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Analysis of Structural and Photocatalytical Properties of Anatase, Rutile and Mixed Phase TiO_2 Films Deposited by Pulsed-Direct Current and Radio Frequency Magnetron Co-Sputtering

S. Varnagiris, M. Urbonavicius, S. Tuckute, M. Lelis, K. Bockute

***Abstract*—**Amongst many water purification techniques, TiO_2 photocatalysis is recognized as one of the most promising sustainable methods. It is known that for photocatalytical applications anatase is the most suitable TiO_2 phase, however heterojunction of anatase/rutile phases could improve the photocatalytical activity of TiO_2 even further. Despite the relative simplicity of TiO_2 different synthesis methods lead to the highly dispersed crystal phases and photocatalytic activity of the corresponding samples. Accordingly, suggestions and investigations of various innovative methods of TiO_2 synthesis are still needed. In this work structural and photocatalytical properties of TiO_2 films deposited by the unconventional method of simultaneous co-sputtering from two magnetrons powered by pulsed-Direct Current (pDC) and Radio Frequency (RF) power sources with negative bias voltage have been studied. More specifically, TiO_2 film thickness, microstructure, surface roughness, crystal structure, optical transmittance and photocatalytical properties were investigated by profilometer, scanning electron microscope, atomic force microscope, X-ray diffractometer and UV-Vis spectrophotometer respectively. The proposed unconventional two magnetron co-sputtering based TiO_2 film formation method showed very promising results for crystalline TiO_2 film formation while keeping process temperatures below 100 °C. XRD analysis revealed that by using proper combination of power source type and bias voltage various TiO_2 phases (amorphous, anatase, rutile or their mixture) can be synthesized selectively. Moreover, strong dependency between power source type and surface roughness, as well as between the bias voltage and band gap value of TiO_2 films was observed. Interestingly, TiO_2 films deposited by two magnetron co-sputtering without bias voltage had one of the highest band gap values between the investigated films but its photocatalytic activity was superior compared to all other samples. It is suggested that this is due to the dominating nanocrystalline anatase phase with various exposed surfaces including photocatalytically the most active {001}.

***Keywords*—**Films, magnetron co-sputtering, photocatalysis, TiO_2.

I. Introduction

TITANIUM dioxide (TiO_2) is recognized as industrially important material for its advantageous properties including non-toxic nature, chemical stability, optical transmittance, etc. TiO_2 can exist as an amorphous material or in one of the three crystalline phases: brookite, rutile and anatase. However, only the last two phases have practical applications including paint production, optical coatings, drugs, cosmetics, dielectric applications, dye-sensitized solar cells, etc. [1]. Besides, due to the relatively favorable band gap between valence and conduction bands, non-toxicity and photo-stability [2], [3], TiO_2 is promising candidate for various photocatalytical applications. Amongst them photocatalysis-based waste-water cleaning is recognized as one of the most researched areas. During the years a lot of advancement has been done but still there are a lot of challenges, which have to be solved. For instance, photocatalytically the most active TiO_2 materials have been synthesized in the form of powders, however, for practical TiO_2 application of waste-water cleaning it has to be immobilized on suitable substrates in order to overcome issues of photocatalyst collection after its usage [4]. Accordingly, TiO_2 films also attract a lot of interest.

There is a big variety of deposition methods that can be used to prepare TiO_2 films, such as electron-beam evaporation, ion-beam assisted deposition, magnetron sputtering, sol-gel methods or plasma enhanced chemical vapor deposition. Among these methods, magnetron sputtering (MS) is appreciated for production of high-quality coatings, scalability, versatility, uniformity and repeatability [5]. Traditionally, TiO_2 deposition by reactive MS is done using one of two types of power sources: RF or p-DC. Researchers showed that both type of power sources can be successfully used for various phase TiO_2 films' deposition. However, formation of TiO_2 films with needed phases or their mixtures requires different type of power source, changes in annealing temperature or even larger scale deposition system modification [6], [7]. This is inconvenient because most of the system modifications are time consuming. Moreover, as mentioned before, even slight modifications of TiO_2 synthesis conditions affect numerous parameters (surface roughness, post-processing methods, presence of impurities/dopants, crystalline phase, crystallographic orientation, etc.), which can affect the ultimate photocatalytic performance of the deposited films. The possibility to simultaneous control all mentioned parameters is one of the main interests for researchers in the TiO_2 deposition process.

