XRD and XPS Analysis of TiO$_2$ Thin Films Annealed in Different Environments

Tamara Potlog$^1$, Petru Dumitriu$^1$, Marius Dobromir$^2$ and Dumitru Luca$^2$

$^1$. Department of Physics and Engineering, Moldova State University, MD 2009, Chisinau Moldova
$^2$. Faculty of Physics, Alexandru Ioan Cuza University, Iasi 700506, Romania

Received: June 18, 2014 / Accepted: June 23, 2014 / Published: June 25, 2014.

Abstract: Undoped and Nb-doped TiO$_2$ thin films have been fabricated on glass substrate by RF magnetron sputtering. The morphologic, structural and surface composition of these films before and after annealing in different environments were investigated by atomic force microscopy (AFM) imaging, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The XRD data reveal that the crystallinity is improved when the films are Nb-doped and annealed in H$_2$ environment. The TiO$_2$ thin films annealed in H$_2$ environment exhibit only the anatase phase. The XPS analysis of TiO$_2$ with Nb indicates the maximum shift in binding energy of the Ti 2p peak. A mechanism for the incorporation of Nb in the TiO$_2$ lattice has been proposed.

Key words: TiO$_2$ thin films, doping effect, H$_2$ annealing, XRD, XPS analysis.

1. Introduction

TiO$_2$ is a large bandgap semiconductor, commonly investigated more in rutile and anatase phases, has been extensively studied worldwide. Its response to UV light has led to the emergence of the photocatalysis research field [1-3]. New opportunities for the applications of the TiO$_2$ materials lie nowadays in more challenging areas, such as energy conversion and storage. Mesoscopic TiO$_2$ film is a major component of dye-sensitized solar cells [4, 5], organic photovoltaics [6] and quantum dot sensitized solar cells [7, 8]. Furubayashi et al. recently reported that Nb-doped TiO$_2$ could be used as a new transparent conducting oxide (TCO) material [9]. The incorporation of Nb metal ion in TiO$_2$ lattice acts as a donor type impurity and leads to a decrease in the resistivity of the semiconductor [10], which is critical for window layer in the fabrication of the photovoltaic devices based on hetero-junctions. In order to extend the light absorption spectrum into visible region in solar cells, we try to modify the properties of some TiO$_2$ films by using the Nb$_2$O$_5$ as dopant. In this paper we report the effect of annealing in different media on the structural properties and composition of the films by XRD and XPS and the mechanism for the incorporation of Nb in the TiO$_2$ lattice.

2. Experiments

TiO$_2$ thin films were prepared on glass substrates by radio frequency (RF) magnetron sputtering of a Ti target of 99.5% purity, 76.2 mm in diameter. Additionally, TiO$_2$ thin films doped with oxide powder Nb$_2$O$_5$ of 99.999% purity were prepared. The sputtering was performed under a mixture of 5 standard cubic centimeters per minute (sccm) of Ar (99.99%) and 1 sccm of O$_2$ (99.99%) atmosphere supplied as working and reactive gases, respectively, through independent mass-flow controllers. The sputtering chamber was evacuated down to $1 \times 10^{-5}$ mbar by the turbo molecular pump and the working pressure was kept at about $5 \times 10^{-3}$ mbar.
During the depositions, the RF power was 100 W and the substrates were kept at room temperature using the same deposition time of 8 h. The distance between the target and the substrate was kept constant at 6 cm. Before the deposition, the glass substrates were sequentially cleaned in an ultrasonic bath with acetone then ethanol. Finally, the substrates were rinsed with distilled water and dried. After the deposition, the undoped and Nb-doped TiO2 films were vacuum-annealed in hydrogen environment. The first set of undoped TiO2 films was vacuum-annealed at 420 °C for 30 min in the deposition chamber at a pressure of $4.0 \times 10^{-5}$ mbar and in hydrogen atmosphere at a pressure of $2.0 \times 10^{-3}$ mbar. A second set of Nb-doped TiO2 films was annealed at 420 °C for 30 min in hydrogen atmosphere at the same pressure, as the first set. We denote the first set of pristine TiO2 films as MD-2 and the second one as TiNbO-2.

