

PHOTOCATALYTIC ACTIVITY OF TiO₂ FILMS DEPOSITED BY REACTIVE MULTI-PULSE HiPIMS AT DIFFERENT SUBSTRATE TEMPERATURE VALUES

A. BEȘLEAGĂ¹, A. DEMETER¹, G.B. RUSU², P. DINCĂ³ and L. SIRGHI^{1,*}

¹“Alexandru Ioan Cuza” University of Iasi, Faculty of Physics,
Iasi Plasma Advanced Research Center (iPARC),
Blvd. Carol I nr. 11, Iasi-700506, Romania

²“Ion Ionescu de la Brad” University of Agricultural Sciences and Veterinary Medicine
of Iasi, Faculty of Agriculture, Department of Pedotechnics, Sadoveanu Alley nr. 3,
Iasi-700490, Romania

³National Institute for Laser, Plasma and Radiation Physics, Atomistilor nr. 409,
Bucharest-077125, Romania

*E-mail: lsirghi@uaic.ro

Received July 11, 2017

Abstract. Reactive high power impulse magnetron sputtering (HiPIMS) operated in multi-pulse mode was used to grow titanium dioxide (TiO₂) thin films on quartz at different substrate temperature values. The films were characterized by X-Ray diffraction, atomic force microscopy, Raman spectroscopy and UV-Vis transmission spectroscopy techniques to investigate the influence of substrate temperature on the microstructure and optical properties of the deposited thin films. In particular, the substrate temperature affected the crystallinity, energy band gap, hydrophilicity induced by UV light irradiation and photocatalytic activity of the deposited films. The photocatalytic activity was evaluated by experiments of degradation under visible light irradiation of the methylene blue molecules in water. It is shown that the photocatalytic activity gradually increases with the value of the substrate temperature used in depositions. By increase of the substrate temperature, the structure of the deposited films changed from amorphous to crystalline anatase phase, while the optical band gap gradually decrease from 3.2 eV to 2.8 eV. These changes in microstructure and optical properties are considered as the main causes of the significant improvement by substrate heating of the visible light photocatalytic activity of the TiO₂ thin films.

Key words: photocatalytic activity, dye molecule decomposition, HiPIMS, TiO₂ thin films.

1. INTRODUCTION

Among other semiconductors, titanium dioxide (TiO₂) shows excellent photocatalytic activity under UV light irradiation for oxidative degradation of environmental pollutants [1]. Significant efforts have been devoted in the last decades to improve the utilization of solar energy by extending the optical absorption of this material into the visible wavelength region, thus enhancing the photocatalytic

activity in visible light. Developments of TiO₂ photocatalysts that operate effectively under visible light or solar light irradiation are still a challenge for large-scale utilization of TiO₂ photocatalysts. Approaches followed to improve the visible light photocatalytic activity include creation of nanostructured TiO₂ coatings (nanoparticles, nanorods, nanopores, nanopatterns, etc.) [2]. The use of nanosized particles enhances the photocatalytic activity in visible light due to increased effective area, thus providing at the same volume more surface atoms to promote the redox reactions, and decreased energy gap at nanoparticle surfaces. Recently, we fabricated TiO₂ 2D nanopatterns with improved photocatalytic activity in visible light by using HiPIMS deposition of nanopatterned Ti films with colloidal masks, followed by thermal oxidation of the nanopatterned films [3]. Besides fabrication of nonosized TiO₂ photocatalyst, high density and crystalline coatings is desired for improving of the photocatalytic activity due to density reduction of defects acting as charge recombination centers. The High Power Impulse Magnetron Sputtering (HiPIMS) deposition technique is known to produce coatings with high density microstructures due to the delivery of highly ionized deposition particle flux to the growing films [4]. Recently, it has been shown that the HiPIMS operating in multi-pulse mode (m-HiPIMS) has the advantages of a higher ionization degree of the sputtered material and of an important reduction of metal ion back-attraction. These effects enhance the quality (higher crystalline order, smaller roughness, higher compactness) and increase the deposition rate of the thin films [5, 6]. Compared to the standard HiPIMS operation mode, in the multi-pulse mode a single discharge pulse is divided in a number of micropulses with the same amplitude, separated by an optimum delay time. It was proved that HiPIMS operating with very short voltage pulses reduces significantly the gas rarefaction and self-sputtering effects, favors the production of ions in plasma volume (away from target) and prevents ion back-attraction [7, 8]. The high electron density in the reactive HiPIMS discharge enhances the dissociation of the molecular gases and improves their reactivity which is beneficial for the deposition process of compound materials [9]. Recently, reactive HiPIMS operated in multi-pulse mode has been used to deposit amorphous TiO_x thin films with variable stoichiometry ($1.63 < x < 2$) [10]. It has been found that the post deposition annealing treatment of the deposited films leads to the formation of TiO₂ anatase and Ti₄O₇ phases and significantly enhances the photocatalytic activity in visible light. Beside improvements of the visible-light photocatalytic activity and crystalline order, it has been demonstrated that a post-deposition annealing treatment in nitrogen atmosphere leads to formation of the titanium oxynitride phases with improved chemical stability [11].