S. Varnagiris is with the Lithuanian Energy Institute, 3 Breslaujos st., LT-44403 Kaunas, Lithuania (phone: +37066243136; e-mail: sarunas.varnagiris@lei.lt).

M. Urbonavicius, S. Tuckute, and M. Lelis are with the Lithuanian Energy Institute, 3 Breslaujos st., LT-44403 Kaunas, Lithuania (e-mail: marius.urbonavicius@lei.lt, simona.tuckute@lei.lt, martynas.lelis@lei.lt).

K. Bockute is with the Kaunas University of Technology, 50 Studentu st., LT-51368 Kaunas, Lithuania (e-mail: kristina.bockute@ktu.lt).

While using MS to deposit TiO_2 films, researchers usually variate i) working gas pressure and composition (traditionally deposition is done in Ar:O mixtures); ii) magnetron power source type and its operating parameters; and iii) pre- or post-annealing of the samples. Effects of most of these parameters are generally known and widely documented [8]. Reference [9] showed that phase composition and preferred orientation of the TiO_2 films can be controlled by adjusting the negative bias voltage during MS. Similar results were observed by [10], which revealed that adding of bias voltage allows to control grain size and surface roughness.

In this work, different phase TiO_2 thin films were deposited by using innovative two magnetron co-sputtering from two identical magnetrons with Ti cathodes powered by p-DC and RF power sources at temperatures below 100 ºC. In addition, the influence of negative bias voltage on TiO_2 phase, crystalline size, surface morphology, roughness and band gap were analyzed. Photocatalytic activity of deposited TiO_2 samples was evaluated by measuring the bleaching of methylene blue (MB) solution.

II. Material and Methods

A. Deposition of TiO_2 Films

TiO_2 film deposition was performed using two identical magnetrons with titanium targets (76 mm diameter, 99.99 purity, Kurt. J. Lesker Company) powered by different types of dedicated power source. Advanced Energy MDX-1K power supply was connected to the Advanced Energy Sparc-le 20 DC Pulsing ARC Handling unit and this system was used to provide p-DC power to the first magnetron. The second magnetron was operated with Kurt J. Lesker R301 RF power supply. More details on the reactive two magnetron co-sputtering technique are provided at [11].

TABLE I
MS Parameters

Type of deposition	Power source		
	pDC, W	RF, W	BIAS, V
pDC	300	-	-
RF	-	200	-
pDC_RF	300	200	-
pDC_RF_30V BIAS	300	200	30
pDC_RF_60V BIAS	300	200	60

Borosilicate glass discs (diameter - 30 mm) were used as substrates for TiO_2 film formation. The distance between the sample and the centers of Ti cathodes was fixed at 70 mm. The reactive gas mixture with the ratio O_2/Ar = 1/4 (purity of both used gases was 99.999%) was used for all samples while total gas pressure was kept constant at 6×10^{-3} mbar. The deposition time varied in the range from 60 min to 150 min in order to reach similar thickness for all samples which was approximately 500 nm. The power of p-DC and RF sources were preselected experimentally by finding optimal deposition condition and fixed at 300 W and 200 W for p-DC and RF sources respectively. Additionally, negative BIAS voltage (30 V and 60 V) was applied for selected experiments (see Table I). All TiO_2 film deposition processes were performed without sample heating and temperatures did not reach 100 ºC.

B. Characterization of TiO_2 Films

Thickness of as-deposited TiO_2 films was measured using stylus profiler (Ambios XP-200). The microstructure analysis was performed by Scanning Electron Microscope (Hitachi S-3400 N) using secondary electron detector. Surface roughness was evaluated by an atomic force microscope (AFM, Microtestmachines NT-206). Crystal structure was determined by X-Ray diffraction (XRD, Bruker 8) operating with Cu Kα radiation. The crystallite sizes were evaluated by Topas 4.1 software with Lorentzian convolution. UV-VIS spectrophotometer (Jasco V-650) was used for optical transmittance measurement at normal incidence from 200 nm to 900 nm. The optical energy band gaps were evaluated by:

$$\alpha h\vartheta = B(h\vartheta - E_g)^2 \quad (1)$$

where α is the Tauc plots adsorption coefficient, B is band-tailing parameter, hv is photon energy and Eg – optical band gap.