The crystal structure was studied by X-ray diffraction (XRD) using a Bruker-AXS, D8 Advance diffractometer (CuKα radiation, 40 mA, 40 kV). The weight percentage of the anatase phase ($W_A$) was calculated with the relation [11]:

$$W_A = \frac{1}{1 + 1.265 \frac{I_R}{I_A}}$$

where, $I_A$ denotes the intensity of the strongest anatase reflection and $I_R$ is the intensity of the strongest rutile reflection.

The elemental composition in the surface region was investigated by X-ray photoelectron spectroscopy (XPS). The spectra were measured using a Physical Electronics PHI 5000 Versa Probe instrument, equipped with a monochromated AlKα X-ray source (1,486.6 eV). The photoelectrons were collected at a take-off angle of 45°. The surface quantification was done following the standard procedure [12] using the Ti 2p, O 1s, and Nb 3d high-resolution XPS spectra. Peak deconvolution has been done using the PHI-MULTIPAK software. The elemental atomic concentration was calculated from the peak surface areas, taking into account the sensitivity factors of the analyzed elements [13].

3. Results and Discussion

3.1 Morphological and Structural Studies of TiO2 Thin Films

The diffraction pattern for the first set of undoped TiO2 films is shown in Fig. 1. The various diffraction peaks could be assigned to reflections corresponding to the anatase and rutile phases of TiO2 [14] for the as-deposited and the vacuum-annealed films. For the as-deposited TiO2 film, the weight percentage of the anatase phase ($W_A$) is 59.3%. For the vacuum-annealed film the weight percentage of the anatase phase ($W_A$) increases to 62%. The TiO2 films annealed in H2 atmosphere exhibit only the anatase phase.

The diffraction spectra of the second set of Nb-doped TiO2 films are depicted in Fig. 2. The XRD data show that the crystallinity is improved when the films are doped.

Annealing at 420 °C in H2 atmosphere results in an increase in the intensity of the diffraction peak located at $2\theta = 25.2^\circ$. No characteristic peaks of Nb2O5 were observed in Nb-doped TiO2 thin films. Instead, it is found that the peak position of (101) anatase plane shifts to smaller diffraction angle values. This may be ascribed to the exchange of Nb with Ti in the TiO2 lattice [15] and the formation of the TiNbO phase with different concentrations.
We suppose that the primary hydrogen annealing mechanism is the chemisorption of the dissociated hydrogen on the surface of the films. The half width of all the peaks of the Nb-doped and annealed TiO₂ thin films increases. The crystallite size was calculated by Scherer equation using anatase (101) and (110) rutile phases. As shown in Table 1, for samples annealed in H₂ atmosphere at 420 °C the estimated crystallite size for the anatase phase increases for both sets.

Figs. 3 and 4 show the AFM images of Nb-doped TiO₂ films as-grown at room temperature and annealed at 420 °C for 30 min in hydrogen atmosphere. The AFM measurements reveal a net discrepancy and indicate an increase of crystallinity of the annealed films. The as-deposited TiO₂ film exhibits a smooth surface with non-uniform grains. After annealing, the surface becomes homogeneous and is composed of many nanocrystalline grains.

### 3.2 X-Ray Photoelectron Spectroscopy Analysis

Fig. 5 shows the survey XPS spectra of the first set of TiO₂ films in the whole binding energy region. The characteristic peaks of C 1s, O 1s and Ti 2p are present.

| Sample          | θ (°) | Intensity (arb. units) | Phase name | d (Å) | D (nm) |
|-----------------|-------|------------------------|------------|-------|--------|
| MD-2.5 (unannealed) | 25.508 | 601*                   | (101) Anatase | 1.7954 | 51.0   |
|                 | 27.438 | 283                    | (110) Rutile | 3.3228 | 44.1   |
|                 | 48.042 | 170                    | (200) Anatase | 3.1042 |        |
| MD-2.1 (vacuum, 420 °C) | 25.503 | 556*                   | (101) Anatase | 1.7967 |        |
|                 | 27.438 | 386                    | (110) Rutile | 3.3304 | 51.5   |
|                 | 48.043 | 204                    | (200) Anatase | 3.1003 |        |
| MD-2.4 (H₂, 420 °C) | 25.508 | 636*                   | (101) Anatase | 1.7981 |        |
|                 | 37.793 | 186                    | (004) Anatase | 2.5118 | 88.4   |
|                 | 48.048 | 162                    | (200) Anatase | 3.1064 |        |
| TiNbO₂-2.1 (unannealed) | 25.192 | 3643*                  | (101) Anatase | 1.8121 | 47.4   |
|                 | 27.432 | 246                    | (110) Rutile | 3.3591 |        |
|                 | 37.789 | 156                    | (004) Anatase | 3.7975 |        |
|                 | 47.783 | 749                    | (200) Anatase | 4.1726 |        |
| TiNbO₂-2.5 (H₂, 420 °C) | 25.162 | 4126*                  | (101) Anatase | 1.8141 | 55.2   |
|                 | 27.420 | 226                    | (110) Rutile | 3.3738 |        |
|                 | 37.792 | 207                    | (004) Anatase | 3.7975 |        |
|                 | 47.747 | 827                    | (200) Anatase | 4.1783 |        |
XRD and XPS Analysis of TiO$_2$ Thin Films Annealed in Different Environments