In the present work, we investigate the effect of the substrate temperature on the crystalline structure and photocatalytic activity of TiO₂ thin films deposited by reactive m-HiPIMS. In contrast with the previous work [10], where substoichiometric TiO_x thin films were deposited at low value of gas pressure (0.8 Pa) on substrates at room temperature at variable pulsing frequency, in this work we use a relatively

low (constant) value of pulsing frequency at a higher value of gas pressure (6.6 Pa) and change the value of the substrate temperature. Therefore, in the present study the deposition gas have enough oxygen to yield stoichiometric TiO₂ compound films.

2. EXPERIMENTAL SET-UP

TiO₂ thin films were deposited on quartz at different substrate temperatures by reactive m-HiPIMS of a pure Ti target. The Ti target was sputtered in Ar/O₂ gas mixture (0.2% O₂ of the total mass flow rate of 50 sccm) at the total gas pressure of 6.66 Pa. Sequences consisting of 3 micro-pulses (each voltage pulse with an amplitude of -1 kV, duration of 3 μs and separated by a delay time of 50 μs) were applied on the Ti target with a repetition frequency of 900 Hz. In contrast with the previous work [10], where the use of much lower gas pressure (0.8 Pa) and longer micro-pulses (5 μs) determined deposition of substoichiometric TiO_x films, the values of gas pressure, micro-pulse duration and pulse repetition frequency used in the present work determine operation of the m-HiPIMS in compound target sputtering regime, which favors deposition of stoichiometric TiO₂ thin films. Details on the m-HiPIMS setup and discharge pulsing scheme are found in previously published paper [10]. Thin films with thickness of about 300 nm were obtained by setting the deposition time to one hour, while the substrate temperature was ranged from RT to 600°C by means a programmable port-substrate heater. The films thickness was estimated by measuring deposition rate using a quartz crystal microbalance, placed near the substrate. The properties of the deposited films were investigated by Atomic Force Microscopy (AFM) for morphological characterization of the film surface, X-Ray Diffraction (XRD) and Raman spectroscopy (RS) for structural characterization, and UV-Vis transmission spectroscopy for optical properties.

The photocatalytic activity of the TiO₂ coatings deposited at different substrate temperatures was evaluated by measuring the decrease in concentration of methylene blue (MB) dye in aqueous solutions under visible light irradiation. Prior to these measurements, an amount of 45 ml of MB solution with the volume concentration $C_0 = 440$ ppm was prepared. The concentration of MB in the solution subjected to photocatalytic degradation was determined by measurements of optical absorbance in the 400–800 nm range, we have considered the intensity of the main absorbance peak at 664 nm, using a UV-VIS spectrophotometer (Evolution 300 from Thermo Scientific). The UV-VIS spectrophotometer was first calibrated in order to determine the relationship between the absorbance peak intensity and MB concentration. The photocatalytic degradation setup consisted of a visible-light lamp that irradiated a glass Petri dish with the TiO₂ substrates immersed in a small amount (5 ml) of MB solution. Degradation of MB in control experiments consisting in visible-light irradiation of the same amount of solution in the Petri dish without the TiO₂ substrates was used as reference. Prior to visible light irradiation, the TiO₂ substrates were

immersed in solution and left in dark for 5 minutes. Then, the substrates and the MB solution were irradiated with visible light ($\lambda > 400$ nm) at a constant power density of 60 mW/cm^2 for different irradiation time (from 5 to 120 minutes). The decomposition of MB in the absence of any catalyst material was used as control. The photocatalytic activity of TiO_2 thin films under UV light irradiation was evaluated by water contact angle measurements (WCA). The measurements were conducted at room temperature by analysis the height profiles of digital images of small sessile drops ($1 \mu\text{l}$) of deionized water deposited on the TiO_2 surface after irradiation with UV light. The probes were radiated by a UV lamp (TUV T8 from Philips) at a power density of 1.8 mWcm^{-2} .