C. Testing of Photocatalytic TiO_2 Properties

Photocatalytic properties of TiO_2 films were tested by investigating bleaching of the aqueous MB (Reachem Slovakia s.r.o.) solution under UV-B (PL-S 9W/01/2p 1CT) irradiation. The distance between the light source and the sample was 8.5 cm. The lamp irradiation intensity on the surface of TiO_2 sample was approximately 2.5 mW/cm^2 (measured using Thorlabs PM16–401 Power meter). 15 ml MB (7.5 mg/l) solution was syringed above the sample and kept in the dark for 24 hours before the experiment. In order to minimize the evaporation of MB solution, the glass container was covered by 500 μm thick fused silica disc. Magnetic stirrer was used in order to ensure equal mixing of MB solution during the experiment.

III. Results and Discussion

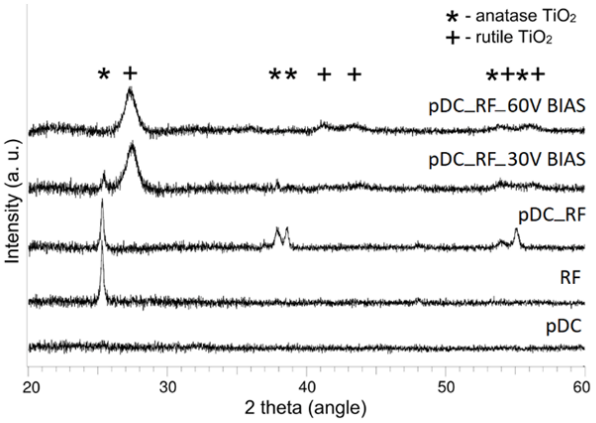

Fig. 1 XRD patterns of TiO_2 films using different combination of deposition parameters

XRD results of TiO_2 films deposited by pDC, RF, their

combination (pDC_RF) and their combination with BIAS voltage (pDC_RF_30V BIAS and pDC_RF_30V BIAS) are presented in Fig. 1. It was observed that amorphous TiO_2 phase was deposited by pDC power source when the power was set at 300 W. Contrarily, clear peak corresponding to anatase TiO_2 phase (101) was deposited by RF power source even at lower power of 200 W. TiO_2 anatase phase with additional anatase peaks ((004), (112) and (105)) was deposited by combination of pDC and RF power sources. It is known that the main (101) and additional (004) anatase orientations are attributed to {101} and {001} facets respectively [11]. Reference [12] showed that TiO_2 crystals with dominant {001} facet have nearly two times higher photocatalytic activity compared to {101} surface. Moreover, such formation of additional anatase phases invoked increment of surface roughness from 1.6 nm (RF) to 4.3 nm (pDC_RF) (see Fig. 2). The heterojunction of anatase and rutile phases was observed by using combination of pDC and RF power sources with 30 V bias voltage. In this case, surface roughness increased to 7.9 nm. Further increment of bias voltage (60 V) increased the energetics of the process and contributed to deposit thermodynamically the most stable rutile phase with 1.1 nm roughness.

