By comparing the concentration decrease for solutions without titanium oxide layer and with titanium oxide layer three photoactivity regions can be distinguished: (i) neglecting, (ii) middle and (iii) high. Altogether, a relatively low photocatalytic activity is to be observed. This can be connected with the phase composition. The layers consist mainly of Rutile and the photocatalytic activity of anatase is usually higher compared to Rutile. The results obtained for three different samples are presented in figure 5.
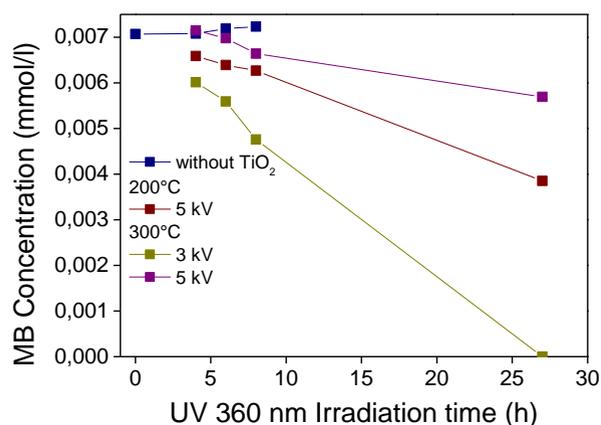

Figure 5: Photocatalytic degradation of Methylene blue from titanium dioxide layers deposited on (100) silicon substrate.

The absorption of the solution without titanium oxide doesn't show any photo-chemical reduction reaction of Methylene blue within the error by the absorption measurement.

Therefore, the observed decrease of the absorption results from the photocatalytic activity of the titanium dioxide layers. The sample, which was produced with a pulse voltage of 5 kV and

a substrate temperature of 300 °C, doesn't show any photocatalytic activity. The sample at 3 kV and 300°C shows the highest activity. The results from the contact angle measurements and the decolorization of the Methylene blue show the correlation of both effects. The disappearance of the photoactivity cannot be explained with the results of this work due to characteristic structural layer properties. Regarding the structure of the layers, that shows an extreme distinction in photoactive properties, no differences were observed. Furthermore, no difference in the phase composition was observed.

A summary of these results on the photoactivity is schematically presented in Fig. 6, using the published phase formation behavior [9] as a reference. 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 caveats have to be considered.

Figure 4: Identification of process window to obtain photoactive thin films using the
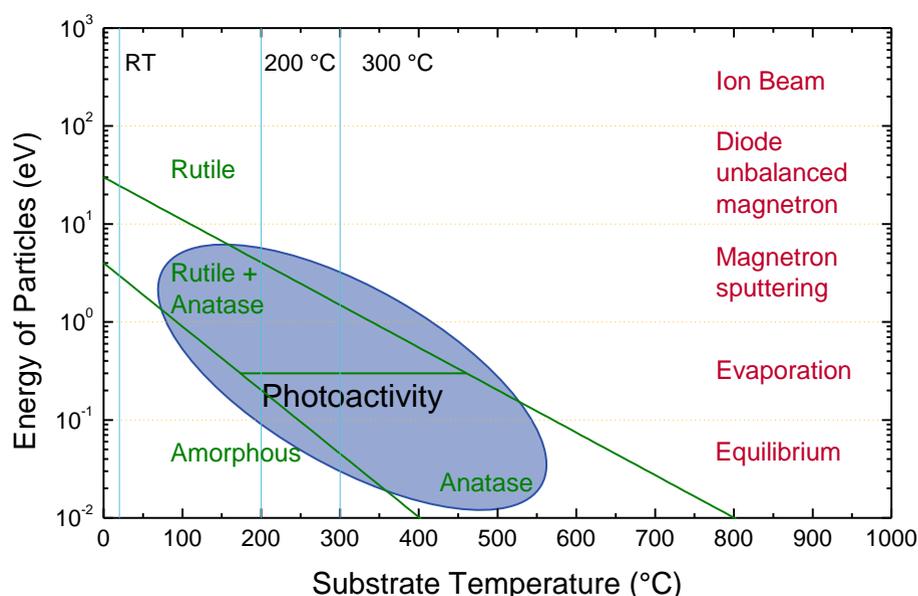
correlation between phase composition and temperature/energy [9].

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 [13] 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. 14 and here.

Second, the published model [9] is purely empirical and summarizes the experimental observations. The replacement of substrate temperature with energy roughly implies an increase in the energy by a factor of 10 for a decrease of 300 °C. This logarithmic scale is counter-intuitive as a linear reduction of temperature should be compensated by a linear increase in energy.

As a corollary, 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 structrued 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.

BIBLIOGRAPHY

[1]   M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[2]   K. Rajeshwar, C.R. Chenthamarakshan, S. Goeringer, M. Djukic, Pure Appl. Chem. 73 (2001) 1849.
[3]   A. Fujishima, K. Honda, Nature 238 (1972) 37.
[4]   W. Hofmeister, E. Tillmanns, W.H. Bauer, Acta Crystallogr. C 40 (1984) 1510.
[5]   J.-D. Liao, H.-J. Chen, C.-W. Chang, S.-M. Chiu, Z.-S. Chen, Thin Solid Films 515 (2006) 176.
[6]   J.T. Chang, C.W. Su, J.L. He, Surf. Coat. Technol. 200 (2006) 3027.
[7]   I.M. Brookes, C.A. Muryn, G. Thornton, Phys. Rev. Lett. 87 (2001) 266103.
[8]   P.C. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, Appl. Environ. Microbiol. 65 (1999) 4094.
[9]   P. Löbl,. M. Huppertz, D. Mergel, Thin Solid Films 251 (1994) 72.
[10]   O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. 32, (2004) 33.
[11]   A. Anders (Ed.), Handbook of Plasma Immersion Ion Implantation and Deposition, John Wiley & Sons, New York, 2000.
[12]   A. Anders, Phys. Rev. E 55 (1997) 969.
[13]   G. Thorwarth, S. Mändl, B. Rauschenbach, Surf. Coat. Technol. 128/129 (2000) 116.
[14]   S. Mändl, W. Attenberger, B. Stritzker, B. Rauschenbach, Surf. Coat. Technol. 196 (2005) 76.
[15]   A. Anders, Surf. Coat. Technol. 136 (2001) 85.
[16]   K. Nonnenmacher, Master Thesis, Universität Leipzig, 2008.
[17]   K. Guan, Surf. Coat. Technol. 191, 155 (2005)
[18]   A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, and J.M. Herrmann, Appl. Cat. B 31, 145 (2001)