JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 15, No. 5- 6, May – June 2013, p. 519 - 522

Nb-doped TiO_2 thin films deposited by spray pyrolysis method

C. ADOMNITEI, D. LUCA, M. GIRTAN[a], I. SANDU[b], V. NICA, A.V. SANDU[c], D. MARDARE*
"Alexandru Ioan Cuza" University, Faculty of Physics, 11 Carol I Blvd., 700506 Iasi Romania
[a]Photonics Laboratory, Angers University, 2, Bd. Lavoisier, 49045, Angers, France
[b]ARHEOINVEST Interdisciplinary Platform, "Alexandru Ioan Cuza" University of Iasi, 22 Blvd. Carol I, 700506, Iasi, Romania
[c]Faculty of Materials Science and Engineering, "Gheorghe Asachi" Technical University of Iasi, 64 Blvd. D. Mangeron, 700050, Iasi, Romania

Undoped TiO_2 and Nb-doped TiO_2 thin films have been deposited by spray pyrolysis method on ITO/glass substrates. All the as-deposited films are amorphous, as shown by X-Ray Diffraction. Under certain conditions of heat-treatment in air, the films deposited by pyrolysis became pure anatase. The hydrophilic properties of all the films were investigated, and a comparison was made as a function of the heat treatment, and as a function of Nb doping. Contact angles lower then 3 deg. have been obtained, after irradiation times specific for each film

(Received March 29, 2013; accepted June 12, 2013)

Keywords: Nb-doped TiO_2, Spray pyrolysis, Hydrophilic properties, SEM-EDX, XRD

1. Introduction

Since the humanity confronts with global problems such as: green house effect, ozon depletion, etc., phenomena that have increased in intensity in the last few years, an important responsibility is attributed nowadays to the environmental protection. In this respect, concern for the development of less polluting alternative technologies has increased all over the world. It is necessary to develop new applications based on the oxidation process because many pollutants are organic compounds which resist to chemical or biological treatments [1,2]. One of the most promising method that can be used in the degradation of different polluting organic compounds existing in water or air, is photocatalysis. The discovery made in 1972 by Fujishima and Honda of the photodecomposition of water on a titanium dioxide electrode (without the use of electricity) marked the beginning a new era in photocatalysis [3,4]. Titanium dioxide is considered by some researchers that it is, it was, and it will be the best photocatalyst, due to its low cost, non-toxicity, high oxidation potential, transparency in the visible domain, excellent chemical and mechanical stability in unfriendly environment, or in a large number of solvents, etc. [3-7]. In 1995 Fujishima and his group of researchers have discovered that TiO_2 thin films surface exposed to sunlight became superhydrophilic (contact angles lower then 10 deg.). This property led to the development of technologies for self-cleaning and anti-fog materials. However, one of the drawbacks would be that TiO_2 does not absorb the visible sunlight, due to the large optical band gap of these materials (about 3.2eV for anatase) that requires the activation with near-UV light radiation ($\lambda < 388$ nm); this makes the process less efficient, since only about 3 % of solar energy spectrum is near-UV. In the mean time, it was reported [8] that the electron-hole lifetime values (responsible in the redox processes) are directly proportional to the bandgap values. Many groups of researchers are working to remedy this problem, managing the expansion of TiO_2 absorption from near-UV light to the visible light [9-11].

A rapid evaluation of the films photocatalytic activity, can be indirectly done via hydrophilicity measurements, as long as the surface hydrophilicity is intimately associated with their oxidizing capacity, despite different mechanisms that rule these two features [4].

In this paper we have studied the structural and hydrophilic properties of the undoped TiO_2 and Nb-doped TiO_2 thin films, deposited by spray pyrolysis.

2. Experimental part

Undoped and Nb-doped titanium oxide thin films were obtained by spraying an appropriate solution from a sprayer, placed at 18 cm in front of a heated substrate holder (inclined at 55° with respect with the horizontal plane). The deposition was made on glass covered by 150 nm transparent indium tin oxide (ITO) (from Merck Balzers), heated at 100 ºC, and it was performed by repeating three identical procedures, with a 10 min break between them (for each substrate in part). A procedure involved three steps, each consisting of 10 s spraying, followed by 20 s pause.

The solution used to obtain the undoped thin films consists in a mixture of 6 mL ethyl alcohol (95%), 0.5 mL $Ti(OC_4H_6)_4$ and 0.5 mL HCl (used as stabilizer), vigorously stirred for 10 hours in N_2 atmosphere. The solutions with the increasing Nb content were obtained by adding to the previous mixture, increasing amounts of $Nb(OC_2H_5)_5$.