Phase composition and crystallinity were characterized by X-ray diffraction (LabX XRD-6000 from Shimadzu Co.) with $\text{Cu-K}\alpha$ X-ray radiation having a characteristic wavelength of 1.54059 \AA . The powder X-ray diffractometer was set up in the Bragg–Brentano configuration and the samples were analysed in the range of $2\theta = 10^\circ\text{--}50^\circ$, with a scanning rate of $4^\circ/\text{min}$. The Raman spectrometer (Renishaw inVia Raman Microscope) was used in the back-scattering configuration to collect spectra at room temperature in the range $100\text{--}1000 \text{ cm}^{-1}$ of the films excited at 532 nm by a diode laser. The scattered light was detected by a water-cooled charge coupled device detector. The optical properties of the deposited films were investigated by ultraviolet-visible (UV–Vis) transmission spectroscopy in the range of $200\text{--}1100 \text{ nm}$. The optical band gap of the TiO_2 thin films deposited at different substrate temperatures was estimated from the Tauc plots [12] obtained from the optical transmittance. The topography images and roughness of the deposited film surfaces have been obtained by atomic force microscopy (AFM) measurements performed in non-contact mode with a silicon AFM probe (NSG 03 from NT-MDT) with a sharpened tip (nominal curvature radius of 10 nm) and a stiff cantilever.

3. RESULTS AND DISCUSSION

XPS measurements (not shown here) revealed that TiO_2 thin film deposited at RT is stoichiometric. By taking into account that the reactivity of growing thin films increases as substrate temperature increases, we can state that all the deposited TiO_2 thin films are stoichiometric.

The photocatalytic activity of the samples for degradation of an organic compound dissolved in water was confirmed by photocatalytic degradation of methylene blue (MB) dye in water under visible light ($400\text{--}800 \text{ nm}$) irradiation. Figure 1 illustrates the photocatalytic degradation of MB molecules in water under visible light irradiation for five TiO_2 coatings deposited at different values of the substrate temperature. The MB photocatalytic degradation is expressed by the variation with the irradiation time of the C/C_0 ratio, where C is the volume concentration of

MB measured after a certain irradiation time and C_0 is the initial concentration of MB solution ($C_0 = 440$ ppm). In these plots, a higher photocatalytic activity is associated with a steeper decrease of MB concentration with the irradiation time. The degradation of MB is slow for all films because they absorb mainly in UV range (see results of light absorption spectra presented in Fig. 5) and are transparent for visible light. However, the films are slightly activated by the light at the edge of the visible spectrum (400 nm) of the light source and the films deposited at higher substrate temperature values showed a slightly better photocatalytic activity due to their smaller optical bandgap.

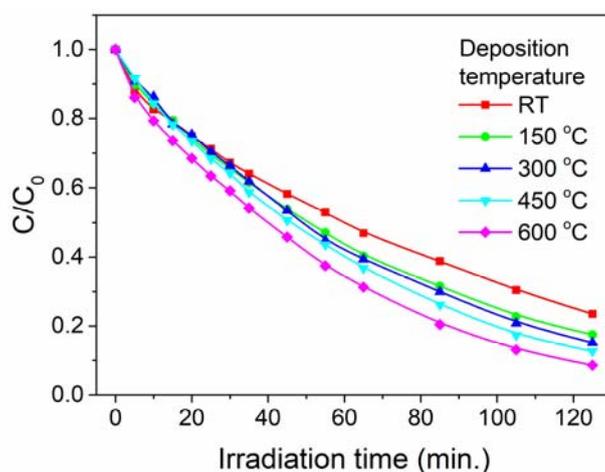


Fig. 1 – MB degradation under visible light irradiation for TiO₂ coatings deposited at different substrate temperature values.

