Characterization of doped TiO_2 thin films obtained by pulsed laser deposition

M. DOBROMIR, A.-V. MANOLE[a,*], L. URSU[b], C. URSU[b], M. NEAGU[a], D. LUCA[a]
Department of Sciences, "Alexandru Ioan Cuza" University, 11 Carol I Blvd., 700107 Iasi, Romania
[a]Faculty of Physics, "Alexandru Ioan Cuza" University, 11 Carol I Blvd., 700506, Iasi Romania
[b]"Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, 700487 Iasi, Romania

N-doped TiO_2 thin films were synthesized by pulsed laser deposition using a TiO_2 target in nitrogen atmosphere and glass slides substrates heated at 250°C. The samples were characterized by atomic force microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, ellipsometry and contact angle measurements. The root mean square roughness is increasing with the increase of pulses number. Even if increased surface roughness is known to intensify the hydrophilic behavior of TiO_2, the samples do not present the photoinduced superhydrophilic conversion process. The optical constants values are suggesting that the PLD technique is suitable to obtain thin films for optical coatings.

(Received December 8, 2012; accepted June 12, 2013)

Keywords: N-doped TiO_2, Pulsed laser deposition, XPS, Ellipsometry, Contact angle

1. Introduction

Pristine titanium dioxide materials have been under intensive research during the last decades. The exceptional combination of mechanical, chemical, electrical and optical properties led to the development of various environmental, optical coatings and energy - related applications [1]. Under UV illumination, the TiO_2 surface becomes self-cleaning, self-sterilizing, photocatalytic, superhydrophilic, to mention only a few features in a long list [1]. Unfortunately, the amount of the UV energy within the solar light spectrum is less than 5%, therefore the efficiency of the photocatalytic activity of the titania surface is pretty limited. It is now well documented that one of the possibilities for increasing the activation efficiency of the TiO_2-based photocatalysts is to find opportunities to extend their photoactivation in the visible range. This can be achieved, among others, by enhancing the oxygen vacancy concentration in the surface region [2] or by doping the materials with rare earths, transition metals or non-metals [1-3]. In this latter case, nitrogen doping proved to be one of the most efficient ways to shift the materials' absorption edge of the incident light from approx. 390 nm towards 400-500 nm wavelength range [1-3].

Various growth techniques have been used to prepare titania films, such as plasma vapor deposition, laser ablation, ion implantation, chemical vapor deposition, sol-gel etc. [4-8]. Among them the PLD offers the advantage of thin films preparation with good adherence on the substrate and allows the control of the crystalline phase of the synthesized materials [9, 10].

The aim of this paper is to synthesize by pulsed laser deposition method and characterize N-doped TiO_2 thin films. The chemical surface analyses prove the formation of the Ti-O-N and N-Ti-N bonds at the sample's surface. The dopant concentration of the samples varies between 2.2 and 3.8 at%. The anatase crystalline phase formation was confirmed by Raman spectroscopy and by the high refractive index values determined from ellipsometric measurements. Thus the PLD technique can be suitable for obtaining thin films with applications as optical coatings. Even if the root mean square roughness is increasing with laser pulse number the samples do not present the photoinduced hydrophilic conversion.

2. Experimental details

The nitrogen doped TiO_2 thin films were deposited by laser ablation method in the Excel Instruments Mumbai 93 device using as excitation source the radiation provided from an KrF excimer laser (λ = 248 nm), Coherent COMPex Prov TM 250F. Thin films were deposited on glass substrates located at a distance of 3 cm from the stoichiometric TiO_2 material used as target (Furuuchi Chemicals, 99.99% purity). The target was mounted on a special holder, which is rotated during deposition at a constant speed. During deposition time the glass substrates were heated at 250° C. Before deposition, the substrates were successively sonicated in acetone and ethyl alcohol and dried in air. By using a quartz lens the laser beam is focused onto the target at an incidence angle of 45°. The laser spot area on the target surface was about 6 mm^2 and the laser pulse energy 177 mJ. According to these values the laser fluence onto the target surface was 2.95 J/cm^2. For the deposition of three thin films sets we applied 10000, 3000 and 1500 subsequent laser pulses with a 10 Hz repetition rate (see Table 1).

Table 1. The deposition parameters of the samples.

Samples	Laser pulses number	Repetition rate (Hz)	Fluence (J/cm^2)
S1	10000	10	2.95
S2	3000	10	2.95
S3	1500	10	2.95

The deposition chamber was evacuated by a vacuum line up to a base pressure of 2×10^{-6} mbar. The mass flow rate of the nitrogen (5 sccm) was adjusted using a MKS - PR4000B-F2V2 mass flow rate controller. The total pressure during all deposition runs was kept constant at a value of 6×10^{-3} mbar.