To obtain polycrystalline structures, the as-deposited thin films were thermally treated. Heat treatment was performed using a furnace tube Barnstead F21130-33 and consisted of: heating the obtained films with 2 ºC/min temperature rate, followed by the annealing (120 min at 400 ºC) and a cooling down to room temperature. We denote the thermal untreated samples by S_0n, S_1n, S_2n, and those heat treated, by S_0t, S_1t, S_2t. S_0 notation refers to the undoped samples, while S_1, S_2 refer to Nb-doped samples with increasing Nb content, 0.2wt.% and 0.6wt.% respectively.

Thin films structure was investigated by X-ray diffractometry (XRD), in standard θ-2θ configuration with a SHIMADZU 6000 diffractometer (CuK$_\alpha$ radiation, 40kV, 30mA).

The average crystallite size value, D_A, of the heat-treated films, calculated with the Debye-Scherrer formula [12]:

$$D_A = \frac{0.9\lambda}{B_{1/2}\cos\theta} \tag{1}$$

where $B_{1/2}$ is the width measured at half height of the diffraction peak (in radians), θ is the Bragg angle, and λ is the wavelength of X radiation (here, λ = 1.54Å).

Scanning electron microscopy (SEM) analysis was performed for the investigation of the films surface morphology, by using a SEM VEGA II LSH scanning electron microscope manufactured by the TESCAN Co., the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by the BRUKER/ROENTEC Co., Germany.

To determine if the studied surface area is hydrophilic or hydrophobic, contact angle measurements between films surface and de-ionized water have been performed, by using a home-built goniometer allowing advancing- and receding-angle measurements in the sessile drop arrangement. The motorized syringe (Hamilton, 10 µL) of the set-up, operated by a computer, allowed controlling drop volume with 500 nL accuracy. The drop image was acquired by a CCD camera (752 pixels x 582 pixels) attached to the microscope, then transferred to the computer for processing with an image analysis software. Measurements were made at a room temperature (20ºC) under 65 % environment humidity conditions. We have chosen drop volumes of 500 nL, thus avoiding accidental drop shape alteration due to the gravitational force and to diminish the evaporation effects.

The photoactivation of the films surface was performed by irradiating the samples with UV light, from a high-pressure mercury lamp (150W) ensuring a flux of 1mW/cm^2 at samples surface, until the saturation of the photoactivation was reached (contact angle decreased below 3 degrees). The measurements were made at 5 min intervals of irradiation, and each final value of the contact angle was obtained by averaging three contact angle values measured at different locations on the films surface. Then, by keeping the samples in darkness, the contact angles were monitored during the back-reaction time, every 12 hours, until they approached to the value of contact angle taken before irradiation with UV light.

3. Results and discussion

X-ray diffraction (XRD) measurements indicate that the initially deposited samples are amorphous. After heat treatment they become pure anatase (Fig. 1). An anatase surface is desired in photocatalysis because is more open than the surface of significantly denser rutile, and it has a higher oxidizing power and a higher density of oxygen bridging sites [13].

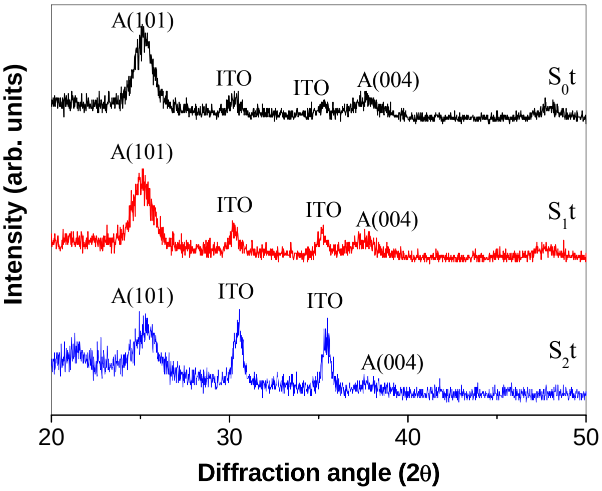

Fig. 1. XRD patterns for the heat treated samples: undoped (S_0t) film and Nb-doped films (S_1t, S_2t). The peaks of the anatase phase: A(101) and A(004), as well as the peaks of the ITO substrate can be observed in the XRD patterns.

The average crystallite size of the anatase phase, calculated with the relation (1), are under 10nm, and a slight decrease was observed with the increase of the Nb content, from about 8.2 nm (S_0t), till 7.0 nm (S_1t) and 5.8 nm (S_2t).

From the SEM images presented in figure 2 (a,b) for the S_2t film (0.6 wt.% Nb, annealed at 400°C), a compact structure can be observed.

