PREPARATION AND CHARACTERIZATION OF TiO_2 THIN FILMS FOR UV SENSOR

LIDIYA BEDIKYAN[1], STOIL ZAKHARIEV[1], PAVEL KEJZLAR[2]
LUKAS VOLESKY[2], MARGARITA ZAKHARIEVA[1]
NIKOLAY PETKOV[1], PETR LOUDA[2]
[1]Central Laboratory of Applied Physics
– Bulgarian Academy of Sciences, Plovdiv, Bulgaria
[2]Institute for Nanomaterials, Advanced Technology and Innovation
Technical University of Liberec, Czech Republic

DOI: 10.17973/MMSJ.2015_12_201520

e-mail: lid_bed@yahoo.com

Nanosized TiO_2 thin films were deposited by conventional vacuum thermal evaporation and triode-cathode sputtering of Ti on silicon and quartz substrates. To form TiO_2 a high temperature annealing of the Ti films was carried out in the range of 450÷800 °C. The optical properties of TiO_2 were studied by measuring UV-VIS transmittance spectra and the indirect band gap was evaluated. Scanning electron microscope (SEM), atomic force microscope (AFM) and energy-dispersive spectroscopy were employed for surface and structure analysis. Structures for UV sensors were formed by thermal evaporation of various combing contacts on the TiO_2/Si substrates. The photoresponse of the structures was detected in the wavelength range of 235÷420 nm. An increase in photocurrent with an order of magnitude was detected by exposing samples to UVA illumination and applying 6÷10 V bias voltage. The obtained results indicated that the studied structures are suitable for UV sensors.

KEYWORDS
titanium dioxide, spectral characteristics, band gap
surface analysis, UV sensor.

1. INTRODUCTION

Titanium dioxide (TiO_2) is a photosensitive semiconductor widely used in photocatalytic processes, photovoltaics and photosensors. Its light sensitivity can also be used for design of gas and humidity sensors, as well as other types of sensors. Due to the wide band gap of 3.0 eV and 3.3 eV of the TiO_2 crystalline phases rutile and anatase, respectively, this material is sensitive to the illumination in the wavelength range of 320÷400 nm, which renders the TiO_2 – based photodiodes suitable for UV sensors [Hossein-Babaei 2012, Kargan 2012, Tian 2015, Xie 2013].

In the present study, the TiO_2 thin films were prepared using two physical methods of deposition. Optical transmittance characteristics were studied. Band gap energy for the indirect transitions was evaluated by the transmittance spectra vs. photon energy. The analysis of the quantitative composition, morphology and topography of the films was carried out using scanning electron microscope (SEM) and atomic force microscope (AFM).

2. EXPERIMENTAL

The preparation of the TiO_2 films was a two step process. First, Ti films were deposited, as two methods were used: conventional thermal evaporation of titanium and cathode-triode sputtering of preliminary ion purificated titanium target. The sputtering proceeded in argon with pressure of 2 ÷ 6.10^{-3} mbar. The substrates were optical quartz, glass ceramic (sital) and crystalline silicon n-Si (100) with a specific resistivity of about 6 ÷ 9 Ω.cm. The temperature of the substrates was up to 100 °C. The second step was the formation of TiO_2 films by thermal annealing for several hours in dry air using a resistance furnace. The annealing temperature varied from 450 °C to 800 °C. Each experiment included three types of substrates. The obtained TiO_2 films were uniform, with a good adhesion and thickness from 100 nm to 300 nm. The adhesion could be improved by increasing the annealing temperature. Films showed rather smooth and compact surface in both deposition methods. It was suggested that at the annealing temperature of 450 °C anatase phase was formed, and at the temperatures above 600 °C – rutile phase [Fu 2006, Sreemany 2010, Huang 2011].

Optical properties of TiO_2 were investigated by the spectral characteristics of transmittance measured with a spectrophotometer UV-VIS SPECTROMOM 195D within a range of wavelengths of 200 ÷ 900 nm. The films were with high transmittance up to 95% for both deposition methods.

Scanning electron microscope (SEM) and atomic force microscope (AFM) with JPK NanoWizard III head were employed for surface and structure analysis.

SEM analysis was carried out using an ultra-high-resolution field emission scanning electron microscope Zeiss Ultra Plus equipped with microanalytic system (EDX+WDX+EBSD) and energy-dispersive detector Oxford X-Max20 for evaluation of local chemical composition. SEM operated with SmartSEM software, EDX analysis used SW AZtec 2.1.

3. RESULTS AND DISCUSSION

The absorption coefficient α and the band gap energy ΔEg were calculated by shortwave end of the transmittance spectra. Ignoring reflection which was minimal, absorption coefficient is calculated as follows:

$$\alpha = \ln(1/T)/d, \text{ eV/m} \quad (1)$$

where T is transmittance; d – film thickness.

