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Article *in* Advanced Materials Research · July 2015

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Advanced Materials Research Vol 1117 (2015) pp 139-142
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doi:10.4028/www.scientific.net/AMR.1117.139

Submitted: 2014-09-26
Accepted: 2015-02-28

Synthesis and characterization of Nb-doped TiO_2 thin films prepared by RF magnetron sputtering

Marius Dobromir[1,a], Radu-Paul Apetrei[1,b*], Aleksander V. Rogachev[2, c], Dmitry L. Kovalenko[2, d] and Dumitru Luca[1, e]

[1]Faculty of Physics, Alexandru Ioan Cuza University of Iasi, 11 Carol I Blvd., 700506-Iasi, Romania

[2]Advanced Materials Research Laboratory, Francisk Skorina Gomel State University, 104 Sovetskaya Str., 246019-Gomel, Belarus

[a]marius.dobromir@uaic.ro, [b]rapetrei@uaic.ro, [c]rogachevav@mail.ru, [d]dkov@gsu.by, [e]dumitru.luca@uaic.ro

Keywords: Nb-doped TiO_2, thin films, RF magnetron sputtering

Abstract. Amorphous Nb-doped TiO_2 thin films were deposited on (100) Si and glass substrates at room temperature by RF magnetron sputtering and a mosaic-type Nb_2O_5-TiO_2 sputtering target. To adjust the amount of the niobium dopant in the film samples, appropriate numbers of Nb_2O_5 pellets were placed on the circular area of the magnetron target with intensive sputtering. By adjusting the discharge conditions and the number of niobium oxide pellets, films with dopant content varying between 0 and 16.2 at.% were prepared, as demonstrated by X-ray photoelectron spectroscopy data. The X-ray diffraction patterns of the as-deposited samples showed the lack of crystalline ordering in the samples. Surfaces roughness and energy band gap values increase with dopant concentration, as showed by atomic force microscopy and UV-Vis spectroscopy measurements.

Introduction

Titanium dioxide (TiO_2) is a material with attractive properties, such as high oxidative power, large band gap, and high dielectric constant [1]. The electrical conductivity of TiO_2 can be highly improved, not altering the optical transparency by doping it with niobium (denoted later on as Nb:TiO_2 or TNO), mainly when conditions are adjusted so as the anatase ordering to prevail. The TNO materials belong to the class of transparent conductive oxides (TCO), being denoted as "transparent metals" by Furubayashi and co-workers [2]. It has been demonstrated that doping titanium dioxide with Nb keeps the optical transparency almost unaffected ($T > 90\%$), thus making this class of material as similar to Sn:In_2O_3 (ITO), but lacking the drawbacks of the later one. Nb-doped anatase TiO_2 materials are nowadays one of the most studied transparent conductive oxides (TCO), with reported resistivity values in the range of 10^{-4} Ω cm, provided that they are either epitaxially grown on single crystal surfaces with low mismatch with the films [3], or on buffer layers with anatase ordering between the films and (amorphous) substrates [4]. Both approaches involve substrate temperature in excess of 250 °C, therefore they remain out of question for depositing TNO films on polymer substrates. Further investigations are necessary to lower the deposition temperature of the films, while keeping the film resistivity in the 10^{-3} – 10^{-4} Ω cm range.

The aim of this paper was to synthesize and characterize Nb-doped TiO_2 thin films prepared by RF magnetron sputtering. For characterization, the surface elemental composition and valence band measurements were performed using X-ray photoelectron spectroscopy (XPS) and Valence Band X-ray photoelectron spectroscopy (VB-XPS). An atomic force microscope (AFM) was used to observe surface morphology. The film structure was derived from X-ray diffraction (XRD) data, while the optical properties and energy band gap values of the thin films were determined by UV-Vis spectro-photometry. The results showed that the optical band gap of the TNO films increased upon doping.

