Characterization of RF-Sputtered Ultra-Thin WO_3 Films Grown on TiO_2 Surface

M. Dobromir[*], A. Manole[**], R. Apetrei[***] and D. Luca[****]

[*]Department of Sciences, "Al. I. Cuza" University, 700107 Iaşi, România, marius.dobromir@uaic.ro
[**]Faculty of Physics, "Al. I. Cuza" University, 700506 Iaşi, România, alina.v.manole@gmail.com
[***]Faculty of Physics, "Al. I. Cuza" University, 700506 Iaşi, România, rapetrei@uaic.ro
[****]Faculty of Physics, "Al. I. Cuza" University, 700506 Iaşi, România, dumitru.luca@uaic.ro

ABSTRACT

Ultra-thin WO_3/TiO_2 bilayer thin films were deposited on glass and silicon substrates using RF reactive magnetron sputtering. The films structure, morphology, and transmittance were investigated by X-ray diffraction, atomic force microscopy and UV-Vis spectroscopy. The surface elemental composition and electronic structure were determined by X-ray and valence band photoelectron spectroscopy XRD detected the presence of rutile crystalline phase. AFM images reveal changes in surface morphology with the increase of the ultra-thin WO_3 film thickness. Core level and valence band XPS spectra are suggesting a narrowing of the band gap with the increase of tungsten atomic concentration in the surface of the bilayer structure.

Keywords: TiO_2, WO_3, sputtering, bilayer, VBXPS

1 INTRODUCTION

Titanium dioxide (TiO_2) is a well-documented low cost, non-toxic and chemically stable semiconductor photocatalyst. When exposed to UV radiation, its surface becomes self-cleaning, self-sterilizing and super-hydrophilic [1-3]. Although the application range of TiO_2 photocatalysts is broad, it is still limited to UV-light range, due to the large band gap (3.20 eV for the anatase crystalline phase). Aiming at extending the photocatalytic activity of TiO_2 upon irradiation with visible light, doping titania surface with metal [2-4] or non-metal impurities [1-3] or inducing oxygen defects [3] have been investigated. The same goal can be achieved by fabricating multilayer structures using narrow band gap semiconductors [3, 5-7].

In this contribution, we report on TiO_2 and ultra-thin WO_3/TiO_2 bilayers grown by radio frequency (RF) reactive magnetron sputtering. Among other techniques, magnetron sputtering offers easy control of thin films thickness and properties, as well as the advantage of large area uniform deposition. The crystallinity, surface morphology, surface chemical composition and optical properties of the samples were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy.

The current results are significant for the characterization of WO_3/TiO_2 hetero-junctions, a novel approach structure to improve the photocatalytic efficiency of titania-based materials [5].

2 EXPERIMENTAL

The TiO_2 thin films were grown on unheated glass and Si(100) substrates by using plasma-assisted sputtering. The deposition chamber is evacuated up to a pressure of 2.0×10^{-5} mbar. A 3.00" TiO_2 stoichiometric ceramic target (Kurt J. Lesker) was used in a RF magnetron discharge running in a high purity Ar - O_2 gas mixture. The substrates were placed at 6 cm in front of the magnetron cathode disk (Torus® TM3, K. J. Lesker). The gas-flow is controlled by mass-flow regulators and the discharge total pressure during all deposition runs was maintained at 5.0×10^{-3} mbar by using a needle valve. The discharge power from RF Generator, PFG 300 RF, Huttingher was set at 100 W. The deposition time for TiO_2 was 60 min.

In the next step, ultra-thin WO_3 was deposited on TiO_2 in a similar manner using a 3.00" WO_3 stoichiometric ceramic target (Kurt J. Lesker). The thickness of the ultra-thin WO_3 layer deposited on top of the TiO_2 was adjusted by changing the deposition time (20 – 80 s), while the RF power injected in the discharge remained constant (50 W).

Information on films crystallinity were obtained from XRD data, acquired with a Shimadzu LabX XRD-6000 diffractometer (Cu Kα radiation, λ = 1.54182 Å). Films surface morphology was investigated using an NT-MDT Solver Pro-M atomic force microscope operated in tapping mode. The AFM images were analyzed with specialized software – Gwyddion – in order to retrieve statistical data.