Fig. 3 Two-dimensional AFM image of an as-grown Nb-doped TiO$_2$ thin film.

Fig. 4 Two-dimensional AFM images of a Nb-doped TiO$_2$ thin film annealed in H$_2$ atmosphere at 420 °C.

Fig. 5 XPS survey scan spectra of an as-deposited TiO$_2$ film, vacuum-annealed and annealed in H$_2$ atmosphere at 420 °C.

The C 1s peak of the unannealed film is located at a binding energy value of 284.6 eV, while for the sample annealed in H$_2$ it shifts to 285.7 eV.

Fig. 6 shows the high-resolution Ti 2p doublet of the pristine TiO$_2$ films. For the unannealed TiO$_2$ film the spectrum indicates binding energies at 458.5 ± 0.2 eV for Ti 2p$_{3/2}$ and 464.3 ± 0.2 eV for Ti 2p$_{1/2}$, respectively, which are very close to the values of the Ti$^{4+}$ valence state of stoichiometric rutile TiO$_2$ [16, 17].

For the vacuum and H$_2$ annealed films at 420 °C the binding energies of the Ti 2p feature binding energy values shifted towards 459.5 ± 0.2 eV for Ti 2p$_{3/2}$ and 465.2 ± 0.2 eV for Ti 2p$_{1/2}$, also reported in Ref. [18]. We suppose that this shift could be generated by the reduction of Ti$^{4+}$ ions to Ti$^{3+}$ defect states which usually are accompanied by a loss of oxygen from the surface of TiO$_2$.

Liu et al. [19] proposed that the interaction between H$_2$ and TiO$_2$ fell develops in three successive steps. Firstly, hydrogen interacts physically with the adsorbed oxygen on the surface of TiO$_2$. Secondly, electrons are transferred from the H to the O atoms in the lattice of TiO$_2$. Then, the oxygen vacancies are formed when the O atom and the H atom form of H$_2$O or OH groups. Thirdly, when the temperature increased to 420 °C, the interaction between H$_2$ and TiO$_2$ proceeds more drastically, the electrons are transferred from oxygen vacancies to Ti$^{4+}$ ions, and then Ti$^{3+}$ defect states are formed. Zhang et al. [20] irradiated the TiO$_2$/Si films by electron beams and found that the number of Ti$^{3+}$ ions increased and Ti$^{4+}$ ions decreased after the irradiation. The atomic concentration of Ti and...
Table 2  The atomic concentration and the binding energies for the Ti 2p, Nb 3d and O 1s lines.

| Samples               | XPS Peak | %  | XPS Peak | %  |
|----------------------|----------|----|----------|----|
| MD_2_4 (H2, 420 °C)  | O 1s     | 38.1| O 1s     | 60.1|
|                      | C 1s     | 36.7| Ti 2p_3/2| 39.9|
|                      | Ti 2p    | 25.3|          |     |
|                      | O 1s     | 42.8| O 1s     | 74.0|
| MD_2_5 (unannealed) | C 1s     | 42.2|          |     |
|                      | Ti 2p_3/2| 15.0| Ti 2p_3/2| 26.0|
|                      | O 1s     | 38.1| O 1s     | 61.5|
| MD_2_1 (vacuum, 420 °C)| C 1s    | 38.0|          |     |
|                      | Ti 2p_3/2| 23.8| Ti 2p_3/2| 38.5|
|                      | O 1s     | 41.3| O 1s     | 61.6|
| TiNbO_2_1 (unannealed)| C 1s   | 32.9|          |     |
|                      | Ti 2p_3/2| 21.5| Ti 2p_3/2| 32.0|
|                      | Nb 3d    | 4.3 | Nb 3d    | 6.4 |
|                      | O 1s     | 41.5| O 1s     | 59.8|
| TiNbO_2_5 (H2, 420 °C)| C 1s   | 30.5|          |     |
|                      | Ti 2p_3/2| 22.1| Ti 2p_3/2| 31.9|
|                      | Nb 3d    | 5.8 | Nb 3d    | 8.3 |