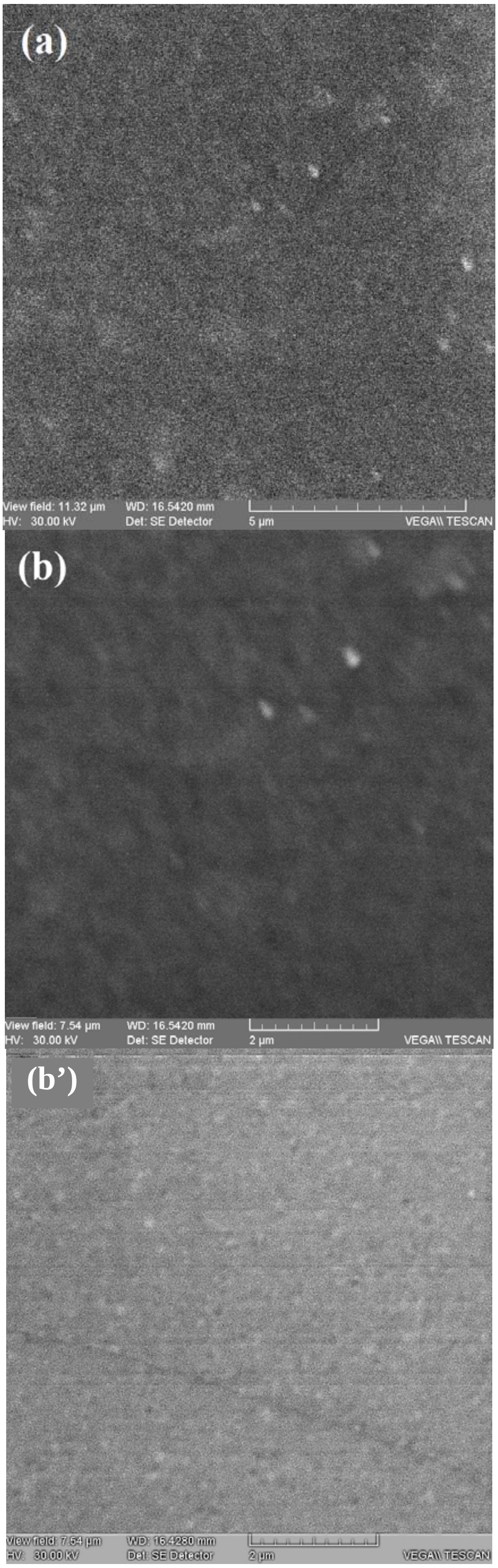

Fig. 2. SEM images of the sample S$_2$t at different scales.

The elemental composition at the film surface, obtained from EDX analysis, is given in Table 1 for the sample S$_2$t. It can be seen the presence of the Nb atoms in the TiO$_2$ matrix.

Table 1. Elemental composition at the surface of S$_2$t sample

Element	Weight [%]	Atomic [%]	Error [%]
Silicon	28.94	24.46	1.44
Calcium	3.98	2.36	1.01
Sodium	4.34	4.48	0.38
Magnesium	1.16	1.13	0.12
Aluminium	0.78	0.69	0.08
Potassium	0.01	0.01	0.03
Titanium	0.66	0.33	0.06
Indium	7.53	1.56	0.97
Tin	7.44	1.49	1.02
Niobium	2.84	0.73	0.26
Oxygen	42.32	62.78	58.84
	100.00	100.00	

The contact angle dependence on the time of irradiation with UV light for the untreated and heat-treated samples is presented in figure 3. One can see that the superhydrophilicity state is reached by all the studied samples.

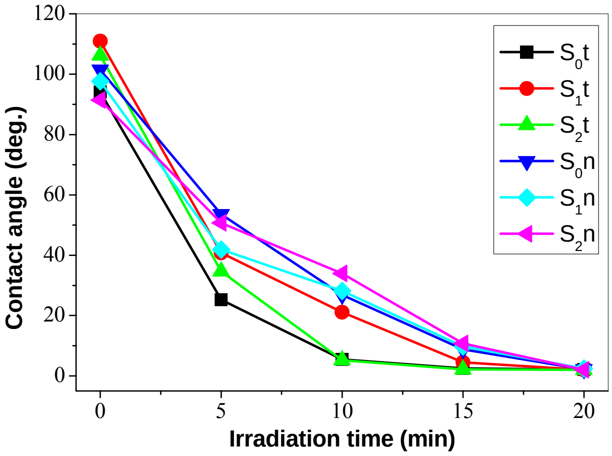

Fig. 3. Contact angle as a function of the irradiation time.