The width of the optical zone was obtained by linear extrapolation of their straight portion to 0 of the graphs of optical absorption $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus photons energy ($h\nu$) for direct and indirect transitions, respectively [Sreemany 2010, Kernazhitsky 2013].

Calculated values of the indirect optical transitions were in the range of 2.96 ÷ 3.01 eV for samples annealed at 650 ÷ 700 °C, for samples annealed at 550 ÷ 600 °C they were in the range of 3.10÷3.15 eV and in the range of 3.2 ÷ 3.3 eV for samples, annealed at 450 °C. The illustration graphs of the energy absorption for the indirect transitions are shown in Fig. 1. The presented data are for the samples with similar thicknesses in the range of 150÷170 nm and annealed at: 650 °C – sample 1, 550 °C – sample 2, 450 °C – sample 3.

Qualitative and quantitative local composition of the films in atomic % and weight % were evaluated using SEM and EDX microanalytic system.

Average results characteristic of sample surface are presented in Table 1. As seen, the films are similar in composition. Samples annealed at low temperature exhibit a higher content of C. In order to avoid the

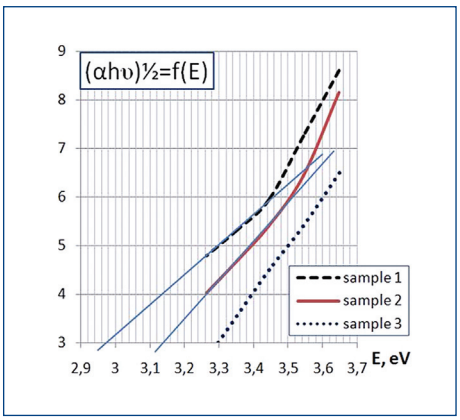

Figure 1. Graphs of the energy absorption for indirect transitions.

Spectrum Label Wt%	C	O	Ti	Spectrum Label At%	C	O	Ti
sample 3, K series	6.60	59.00	34.40	sample 3, K series	11.09	74.42	14.49
sample 2, K series	6.03	57.00	36.98	sample 2, K series	10.38	73.66	15.96
sample 1, K series	5.38	58.08	36.54	sample 1, K series	9.25	74.99	15.76

Table 1. Films composition in atomic % and weight %

inclusion of C, some authors [Chow 2001] advised before scanning the samples to be cleaned with argon at 4 kV.

Surface morphology of the samples annealed at temperatures 550 °C, 650 °C and 800 °C, is presented in Fig. 2 (A, B and C respectively). The increase in the temperature of post annealing leads to the growth of crystallite size and at 800 °C leads to cluster formation.

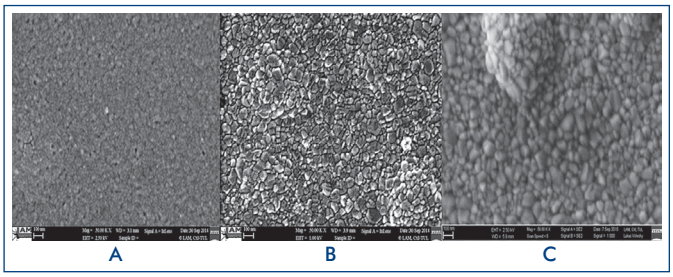

Figure 2. Surface morphology of samples 2(A), 1 (B) and 3 (C).

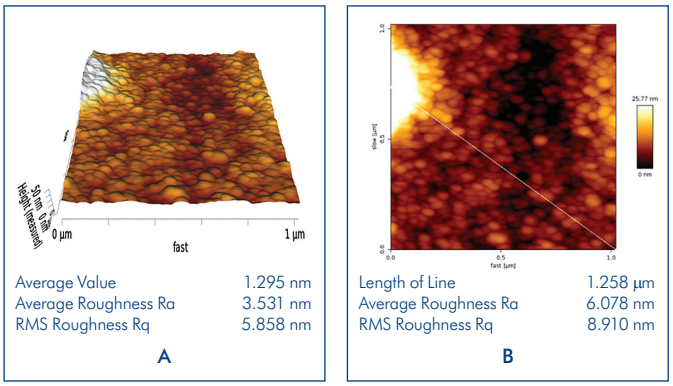

Figure 3. Height measured trace 3D 1 x 1 um and roughness data (A); Line roughness 1 x 1 um and roughness data (B).