The UV light photocatalytic activity of the deposited TiO₂ thin films was investigated by assessing the improvement in hydrophilicity caused by UV light irradiation of the film surfaces. The surface hydrophilicity was characterized by water contact angle measurements. The UV irradiation of samples with enhanced UV light photocatalytic activity increases the surface hydrophilicity due to photocatalytic decomposition of hydrophobic airborne contaminant molecules adsorbed on surface and generation of hydroxyl group by photolysis of water molecules [13].

Experimental results (Fig. 2) show a much faster decrease of the water contact angle of the TiO₂ thin films deposited at high temperature as compared to the TiO₂ films deposited at RT. The surface of TiO₂ deposited at 600°C become super hydrophilic by UV light irradiation, which is probed by a decrease of water contact angle to values below 10° after one hour of irradiation.

The results concerning dependence of the photocatalytic activity on deposition temperature can be correlated to the crystalline structure of the deposited films. The X-ray diffraction patterns of TiO₂ coatings deposited at different substrate

temperature values are shown in Fig. 3. The TiO₂ films deposited at RT and substrate temperature of 150°C and 300°C are amorphous, whereas the films grown at 450°C and 600°C developed crystalline predominantly anatase phase. The intensity of the diffraction peaks increases with the substrate temperature used in depositions, which indicates that increase of the substrate temperature favors depositions of films with a better crystalline order. The average crystallite sizes for TiO₂ films deposited at 450°C and 600°C, estimated from the Debye-Scherrer's formula using the preferred orientation of XRD peak A(101), were 12.5 nm and 17.7 nm, respectively.

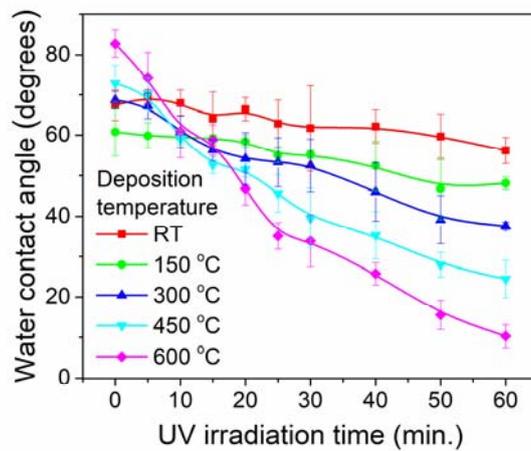


Fig. 2 – Variation of the water contact angle for TiO₂ thin films deposited at different substrate temperature values.

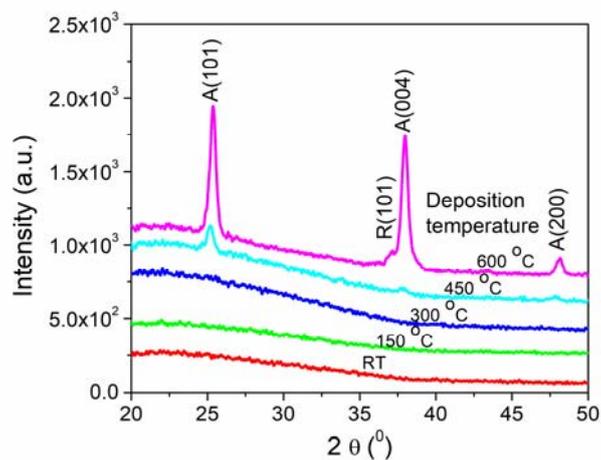


Fig. 3 – XRD patterns of TiO₂ thin films deposited at different substrate temperature values. The patterns are offset for better readability.