Fig. 7  XPS spectra of O1s region of as-deposited TiO2 film, vacuum-annealed and annealed in H2.

O in the TiO2 thin films are shown in Table 2.

We can conclude that the Ti^{4+} ions are reduced by both electron donors such as H2 and lattice oxygen in TiO2 and the binding energy of 459.5 eV may be attributed in this case to Ti^{3+} defect state of anatase TiO2 phase, according to the XRD analysis. Significant increases in the intensity of the Ti 2p peaks are observed, too.

Fig. 7 shows high-resolution O 1s XPS spectrum. For the unannealed TiO2 film, two oxygen chemical species appear, the lower binding energy (BE) at around 529.7 ± 0.2 eV can be attributed to the basic peak of TiO2 lattice oxygen (O_{lat}); the other 532.8 ± 0.2 eV represented the surface weakly bound (or adsorbed) oxygen (OH and molecular O_{2} species). The O 1s spectrum of the vacuum-- and H2- annealed films at 420 °C consists of a main peak with higher intensity at about 530.7 ± 0.2 eV and an obvious shoulder located at about 532.9 ± 0.2 eV, indicating that the detected OH group and molecular O2 may be adsorbed at the surface of the film during annealing. The binding energies of the O 1s signal of the vacuum- and H2- annealed films shifted toward higher binding energies with the same value 1.0 ± 0.2 eV as for Ti 2p spectrum of these films.

Figs. 8-10 depict the high-resolution Nb 3d, Ti 2p and O 1s signals of the unannealed Nb-doped TiO2 films and annealed in H2 atmosphere at 420 °C, respectively. From Table 2 it can be observed that the atomic percentage of the Nb element is different in unannealed TiO2 films, compared to the films after H2 annealing. Therefore, for these samples it is hard to discuss about the influence of the H2 treatment on their structural properties. The Nb 3d binding energy for the unannealed Nb-doped TiO2 film was determined to be 208.2 ± 0.2 eV for Nb 3d_{5/2} and 211.0 ± 0.2 eV for Nb 3d_{3/2}, while for the annealed one in hydrogen, the BE
XRD and XPS Analysis of TiO$_2$ Thin Films Annealed in Different Environments

![XPS spectra of Nb3d region of an as-deposited Nb doped TiO$_2$ film and annealed in H$_2$.](image)

**Fig. 8** XPS spectra of Nb3d region of an as-deposited Nb doped TiO$_2$ film and annealed in H$_2$.

We suppose that this shift are caused by the differences in atomic concentration of Nb (Table 2) and by the effect of annealing in H$_2$ atmosphere..

The Ti 2p XPS spectra (Fig. 9) of unannealed Nb-doped TiO$_2$ films show values of binding energies of $459.7 \pm 0.2$ eV for Ti 2p$_{3/2}$ and $464.9 \pm 0.2$ eV for Ti 2p$_{1/2}$, respectively.

For the film annealed in H$_2$ atmosphere, a slight shift ($\sim 0.2$ eV) towards higher BE values is seen for Ti 2p$_{3/2}$ and ($\sim 0.6$ eV) for Ti 2p$_{1/2}$. The position of the Ti 2p$_{3/2}$ peak (458.8 eV) is close to the value reported for Ti$^{3+}$ states in the anatase phase (458.7 eV) [21]. We believe that the H$_2$ annealing changes the Ti$^{3+}$/Ti$^{4+}$ ratio in the TiO$_2$ thin film. Both 2p$_{1/2}$ and 2p$_{3/2}$ binding energies showed a change in Ti$^{3+}$ states and the Ti$^{4+}$ ions, as a consequence of the H$_2$ treatment.