The surface elemental composition was determined from XPS measurements, which included survey scans and core level spectra of TiO_2 reference and WO_3/TiO_2 bilayers, by using an ULVAC-PHI, 5000 VersaProbe spectrometer. Also, valence band X-ray photoelectron spectroscopy (VBXPS) data were collected in order to determine the electronic structure of the samples [8, 9]. The system is equipped with monochromated Al Kα radiation (hν = 1486.7 eV). The photoelectrons were collected for a take-off angle of 45°. The surface quantification has been carried-out following the standard procedure [10] by using

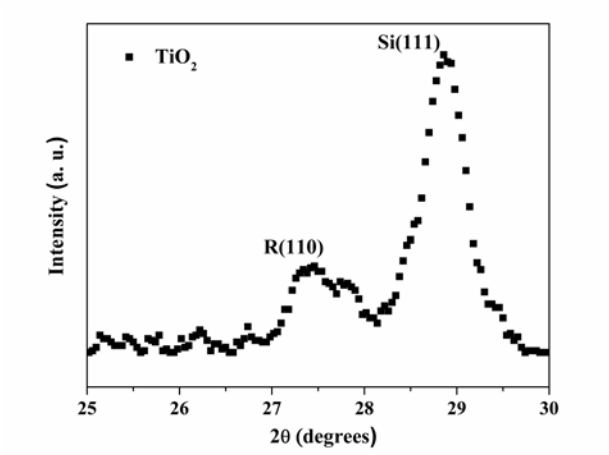
** Corresponding author. Tel: +40 0232202409

the core level spectra of Ti 2p, O 1s and W 4f. The calibration of binding energy (BE) scale was performed with respect to the C 1s peak at 284.6 eV. The spectra deconvolution has been done using the PHI - MultiPak software and the concentration of the elements found in the surface was derived from peak surface areas, taking into account the sensitivity factors of each element [11].

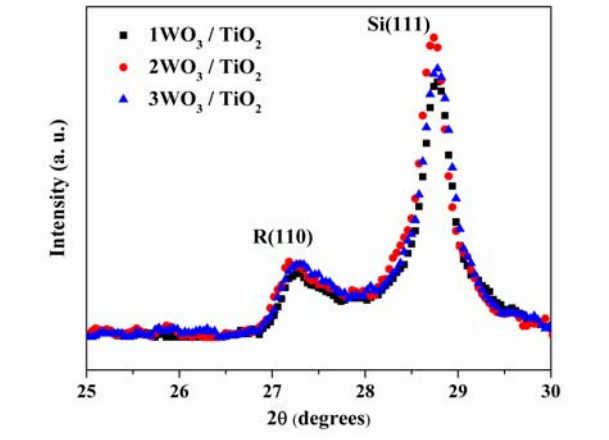
Optical transmittance spectra of films were recorded using an Evolution 300 UV-Vis Thermo Scientific spectrometer (190 - 1100 nm). An AvaSpec-2048 system controlled by the AVASOFT-Thin Film software was used for film thickness measurements.

3 RESULTS AND DISCUSSIONS

Figure 1 shows X-ray diffraction patterns of both reference TiO_2 thin film (Fig. 1a) and WO_3/TiO_2 bilayers (Fig. 1b). The presence of the rutile crystalline phase in all samples is indicated by the diffraction peak at $2\theta = 27.2°$.



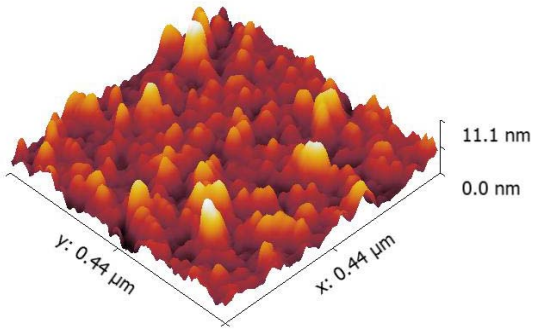
(a)



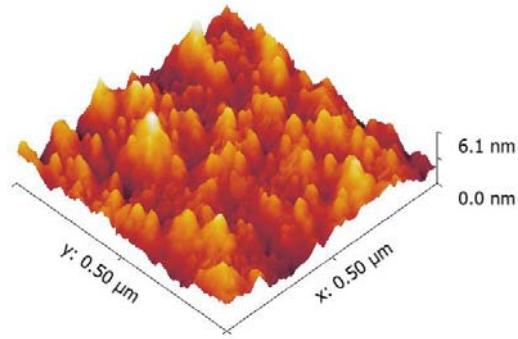
(b)

Figure 1: XRD patterns of reference TiO_2 (a) and WO_3/TiO_2 bilayer (b) thin films. The large signal at $2\theta = 28.7°$ is originated in the single-crystal sample substrate.