The structure of TiO₂ thin films was also investigated by Raman spectroscopy. The Raman spectra of the thin films deposited at different substrate temperature (shown in Fig. 4) are well correlated with the results of the XRD investigation. The typical Raman modes at 144, 398, 448, 515, 612 and 638 cm⁻¹ are assigned to the $E_g(A)$, $B_{1g}(A)$, $E_g(R)$, $A_{1g}(A)$, $A_{1g}(R)$, and $E_g(A)$ modes in anatase and rutile structures [14]. $E_g(A)$, $A_{1g}(A)$ and $B_{1g}(A)$ peaks correspond to the Raman fundamental vibration modes of anatase phase, while $E_g(R)$ and $A_{1g}(R)$ peaks correspond to the Raman-active modes of rutile TiO₂. Additionally, the Raman peak located at ~473 cm⁻¹ corresponds to fused quartz substrate [15]. The Raman spectra of the samples deposited at substrate temperature lower than 450°C correspond to almost amorphous structures, which is in agreement with the results of XRD. The intense Raman peak and band positioned at 144 and 398 cm⁻¹, respectively, have been obtained only for the thin films deposited at substrate temperature higher than 450°C and correspond to a structure with high degree of crystalline order (anatase phase). By increasing the temperature substrate, the intensity of predominant Raman peak ($E_g(A)$ – located at 144 cm⁻¹) gradually increases, showing an improvement of crystallinity. For the other Raman peaks, there is no obvious dependence of their intensity on the substrate temperature, indicating the formation of both anatase and rutile phases in the deposited TiO₂ thin films and a slight phase transition.

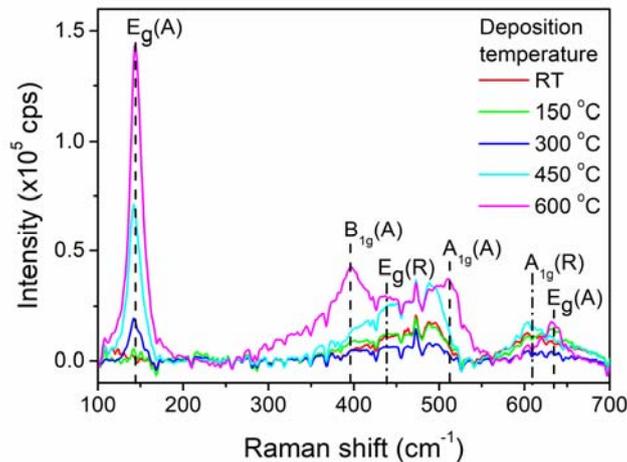


Fig. 4 – Raman spectra of TiO₂ thin films deposited at different substrate temperatures.

The best photocatalytic activity was obtained by the thin films deposited at the highest substrate temperature. The XRD and Raman data for this film showed the best crystalline order with predominant anatase phase. In addition, this sample shows the best absorption of visible light when compared to other films deposited at lower temperatures. The energy band gap (estimated from Tauc plot) decreases by increasing the temperature deposition from 3.2 eV, for the films deposited at RT and 150°C, to 2.8 eV for the film deposited at substrate temperature of 600°C (Fig. 5).

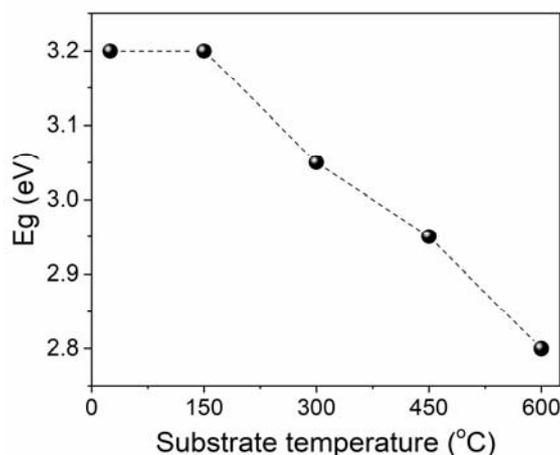


Fig. 5 – Energy band gap of TiO₂ thin films deposited at different substrate temperatures.

The low energy band gap found for the sample deposited at high temperature favors the absorption of visible light and enhances the surface photocatalytic activity in visible light.

In order to analyse and compare the surface roughness of the deposited thin films, three random areas of $3 \times 3 \mu\text{m}^2$ on each sample surface were scanned by AFM (Fig. 6a–e).

The root mean square (RMS) roughness values were calculated using the AFM image processing software. By increase of the substrate temperature, the RMS roughness of the deposited films increases gradually from 3.3 nm to 38.7 nm (Fig. 6f). This corresponds to a change of the film surface morphology characterized by noticeable increase of the grain size and improvement of homogeneity of surface distribution of the grains. The higher roughness and larger grain size obtained at higher substrate temperature can be attributed to higher mobility and diffusivity of adatoms, which lead to a decreased number of nucleation islands and to the suppression of the second nucleation between existing islands. It is worth noting that the influence of surface roughness on the values of water contact angle

is insignificant, the difference between the measured values and the apparent values (according to Wenzel model) being less than 2 degrees. AFM topography images of film surfaces taken after light irradiation (not shown) indicated no noticeable change of film surface morphology as result of light irradiation.