A chemical shift of the BE is known to mean changes in the structure. Since the ionic radius of Nb$^{5+}$ (0.70 Å) is larger than the ionic radius (0.68 Å) of the titanium, we can thus conclude that the Nb is easily built into a lattice, adding electrons. The theoretical calculations of Morgan [22] predict a small-polaronic Ti$^{3+}$ gap state within an Nb-doped TiO$_2$ thin film. For Nb dopant at these concentrations, the defect can be characterized as Nb$^{5+}$ and Ti$^{3+}$/Ti$^{4+}$ ratio.

The peak of the Nb 3d$_{3/2}$ peak corresponds to that of Nb$^{5+}$ oxidation state [23, 24]. Nb$^{5+}$ species, substituting for Ti$^{4+}$ in the crystalline lattice could be a reason for anatase stabilization. To maintain the charge equilibrium, the extra-positive charge due to Nb$^{5+}$ may be compensated by the creation of an equivalent amount of Ti$^{3+}$ ions [25] or by the presence of vacancies in the cation sites [26].

The O 1s XPS spectra of the Nb-doped TiO$_2$ samples showed in Fig. 9 indicate that there a single chemical state. The binding energy of $531.1 \pm 0.2$ eV for unannealed and $530.8 \pm 0.2$ eV for annealed Nb-doped TiO$_2$ films can be attributed to surface species, such as Ti-OH resulting from the chemisorbed water (OH) [27, 28], and to the lattice oxygen (Ti-O), respectively. The shift of the binding energy to small

values are $207.9 \pm 0.2$ eV and $210.8 \pm 0.2$ eV, respectively.
values for the annealed Nb-doped TiO$_2$ film can be attributed to the fact that a part of the OH group is adsorbed from the surface, because the weight percentage of O atoms is reduced from 61.6% to 59.8%.

4. Conclusions

Annealing in hydrogen atmosphere showed substantial improvement of structural properties TiO$_2$ thin films. Undoped thin films of TiO$_2$ are $n$-type conductors with doubly ionized oxygen vacancies as predominant point defects. The XRD data show that the crystallinity is improved when the TiO$_2$ films upon Nb doping. The Nb ions incorporate into the TiO$_2$ lattice. The XPS results indicate that the charge transfer from Nb metal ions to Ti leads to a change in the oxidation state of titanium. The H$_2$ annealing changes the Ti$^{3+}$/Ti$^{4+}$ ratio in the TiO$_2$ thin film.

These results demonstrate that hydrogen annealing is a simple and effective tool to enhance and modify the properties of the original material.

Acknowledgments

This research was supported by the Bilateral Moldova-Romania grant no. 13.820.15.19/RoA.

References

[1] K. Maeda, K. Domen, Photocatalytic water splitting: Recent progress and future challenges, J. Phys. Chem. Lett. 1 (2010) 2655-2661.

[2] W.Y. Teoh, J.A. Scott, R. Amal, Progress in heterogeneous photocatalysis: From classical radical chemistry to engineering nanomaterials and solar reactors, J. Phys. Chem. Lett. 3 (2012) 629-639.

[3] P.V. Kamat, Manipulation of charge transfer across semiconductor interface, J. Phys. Chem. Lett. 3 (2012) 663-672.

[4] L.M. Peter, The Grätzel cell: Where next? J. Phys. Chem. Lett. 2 (2011) 1861-1867.

[5] T. Miyasaka, Toward printable sensitized mesoscopic solar cells: Light-harvesting management with thin TiO$_2$ films, J. Phys. Chem. Lett. 2 (2011) 262-269.

[6] E.L. Ratcliff, B. Zacher, N.R. Armstrong, Selective interlayers and contacts in organic photovoltaic cells, J. Phys. Chem. Lett. 2 (2011) 1337-1350.

[7] I. Mora-Sero, J. Bisquert, Breakthroughs in the development of semiconductor-sensitized solar cells, J. Phys. Chem. Lett. 1 (2010) 3046-3052.

[8] A. Braga, S. Gimenez, I. Concina, A. Vomiero, I. Mora-Sero, Panchromatic sensitized solar cells based on metal sulfide quantum dots grown directly on nanostructured TiO$_2$ electrodes, J. Phys. Chem. Lett. 2 (2011) 454-460.