Experimental details

The film samples were prepared in a home-made RF magnetron (13.56 MHz, 150 W) deposition facility, where a base pressure of 2.5×10^{-3} Pa could be routinely achieved. It was done using a 7.62 mm diameter Ti cathode target in a discharge running in Ar + O_2 gas mixture, on soda lime glass and (100)Si wafers substrates. For the results presented here, four pellets of Nb_2O_5 (5 mm in diameter) were uniformly distributed within the target race-track. The substrate-to-cathode distance was 6 cm. Further details of the deposition configuration are given in ref. [5]. Prior deposition, the substrates were successively sonicated for 6 min in ethanol and in acetone, then dried out in air.

For all the deposition runs, a constant oxygen content (2%) in the discharge gas was maintained by using mass flow rate (MFR) controllers (Ar MFR: 25 sccm and O_2 MFR: 0.5 sccm). The substrate temperature during deposition was not exceeding 70 °C, with non intentional heating (except for the effect of target IR radiation). The deposition time was 240 minutes. Samples with different thickness and Nb content were obtained by varying the total discharge pressure (by throttling the vacuum line) between 5.5×10^{-1} and 2.5 Pa.

The thickness of the deposited layers was measured using an interferential device AvaSpec 2048 (within the 250-1000 nm wavelength range). Optical transmittance spectra were recorded using an Evolution 300 UV-Vis Thermo Scientific spectro-photometer (within the 190-1100 nm wavelength range). XPS and valence band measurements have been done to determine the surface elemental composition of the samples on a Physical Electronics PHI - 5000 Versa Probe instrument, equipped with a monochromated AlK_α X-ray source ($h\upsilon$ = 1486.6 eV). The take-off angle of the photoelectrons was 45^{o}. The structure of thin films was derived from XRD patterns (Shimadzu LabX XRD-6000 diffractometer) using the CuKα radiation, λ = 1.54182 Å in a Bragg-Brentano arrangement. The surface root mean square was measured using an atomic force microscope NT-MDT SolverPro7.

Results and discussion

By adjusting the working pressure, samples with different thickness and Nb content were grown. The main parameters of the films are summarized in Table 1: the total deposition pressure, dopant concentration (% Nb), film thickness (d), surface root mean square roughness (R_{RMS}), optical band gap (E_g) and valence band maxima (VBM) of the thin films.

Table 1: The main parameters of the investigated films

p [Pa]	8.5×10^{-1}	5.5×10^{-1}	8.5×10^{-1}	1	1.4	2.5
sample (% Nb)	0.0	6.7	8.8	10.7	14.2	16.2
d [nm]	255	335	255	225	150	108
E_g [eV]	3.38	3.27	3.36	3.38	3.43	3.45
R_{RMS} [nm]	6.77	8.74	7.76	7.92	9.66	8.89
VBM [eV]	1.95	2.18	2.44	2.33	2.42	2.42

The VB-XPS results indicate that Nb-doping induced a diferences in the VBM values, for doped and undoped samples. The measured thickness of the samples decreases from 335 to 108 nm when increasing the working pressure from 5.5×10^{-1} to 2.5 Pa during deposition runs. The XRD patterns of all synthesized samples in the as-deposited state revealed no crystalline peaks. It is expected to improve the films crystallinity after annealing at 450 °C [6].

Fig. 1 shows the optical transmittance of films with various Nb concentrations. All the samples exhibit nearly the same transmission behavior. The transmittance mean values in the UV - Vis - near IR spectral range varies between 60% and 75%. Transmittance spectra showing the standard min-max shapes have been used to calculate the optical band gaps of the studied thin films.

For wavelengths close to values where loss scattering are dominated by the fundamental absorption of light, the absorption coefficient α can be calculated using the thickness of the film and the optical transmittance [7]. According to ref. [7], in vicinity of fundamental absorption the

indirect allowed transition dominates over the optical absorption, therefore optical band gap values, E_g, can be calculated from the Tauc plots $(\alpha h\upsilon)^{1/2} = f(h\upsilon)$ (see Fig. 2), where $h\upsilon$ is the incident photon energy. The E_g values increase from 3.27 to 3.45 eV with the increase in the Nb concentration from 6.7 to 16.2 at. %. The widening of the E_g can be explained by the Burstein-Möss (BM) effect [8,9], in which the lowest states in the conduction band are blocked, and the transitions can take place only to energies higher than the Fermi energy [10].