The topography and the roughness of the samples were investigated by AFM. Fig. 3, A presents the 3D image and the root mean square roughness of sample 2. Fig. 3, B represents the line roughness of the surface of sample 2 (white line) and the root mean square roughness. The histograms and the surface profiles show a fairly uniformly distribution of the crystallites.

The samples surface is rather smooth with mean square roughness of 5.8 nm ÷ 9.1 nm typical for the annealing temperature under 600 °C [Yang 2007, Senthilkumar 2010]. With the increase of the annealing temperature above 600 °C, the surface mean square roughness increases up to 22.8 nm. The observed increase in the roughness is related to the increase in the crystallite size, which depends on both temperature and duration of the thermal treatment.

In the most published literature, the values for indirect transitions for TiO_2 rutile phase are about 3.0 ÷ 3.1 eV and for TiO_2 anatase phase 3.2 ÷ 3.3 eV [Fu 2006, Yang 2007]. The values obtained in this study are: 2.96 ÷ 3.01 eV for samples, annealed at 650 ÷ 800 °C, 3.10 ÷ 3.15 eV for samples, annealed at 550 ÷ 600 °C and 3.2 ÷ 3.3 eV for samples, annealed at 450 °C. These values suggest the formation of predominantly anatase phase at 450°C and mainly rutile phase at higher temperatures 650 ÷ 800 °C. Annealing at 650 °C influences the size of the crystallites, but obviously prevails the anatase phase. The variation in the width of the band gap can be connected with the increase in the crystallites size. The change in the surface morphology after annealing can be related to possible changes in the ratio of the phases of anatase and rutile and in the amount of oxygen vacations, as well as to the presence of oxides of the type TiO and Ti_2O_3 [Sreemany 2010].

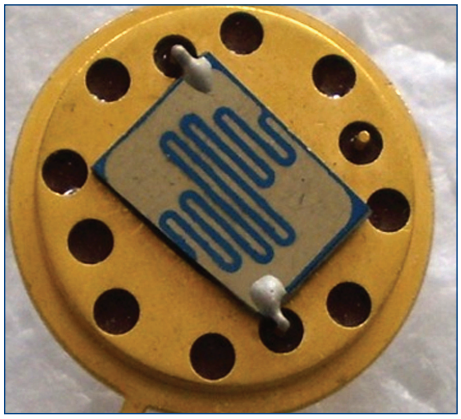

Figure 4. UV sensor structure.

Electrodes of various metals, such as Al, Ni, In and In-Sn were deposited on the obtained TiO_2 films by contact thermal evaporation through a mask. The prepared meandering structures were mounted on golden substrates with conductive Ag paste. Fig. 4 shows a picture of a $Si/TiO_2/Al$ structure.

Fig. 5, A shows the dependence of the dark current of the samples on the applied voltage. The dark and photocurrent-voltage characteristics of the structures were measured in the range of 4 ÷ 30 V. A 50W Hg lamp (wavelength 365 nm) was used for illumination. The best results were obtained with Ni and Al contacts ($Si/TiO_2/Ni$ and $Si/TiO_2/Al$). The photocurrent increases by an order of magnitude in comparison with dark current at a bias voltage in the range of 6 to 10 V.

The photocurrent of the samples as a function of the illumination power and at a constant applied voltage is shown in Fig. 5, B. The spectral characteristics of the photocurrent at 20 V bias voltage show photosensitivity in the range of 235 ÷ 420 nm, with a maximum between 280 and 330 nm. Results are characteristic for both used deposition methods: thermal evaporation and cathode-triode sputtering.

The photoelectric measurements show that the annealing temperature affects the photovoltaic properties [Fu 2006]. Samples with a predominantly anatase phase have better photoelectric properties. The in-crease

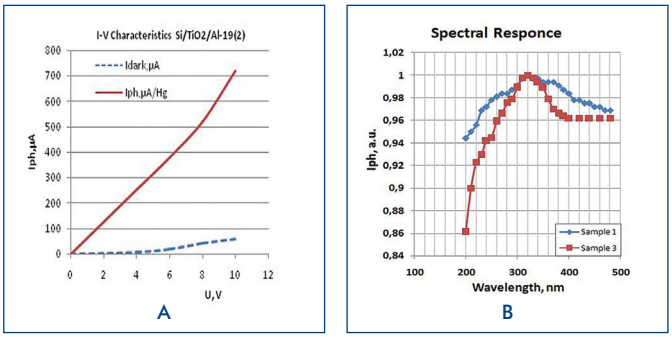

Figure 5. Current-voltage characteristics (A); Spectral characteristics (B).

in the annealing temperature initiates the formation of the rutile phase with a lower photoelectric activity because the wider band gap of anatase results in a more effective recombination of the electron-hole pairs in comparison with that of rutile. Therefore, the current-voltage characteristics of samples with the band gap of 3.3 eV showed a better sensitivity and a significant difference between the dark- and photocurrent. The illumination of the sample with UV radiation at the applied voltage of 6 ÷ 10 V leads to an increase in the photocurrent with an order of magnitude. The spectral characteristics for all samples show a good photosensitivity in the wavelength range of 235 ÷ 420 nm and an essential difference between dark- and photocurrent.