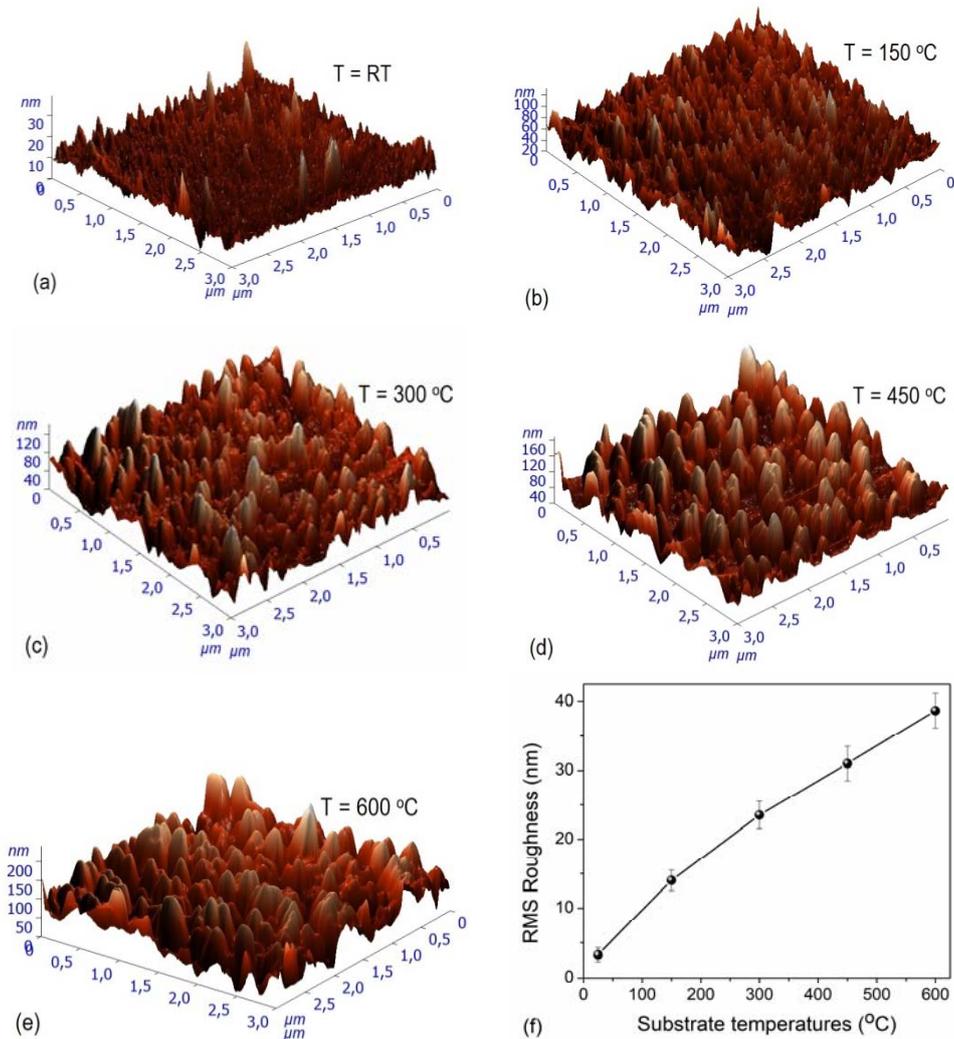


Fig. 6 – 3D AFM (scan size $3 \times 3 \mu\text{m}^2$) images for TiO₂ coatings deposited at different substrate temperatures (a–e) and RMS roughness dependence on the deposition temperature (f).