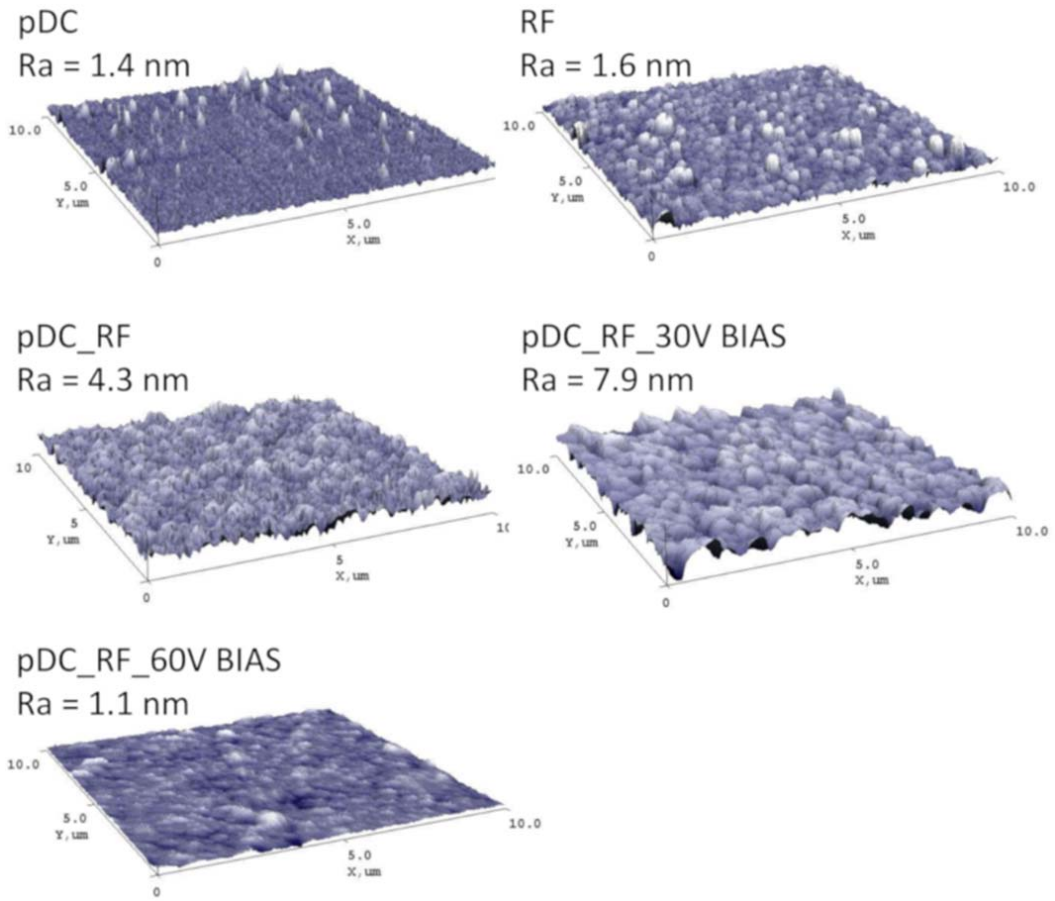

Fig. 2 AFM views and surface roughness of TiO_2 films obtained by using different combination of deposition parameters

Such variation of surface roughness can be influenced by several processes. First of all, formation of amorphous or pure anatase/rutile phases (with expressed one dominant orientation only) induced growth of uniform and smooth films. This caused surface formation with small scale nanometric features. On the other hand, combination of different phases or even different orientations induced formation of domains/grains with expressed boundaries between them. This, in turn, invoked surface irregularities and increase surface roughness. Similar results were observed in [8], where TiO_2 anatase phase with intensive (004) orientation was formed.

TABLE II
CRYSTALLITE SIZE OF ANATASE (101) AND RUTILE (110) PHASES

Type of deposition	Crystalline size, nm		Band gap, eV
	Anatase (101)	Rutile (110)	
pDC	-	-	3.27
RF	48.2	-	3.26
pDC_RF	47.1	-	3.25
pDC_RF_30V BIAS	32.2	9.2	3.12
pDC_RF_60V BIAS	-	8.0	2.99

The analysis of crystallite size was prepared for the most

intensive anatase (101) and rutile (110) peaks. It was revealed that 48.2 nm crystallite size was observed for TiO_2 film deposited by RF power source (see Table II). The combination of pDC_RF power sources had negligible influence on crystallite size (47.1 nm). On the other hand, the addition of bias voltage (30 V) reduced anatase (101) crystallite size to 32.2 nm. The value of rutile (110) crystallite size was obtained at 9.2 nm. Further analysis showed only 8 nm crystalline size for rutile peak, when bias voltage was increased to 60 V.

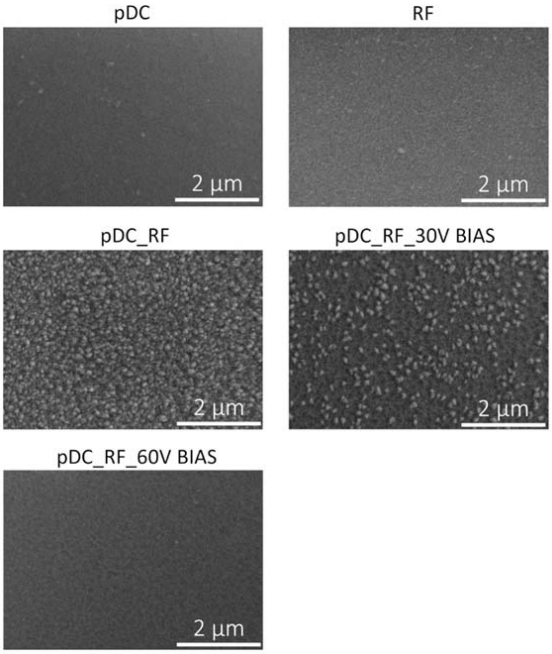

Fig. 3 SEM views of TiO_2 films using different combination of deposition parameters