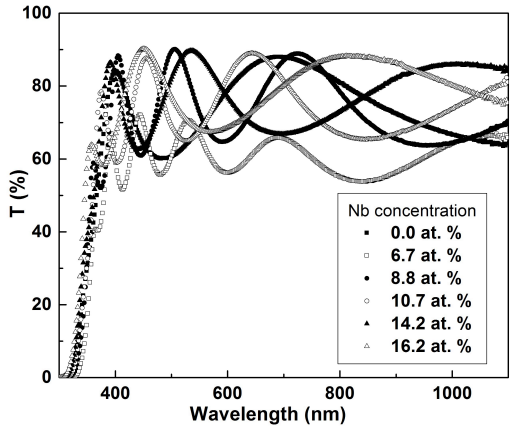

Fig. 1: Transmittance from 190 to 1100 nm of Nb-doped TiO_2 films with various Nb concentrations

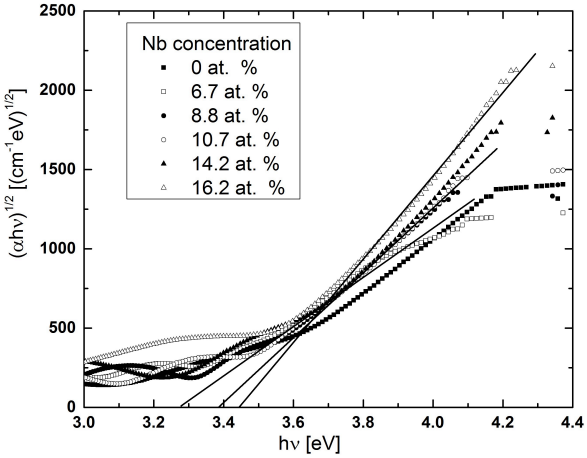

Fig. 2 Tauc plots of the investigated samples

The XPS measurements data show that, in a depth of 10 nm, Ti, O, Nb, and small amounts of C contaminant are present. The dopant atomic concentration varies here between 6.7 and 16.2 at%. Fig. 3 depicts the XPS high-resolutions spectra of the Nb *3d* (a) and Ti *2p* (b) for Nb doped TiO_2 thin films with various dopant concentrations. The intensity of Nb *3d* peaks increases with Nb concentration, while the intensity of Ti *2p* peaks decreases. The binding energies of Nb *3d* (208 eV) and Ti *2p* (459 eV) correspond to Nb^{5+} (207.8 eV) and Ti^{4+} (459.3 eV) states [11]. The oxidation state of titanium in stoichiometrical TiO2 is +4, therefore, niobium (normally in +4 or +5 state) provides one extra electron if it is in +5 state but no electron if it is in +4 state. On the other hand, if titanium is somehow in +3 state, then one hole can be induced. Therefore, to further confirm that the electrons in Nb: TiO2 are introduced by niobium, it is essential to study the valence state of niobium and titanium by means of XPS. The XPS results of the films indicate that Nb exists mainly as Nb^{5+}, whereas Ti exists mainly as Ti^{4+}. Therefore, niobium is indeed the main source of conduction electrons in this system.