Thus, the increase in crystallinity with the deposition temperature is proved by X-Ray Diffraction, Raman spectroscopy and Atomic Force Microscopy (AFM)

measurements and clearly demonstrates to be beneficial for improving the photocatalytic activity of the deposited TiO₂ thin films. The film with the higher degree of crystalline order has longer lifetime of the photogenerated charge carriers due to a reduced density of defects (that act as recombination centers for the photogenerated charged carriers) [16]. This determines a higher density of active surface sites for MB molecule degradation. In addition, large grains and high surface roughness provide a larger surface effective area for surface redox reactions. Therefore, the enhanced photocatalytic activity of TiO₂ films deposited at high substrate temperature can be related to reduction of the defect density, narrowing of energy band gap and enlargement of the surface effective area.

4. CONCLUSION

TiO₂ thin films have been deposited by reactive high power impulse magnetron sputtering technique at different substrate temperature values. The influence of the deposition temperature on microstructure, surface topography, energy band gap, hydrophilicity and photocatalytic activity of the deposited films was investigated by X-Ray Diffraction (XRD), Raman spectroscopy, Atomic Force Microscopy (AFM), UV-Vis transmission spectroscopy, measurements of water contact angle under UV radiation and measurements of the photocatalytic decomposition of an organic dye (methylene blue) in aqueous solution under visible light irradiation. It is shown that the increase of the substrate temperatures over 450°C determined depositions of crystalline TiO₂ thin films with increased photocatalytic activity. The photocatalytic activity is interpreted in correlation with structural, optical and morphological properties of the TiO₂ thin films, which in their turn depend strongly on the deposition temperature. By increase of the substrate temperature, the microstructure of the deposited films changed from amorphous to crystalline anatase and rutile structure, while the optical band gap gradually decrease from 3.2 eV to 2.8 eV. These changes in microstructure (better crystalline order) and optical properties (narrower energy band gap) are considered as the main cause of the improvement of the visible light photocatalytic activity of the films. Another cause is the increase of surface effective area of the films deposited at higher substrate temperature values.

Acknowledgements. This work has been supported by the Romanian National Plan for Research, Development and Innovation, grant JOINT RESEARCH PROJECTS PN-II-ID-JRP-2012-RO-FR-0161.

REFERENCES

1. A. Fujishima, X. Zhang, D.A. Tryk, Surf. Sci. Rep. **63**, 515–582 (2008).
2. Y. Li, T. Sasaki, Y. Shimizu, and N. Koshizaki, J. Am. Chem. Soc. **130**, 14755–14762 (2008).
3. A. Demeter, V. Tiron, N. Lupu, G. Stoian, and L. Sirghi, Nanotechnology **28**, 255302 (2017).

4. I.-L. Velicu, V. Tiron, B.-G. Rusu, G. Popa, Surf. Coat. Technol. **327**, 192–199 (2017).
5. O. Antonin, V. Tiron, C. Costin, G. Popa, T.M. Minea, J. Phys. D: Appl. Phys. **48** 015202 (2015).
6. V. Tiron, I.-L. Velicu, O. Vasilovici, G. Popa, J. Phys. D: Appl. Phys. **48** 495204 (2015).
7. I.-L. Velicu and V. Tiron, Dig. J. Nanomater. Bios **9**, 1513 (2014).
8. I.-L. Velicu, V. Tiron, and G. Popa, Surf. Coat. Technol. **250**, 57 (2014).
9. V. Tiron and L. Sirghi, Surf. Coat. Technol. **282**, 103–106 (2015).
10. V. Tiron, I.-L. Velicu, M. Dobromir, A. Demeter, F. Samoila, C. Ursu, L. Sirghi, Thin Solid Films **603**, 255–261 (2016).
11. A. Demeter, F. Samoila, V. Tiron, D. Stanescu, H. Magnan, M. Straticiuc, I. Burducea and L. Sirghi, Surf. Coat. Technol. **324**, 614–619 (2017).
12. J. Tauc, Mater. Res. Bull. **3**, 37 (1968).
13. A. Mills and M. Crow, Int. J. Photoenergy **2008**, 470670 (2008).
14. S.J. Rigby, A.H.R. Al-Obaidi, S.K. Lee, D. McStay, P.K. Robertson, J. Appl. Surf. Sci. **252**, 7948 (2006).
15. S. Logunov, S. Kuchinsky, J. Appl. Phys. **98**, 053501 (2005).
16. A.L. Linsebigler, G. Lu, and J. T. Yates, Chem. Rev. **95**, 735–758 (1995).