[9] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K.Inaba, G. Kinoda, Y. Hirose, T. Shimada T. Hasegawa, A transparent metal: Nb-doped anatase TiO$_2$, Applied Physics Letters 86 (2005) 252101-1-252101-3.

[10] M.F. Yan, W.W. Rhodes, Effect of cation contaminants in conductive TiO$_2$ ceramics, J. Appl. Phys. 53 (12) (1983) 8809-8818.

[11] JCPDS X-ray powder files data (Data file 05-0522).

[12] J.F. Watts, J. Wolstenholme, An Introduction to Surface Analysis by XPS and AES, John Wiley & Sons, Chichester, 2003.

[13] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy, ULVAC-PHI Japan, Physical Electronics, USA, 1995.

[14] JCPDS Data Cards 00-021-1272 and 00-21-1276, p 521.

[15] R. Sharma, M. Bhatnagar, Improvement of the oxygen gas sensitivity in doped TiO$_2$ thick films Sens. Actuators B 56 (3) (1999) 215-219.

[16] H.S. Kim, S.H. Kang, Effect of hydrogen treatment on anatase TiO$_2$ nanotube arrays for photoelectrochemical water splitting bull, Korean Chem. Soc. 34 (7) (2013) 2067-2072.

[17] H.J. Bae, S.H. Park, A. Nakamura, K. Koike, K. Fujii, H.J. Park, et al., The effect of rapid temperature annealing with N$_2$ and H$_2$ on photoelectrochemical properties of u-TiO$_2$, J. Electrochem. Soc. 160 (11) (2013) H800-H802.

[18] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-Ray Photoelectron Spectroscopy, Perkin Elmer Corp, Publishers, Eden Prairie, MN, 1979, p. 68.

[19] G.X. Liu, F.K. Shan, J.J. Park, W.J. Lee, G.H. Lee, I.S. Kim, et.al., Electrical properties of Ga$_2$O$_3$-based dielectric thin films prepared by plasma enhanced atomic layer deposition (PEALD), J Electroceram 17 (2006) 145-149.

[20] J. Zhang, Y. Wang, Z. Jin, Z. Wu, Z. Zhang, Visible-light photocatalytic behavior of two different N-doped TiO$_2$, Appl. Surf. Sci. 254 (2008) 4462-4466.

[21] M. Sacerdoti, M.C. Dalconi, M.C. Carotta, B. Cavicchi, M. Ferroni, S. Colonna, et al., XAS investigation of tantalum and niobium in nanostructured TiO$_2$ anatase, Journal of Solid State Chemistry 177 (6) (2004) 1781-1788.

[22] B.J. Morgan, D.O. Scanlon, G.W. Watson, Intrinsic n-type defect formation in TiO$_2$: A comparison of rutile and...
anatase from GGA + U Calculations, Journal of Materials Chemistry 19 (2009) 5175-5178.

[23] M.Z. Atashbar, H.T. Sun, B. Gong, W. Wlodarski, R. Lamb, XPS study of Nb-doped oxygen sensing TiO₂ thin films prepared by sol-gel method, Thin Solid Films 326 (1-2) (1998) 238-244.

[24] J.F. Moulder, W.F. Stickle, P.E. Sool, K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie, Minn, USA, 1999.

[25] M. Valigi, D. Cordischi, G. Minelli, P. Natale, P. Porta, A structural, thermogravimetric, magnetic, electron spin resonance, and optical reflectance study of the NbOₓTiO₂ system, Journal of Solid State Chemistry 77 (2) (1988) 255-263.

[26] M. Sacerdoti, M.C. Dalconi, M.C. Carotta, B. Cavicchi, M. Ferroni, S. Colonna, et al., XAS investigation of tantalum and niobium in nanostructured TiO₂ anatase, J. Solid State Chem. 177 (6) (2004) 1781-1788.

[27] M. Park, T.E. Mitchell, A.H. Heuer, Subsolidus equilibria in the TiO₂-SnO₂ system, J. Am. Ceram. Soc. 58 (1975) 43-47.

[28] J.C. Colmenares, M.A. Aramenda, A. Marinas, J.M. Marinas, F.J. Urbano, Synthesis, characterization and photocatalytic activity of different metal-doped titania systems, Appl. Catal. A: Gen. 306 (2006) 120-127.