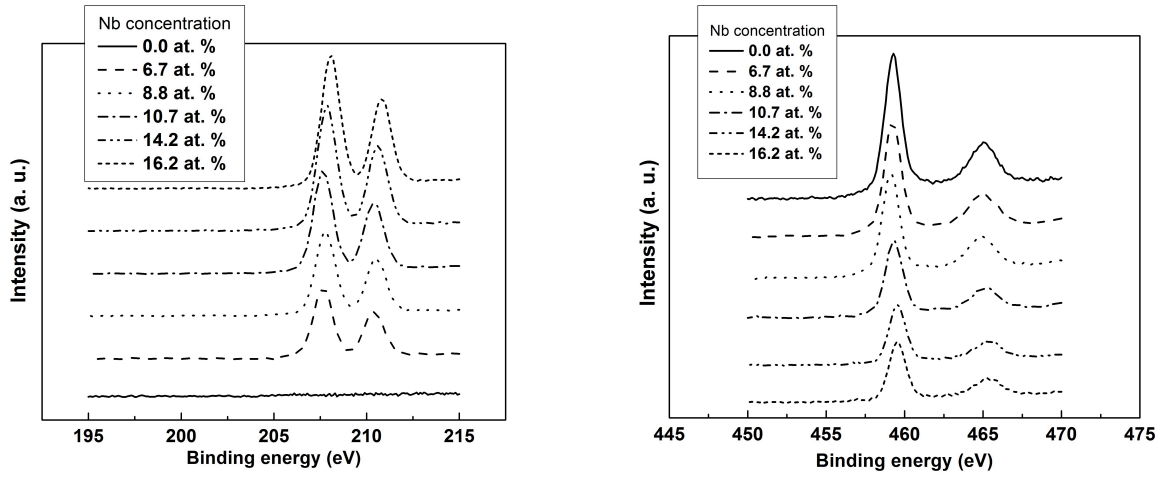

Fig. 3. XPS spectra of (a) Nb 3*d* and (b) Ti 2*p* of the Nb-doped TiO_2 thin films with various Nb concentrations.

Conclusion

Pristine and Nb-doped TiO_2 with dopant concentration ranging between 6.7–16.2 at.% were deposited on single crystal silicon and glass substrates by RF magnetron sputtering. The increase of the roughness and band gap was observed upon doping. The deposition rate of the films decrease with increase in the working pressure. Future work is in progress to establish how the annealing influences the structural and electrical properties of the samples.

Acknowledgements

One of the authors (RPA) acknowledges the financial support of European Social Fund through the Sectorial Operational Program for Human Resources Development 2007–2013, Project POSDRU/159/1.5/S/137750.

References

[1] A. Fujishima, T. N. Rao, D. A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C 1 (2000) 1-24.

[2] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K. Inaba, G. Kinoda, Y. Hirose, T. Shimada, T. Hasegawa, A transparent metal: Nb-doped anatase TiO_2, Appl. Phys. Lett. 86, 252101 (2005**).**

[3] M. A. Gillispie, M. F. A. M. Hest, M. S. Dabney, J. D. Perkins, D. S. Ginley, RF magnetron sputter deposition of transparent conducting Nb-doped TiO_2 films on $SrTiO_3$, J. Appl. Phys. 101 033125 (2007).

[4] N. Yamada, T. Hitosugi, J. Kasai, N. L. H. Hoang, S. Nakao, Y. Hirose, T. Shimada, and T. Hasegawa, Direct growth of transparent conducting Nb-doped anatase TiO_2 polycrystalline films on glass, J. Appl. Phys. 105, 123702 (2009).

[5] D. Luca, D. Mardare, F. Iacomi, C.M. Teodorescu, Increasing surface hydrophilicity of titania thin films by doping, Appl. Surf. Sci. 252 (2006).6122-6126

[6] C.M. Maghanga, G.A. Niklasson, C.G. Granqvist, Optical properties of sputter deposited transparent and conducting TiO_2:Nb films, Thin Solid Films 518 (2009) 1254-1258.

[7] D. Mardare, M. Tasca, M. Delibas, G.I. Rusu, On the structural properties and optical transmittance of TiO_2 r.f. sputtered thin films, Appl. Surf. Sci 156 (2000) 200-206.

[8] E. Burstein, Anomalous Optical Absorption Limit in InSb, Phys. Rev. 93 (1954) 632-633.

[9] T. S. Moss, The Interpretation of the Properties of Indium Antimonide, Proc. Phys. Soc. London, Sect. B 67 (1954) 775-782.

[10] Sato, H. Akizuki, T. Kamiyama, Y. Shigesato, Transparent conductive Nb-doped TiO_2 films deposited by direct-current magnetron sputtering using a TiO_{2-x} target, Thin Solid Films 516 (2008) 5758-6762.

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