Reference [13] investigated the influence of crystallite size on non-porous titania photocatalytic activity. They revealed that crystallite size increased with the film thickness. Moreover, they showed that the lifetime of the electron/hole is lengthened with the larger crystallites as well. This was explained by pair ability to migrate a greater distance in large crystallites than in smaller crystallites. The greater electron-hole recombination distance increased the photocurrent as well as photocatalytic ability. These results can be supplemented by SEM morphology views (Fig. 3). It was observed that samples with amorphous (pDC), anatase (RF) and rutile (pDC_RF_60V BIAS) structures have very uniform and relatively smooth surface. Nevertheless, anatase with various orientations (pDC_RF) showed completely different surface structure. The expressed grains with clear boundaries were observed. Formation of such structure promoted increment of surface roughness. The combination of two different power sources not only stimulated the formation of additional anatase orientations but invoked surface protrusions as well. The surface morphology of sample with anatase and rutile heterojunction (pDC_RF_30V BIAS) revealed formation of less grainy structure. However, bigger grains compared to previous sample were observed. This caused surface formation with the highest roughness.

The optical band gap analysis showed that amorphous TiO_2 phase has the highest band gap (3.27 eV). It is known that anatase phase has higher band gap (~3.2 eV) compared to rutile phase (~3.0 eV) [14]. Similar tendencies were observed by analyzing samples with pure anatase (RF and pDC_RF) and rutile phases (pDC_RF_30V BIAS) with the band gaps of 3.26 eV, 3.25 eV and 2.99 eV respectively (see Table II). The intermediate value of band gap (3.12 eV) was fixed by analyzing sample with the heterojunction of anatase and rutile phases (pDC_RF_60V BIAS). These results revealed that there is a possibility to shift and control band gap of TiO_2 film by applying negative bias voltage.

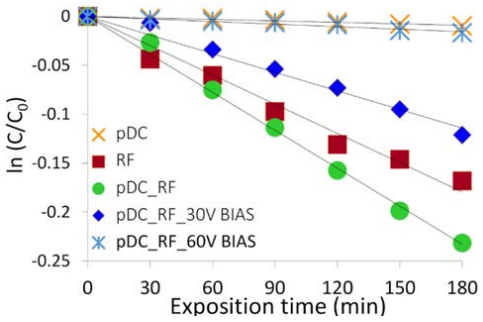

Fig. 4 Photocatalytic degradation of MB dye by TiO_2 films under UV-B irradiation

The results of deposited TiO_2 films' photocatalytical activity are shown in Fig. 4. The clear photocatalytic activity dependency on existence of anatase phase was observed. Samples without anatase phase (amorphous and rutile phases) showed very negligible MB decomposition ratio (0.5×10^{-4} min^{-1} and 0.9×10^{-4} min^{-1}). Significantly higher MB decomposition ratio was observed for the samples where anatase phase was formed. Interestingly, pure anatase phase with one expressed orientation (101) showed higher decomposition ratio (10×10^{-4} min^{-1}) than heterojunction of rutile and anatase phases (6×10^{-4} min^{-1}). This can be explained by Rietveld deconvolution, which showed significantly higher amount of rutile phase compared to anatase (72% and 28% for rutile and anatase phases respectively). Moreover, the sample with additional anatase orientation (004) demonstrated the highest photocatalytical activity (13×10^{-4} min^{-1}). This confirmed previous XRD results that existence of additional anatase surface {001} as well as higher crystalline size improved photocatalytical characteristics.

IV. Conclusions

TiO_2 films were successfully deposited using innovative method: co-sputtering from two similar magnetrons powered by different types of power supplies (RF and pDC) with additional negative bias voltage. XRD revealed that by selecting proper combination of power source and bias voltage various TiO_2 phases (amorphous, anatase, rutile or their mixture) can be synthesized without any additional

modifications of the system set-up. Moreover, roughness and band gap of TiO_2 films can be controlled by proper selection of bias voltage. Films with anatase phase having additional (004) orientation (pDC_RF) showed the highest photocatalytic activity. Such innovative TiO_2 formation method can be applied where various TiO_2 film phases are required especially where substrates temperature cannot exceed 100 °C.

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