Initially, the samples were hydrophobic, with contact angles varying from 92 deg. to 111 deg. After less than 20 minutes of UV irradiation, they reached contact angles lower then 3 degrees, so, they become very rapidly superhydrophilic. Achieving superhydrophilicity states occurs different for heat treated and untreated samples. Thus, the decrease of the contact angle is more pronounced in the first case, and this is certainly due to the presence of the anatase phase in the heat treated samples. A special remark can be made on the S$_2$t sample (0.6 wt.% Nb-doped heat-treated film), that has reached superhydrophilicity after only 10 minutes of UV irradiation. This behavior could be related to its smaller crystallites, which in turn lead to more active surfaces in terms of hydrophilicity [14,15].

Contact angle dependence on the recovery time, after irradiation with UV light (by keeping the films in a dark place), is represented in Fig. 4. One can see that the contact angle slowly returned to near baseline, which is an advantage for these samples obtained by the spray pyrolysis technique. Remarkable are not only the obtaining of contact angles less than 3 degrees in very short times, but also the long recovery time (more than 6 days for the heat treated samples).

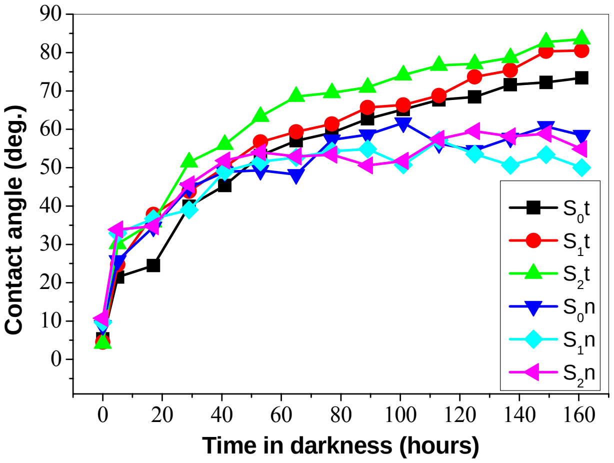

Fig. 4. Contact angle versus time dependences, as monitored during the back-reaction regime.

4. Conclusions

We have obtained amorphous thin films of undoped and Nb-doped TiO_2 with different concentrations of Nb, using the spray pyrolysis method. By heat treatment, the films become polycrystalline, having anatase crystallites which slowly decrease by Nb doping. The heat-treated samples are superior as concern the hydrophilic properties, then their as-deposited counterparts. Remarkable are not only the obtaining of contact angles less than 3 degrees in very short times, but also the long recovery time (more than 6 days for the heat treated samples).

Acknowledgements

This work was supported by CNCSIS Contract PCCE-ID_76/2010.

References

[1] R. Pode, L. Cocheci, E. Popovici, E.M. Seftel, V. Pode, Revista de Chimei, **59**, 898 (2008).
[2] V. Georgescu, D. Bombos, R. Scurtu, I. Spassova, D. Mehandjiev, L.D. Dumitrache, Revista de Chimie (Bucharest), **59**, 243 (2008).
[3] K. Hashimoto, H. Irie, A. Fujishima, Journal of Applied Physics, **44**, 8269 (2005).
[4] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis. Fundamentals and applications, BKC Tokio, 1999.
[5] B. Guo, Z. Liu, L. Hong, H. Jiang, J. Yang-Lee, Thin Solid Films, **479**, 310, (2005).
[6] D. Mardare, G.I. Rusu, J. Optoelectron. Adv. Mater., **6**, 333 (2004).
[7] C. Gümüs , O. M. Ozkendir, H. Kavak, Y. Ufuktepe, J. Optoelectron. Adv. Mater., **8**, 299 (2006)
[8] W.C. Hao, S.K. Zheng, C. Wang, T.M. Wang, Journal of Materials Science Letters, **21**, 1627 (2002).
[9] M. Anpo, Pure and Applied Chemistry, **72**, 1265 (2000).
[10] D. Mardare, F. Iacomi, D. Luca, Thin Solid Films, **515**, 6474 (2007).
[11] S.H. Wang, T.K. Chen, R.K. Koteswara, M.S. Wong, Applied Catalysis B: Environmental **76**, 328 (2007).
[12] P. Klug, L.E. Alexander, X-Ray diffraction procedures, Wiley, New York, p. 515, 1974.
[13] D. Luca, D. Mardare, F. Iacomi, C.M. Teodorescu, Applied Surface Science **252,** 6122 (2006).
[14] D. Mardare, A. Manole, A. Yildiz, D. Luca, Chemical Engineering Communications, **198**, 530 (2011).
[15] J. Bico, C. Marzolin, D. Qu, Europhysics Letters, **47**, 220 (1999).

---

*Corresponding author: dianam@uaic.ro