Film surfaces morphology, as revealed by AFM (Fig. 2), is characterized by root mean square (RMS) values (shown in Table 1) which are gradually decreasing with the increase of the ultra-thin WO_3 film thickness, which is also associated with the increase of the W atomic concentration in the surface of the bilayer structure. The RMS roughness of the reference TiO_2 sample is double in value compared to the one of the $3WO_3/TiO_2$ (Fig. 2)



(a)



(b)

Figure 2: AFM images of reference TiO_2 (a) and $3WO_3/TiO_2$ bilayer (b).

By analyzing the high-resolution XPS spectra and the valence spectra X-ray photoelectron spectroscopy (VSXPS) data, the chemical composition (Table 1) and the valence band maximum (VBM) of the sample were inferred [8, 9]. The XPS core level spectra (not shown) are characteristic to these type of samples.

The VBM of the reference sample is situated at 3.30 eV with respect to the Fermi level (E_F). A shift in BE of 0.5 eV towards lower energies is related to the presence of the top ultra-thin layer of WO_3 (Fig. 3). This result implies a narrowing of the band gap in the case of the bilayer structure.

The thickness of the ultra-thin tungsten oxide layer could not be measured by the used method. Taking into consideration the fact that the electrons detected by the XPS technique have their origin in the first atomic layers and the presence of both W and Ti atoms in all samples, we can assume that the thickness of the WO_3 is less than 10 nm.

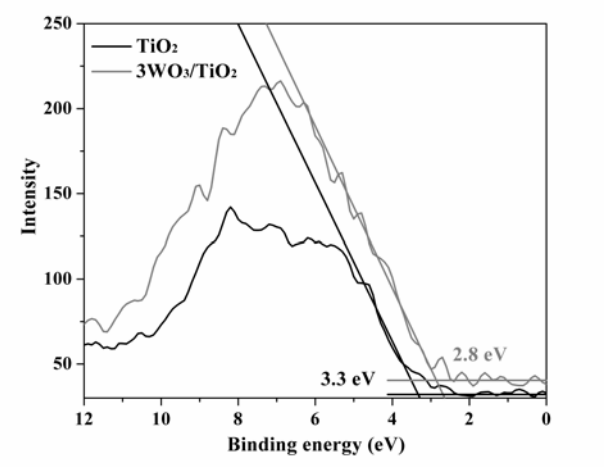
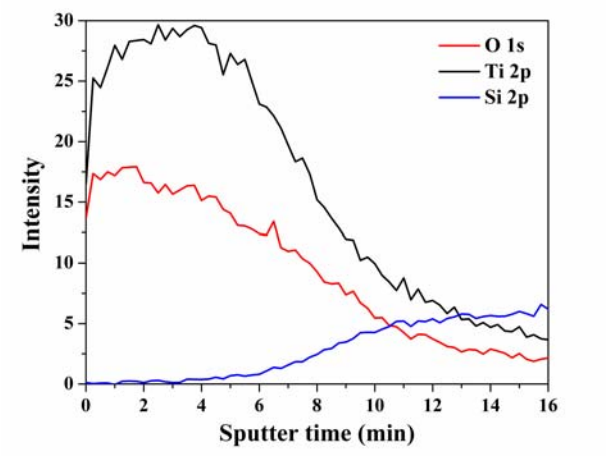
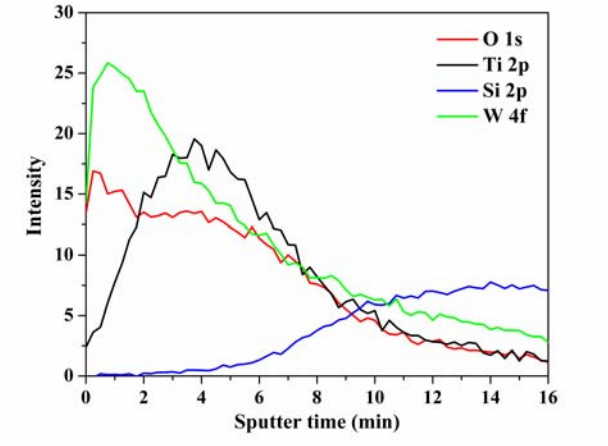


Figure 3: VBM determination by valence band edge liniar fitting of reference TiO_2 and $3WO_3/TiO_2$ bilayer .