4. CONCLUSIONS

In the present study it is shown that TiO_2 films obtained by a two step deposition/annealing process have a photosensitivity, which depends on the annealing temperature. The annealing temperature defines to a high degree the structural composition of the films and the crystallite size. Results are characteristic for both used deposition methods. The collected data show that the thermal annealing of the Ti films at 450 °C in dry air leads to the predominant formation of anatase phase of TiO_2. These films have the widest optical band gap of 3.3 eV and the highest photosensitivity in the UVA region. The best results are obtained with the n-Si/TiO_2/Ni and n-Si/TiO_2/Al structures, which renders them suitable for the UV sensors.

ACKNOWLEDGEMENT

The results of this project LO1201 were obtained with the financial support of the Ministry of Education, Youth and Sports in the framework of the targeted support of the "National Programme for Sustainability I" and the OPR&DI project Centre for Nanomaterials, Advanced Technologies and Innovation CZ.1.05/2.1.00/01.0005.

REFERENCES

[Chow 2001] Chow, L.L.W. et al., Reactive sputtered TiO_2 thin film humidity sensor with negative substrate bias, Sensors and Actuators B, 2001, Vol.76, pp. 310-315. Elsevier ISSN: 0925-4005

[Fu 2006] Fu, Y. and Cao, W., Preparation of transparent TiO_2 nanocrystalline film for UV sensor, Chinese Science Bulletin, 2006, Vol.51, No 14, pp.1657–1661. Springer ISSN: 2095-9281

[Hossein-Babaei 2011] Hossein-Babaei, F. et al., Large area Ag-TiO_2 UV radiation sensor fabricated on a thermally oxidized titanium chip, Sensors and Actuators A: Physical, 2012, Vol. 173, pp. 116–121. Elsevier ISSN: 0924-4247

[Huang 2011] Huang, J. H. and Wong, M. S., Structures and properties of titania thin films annealed under different atmosphere, Thin Solid Films, 2011, Vol. 520, pp.1379–1384. Elsevier ISSN: 0040-6090

[Kargan 2012] Kargan, N.H. et al., Detecting ultra-violet radiation by using titanium dioxide nanoparticles, Soft Nanoscience Letters, 2012, No 2, pp. 29-33. doi:10.4236/snl.2012.23006

[Kernazhitsky 2013] Kernazhitsky, L. et al., Optical absorption of polydisperse TiO_2: Effect of surface doping by transition metal cations, Ukrainian Journal of Physical Optics, 2013, Vol.14, No 1, pp.15-23. ISSN: 1609–1833

[Senthilkumar 2010] Senthilkumar V. et al., Preparation of anatase TiO_2 thin films for dye-sensitized solar cells by DC reactive magnetron sputtering technique, Thin Solid Films, 2010, Vol.519, pp. 991-994. Elsevier ISSN: 0040-6090

[Sreemany 2010] Sreemany, M. et al., A study on structural, optical, electrical and microstructural properties of thin TiO_x films upon thermal oxidation: Effect of substrate temperature and oxidation temperature, Physica B, 2010, Vol.405, pp. 85-93. ISSN: 0921-4526

[Tian 2015] Tian, W. et al., Nanoscale ultraviolet photodetectors based on one-dimentional metal oxide nanostructures, Nano Research, 2015, Vol.8(2), pp. 382-405. Springer ISSN: 1998-0124

[Xie 2013] Xie, Y. et al., A self-powered UV photodetector based on TiO_2 nanorod arrays, Nanoscale Research Letters, 2013, 8:188. Springer doi:10.1186/1556-276X-8–188

[Yang 2007] Yang, H. et al., Microwave-assisted sol-gel synthesis and optical property of TiO_2 thin film, Journal of Optoelectronics and Advanced Materials, August 2007, Vol.9, No 8, pp. 2493-2497. ISSN: 1454-4164

CONTACTS

Assoc.Prof. Lidiya Bedikyan, PhD, Science Secretary
Central Laboratory of Applied Physics
Bulgarian Academy of Sciences
61, Sankt Peterburg Blvd, 4000 Plovdiv Bulgaria
tel.: +359 32 635 019, GSM: 0893 611 032, fax: +359 32 632 810
e-mail: lid_bed@yahoo.com, www.clap-bas.com