Figure 4 depicts the sputter depth profiles of the elements present in the surface of a reference titania sample and of a bilayer structure, as revealed by the XPS spectra taken under Ar^+ surface sputtering (2kV, 1μA 3x3 mm^2).



(a)



(b)

Figure 4: Sputter depth profiles of the reference TiO_2 (a) and $3WO_3/TiO_2$ bilayer (b).

After about 15 minutes of sputtering the highest intensity signal is the one corresponding to the Si 2p state, which means that the deposited thin films were removed from the Si(100) substrate surface.

Sample	Ti at %	O at %	W at %	RMS (nm)
TiO_2	23	77	-	1.5
$1WO_3/TiO_2$	13	78	9	1.3
$2WO_3/TiO_2$	6	76	18	1.1
$3WO_3/TiO_2$	3	76	21	0.8

Table 1: Atomic concentrations of the elements in the surface, RMS values.

The optical transmittance (Fig. 5) of the investigated samples in the visible range is higher than 80%. The deposition of a ultra-thin WO_3 layer on top of the TiO_2 thin film does not introduce significant changes in the registered UV-Vis spectra.

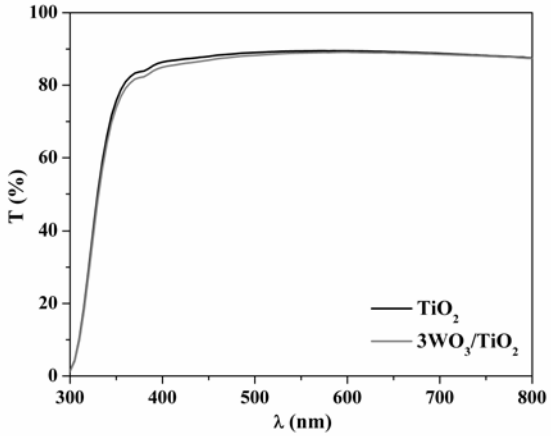


Figure 5: Optical transmittance spectra of reference TiO_2 and $3WO_3/TiO_2$ bilayer

4 CONCLUSIONS

The XRD patterns of both TiO_2 and WO_3/TiO_2 thin films remained unchanged. XPS measurements revealed the presence of both W and Ti atoms in all bilayer samples. The concentration of W in the surface increases with the deposition time up to 21 at %. The WO_3 deposition time affects the surface morphology of the thin films by decreasing the RMS values. The thin films are highly transparent, and the transparency slightly decreased with increasing WO_3 thickness. VBXPS measurements are indicating a narrowing of the band gap with the increase of W content in the surface of the bilayer structure.

ACKNOWLEDGEMENTS

The financial support from the Romanian Ministry of Education, Research and Youth through PCCE ID_76 project and from the EU Structural Funds through POSDRU 89/1.5/S/49944 project is acknowledged.

REFERENCES

[1] A. Fujishima, X. Zhang and D.A. Tryk, Surf. Sci. Rep. 63, 515, 2008.

[2] T.L. Thompson and J.T. Yates Jr., Chem. Rev. 106, 4428, 2006.

[3] M.A. Henderson, Surf. Sci. Rep. 66, 185, 2011.

[4] D. Mardare, A. Yildiz, M. Gîrtan, A. Manole, M. Dobromir, M. Irimia, C. Adomniței, N. Cornei and D. Luca, J. Appl. Phys. 112, 073502, 2012.

[5] M. Miyauchi, A. Nakajima, K. Hashimoto and T. Watanabe, Adv. Mat. 12, 1923, 2000.

[6] C.-H. Liao, C.-W. Huang and J.C.S. Wu, Int. J. Hydrogen Energy 37, 11632, 2012.

[7] Y. Yang, Q. Zhang, B. Zhang, W.B. Mi, L. Chen, L. Li, C. Zhao, E.M. Diallo and X.X. Zhang, Appl. Surf. Sci. 258, 4532, 2012.

[8] X. Cheng, X. Yua and Z. Xing, Appl. Surf. Sci. 258, 3244, 2012.

[9] Y.P. Xie, G. Liu, L. Yin and H.-M. Cheng, J. Mater. Chem. 22, 6746, 2012.

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

[11] J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, "Handbook of X-ray Photolectron Spectrosopy", ULVAC-PHI Japan, Physical Electronics, USA, 1995.