Film surface morphology was investigated using an NT-MDT Solver Pro-M atomic force microscope and images were obtained when the cantilever was operated in constant force mode so that its deflection remains constant. X-ray Photoelectron Spectroscopy (XPS) measurements have been done to determine the surface elemental composition of the samples and the chemical state of O, Ti and N. XPS measurements have been performed on a Physical Electronics PHI 5000 VersaProbe instrument, equipped with a mono-chromated AlK_α X-ray source (hν=1486.6 eV). The take-off angle of the photoelectrons was 45°. The refractive index, *n*, and the extinction coefficient, *k*, were determined using the ellipsometric method. The dependence of the ellipsometric parameters (Δ, Ψ) on the incidence angle was measured using the EL X-01R (DRE-Dr. Riss Ellipsometerbau, GmbH) ellipsometer (λ = 632.8 nm) controlled by the ELX1_02 software. The measurements have been done by ranging the incidence angle of the optical radiation from 50° to 85° with a step of 5°. Contact angle measurements have been done by means of a Data Physics OCA 15EC goniometer, at room temperature and 50% relative humidity, in a sessile drop arrangement.

4. Results and discussion

Fig. 1 presents the AFM 3D images for the nitrogen doped TiO_2 thin films S1 (Fig. 1a), S2 (Fig. 1b) and S3 (Fig. 1c), respectively.

As can be seen from the AFM images, the number of droplets which are characteristic for the pulsed laser deposition is decreasing with the decrease of laser pulses number. The root mean square (RMS) roughness of the samples increases with increasing the number of pulses, thus with decreasing of deposition time (see Fig. 2).

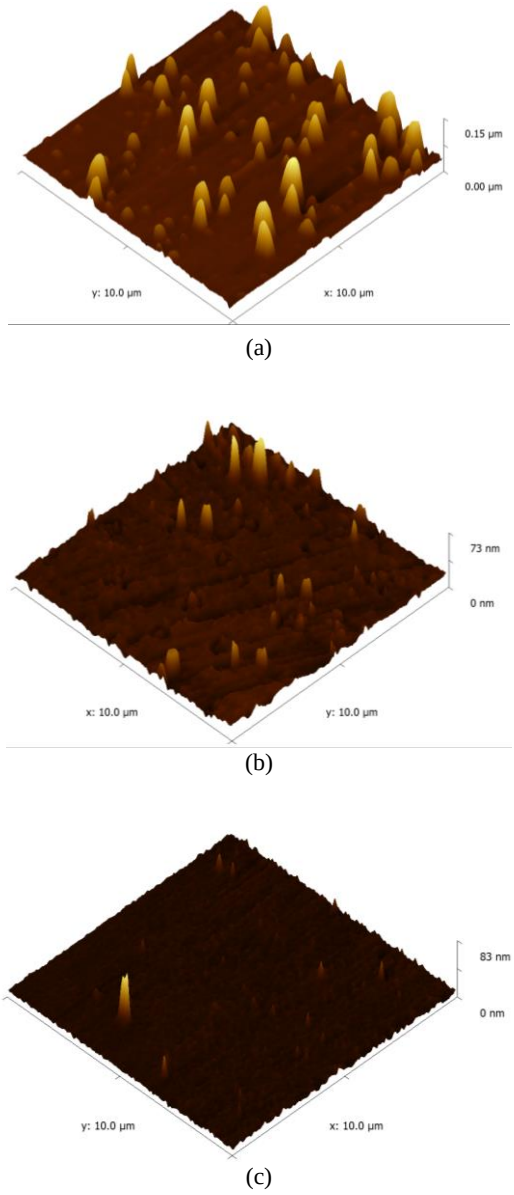


Fig. 1. 3D AFM images of the deposited thin films.

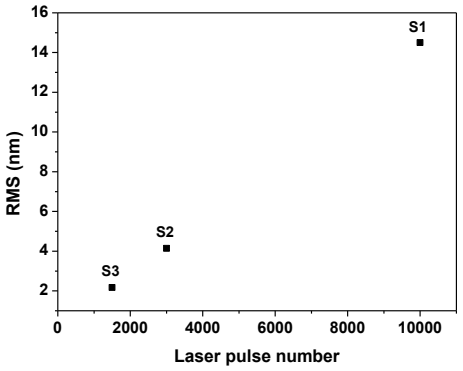


Fig. 2. The dependence of the RMS on the laser pulses number.

The atomic concentration of the nitrogen in the as-deposited thin films decreases with the increase of the laser pulses number (see Table 2). This effect can be explained taking into account the target poisoning with oxygen during deposition time.

Table 2. The atomic concentrations of the elements on the surface's samples.

Samples	Ti (at. %)	O (at. %)	N (at. %)
S1	36.6	61.2	2.2
S2	32.9	64.2	2.9
S3	34.7	61.5	3.8

The deconvolution of the Ti 2*p* high resolution spectra of the sample with intermediate N content showed a binding energy (BE) of the Ti $2p_{3/2}$ peak of 458.7 eV, specific to Ti^{4+} [11]. The Ti $2p_{1/2}$ peak has a higher binding energy 464.4 eV, i.e. with a separation of about 5.7 eV (Fig. 3). The peaks appearing at the binding energies of 456.7 eV and 462.4 eV (Fig. 3) correspond to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of titanium oxy-nitride [12].

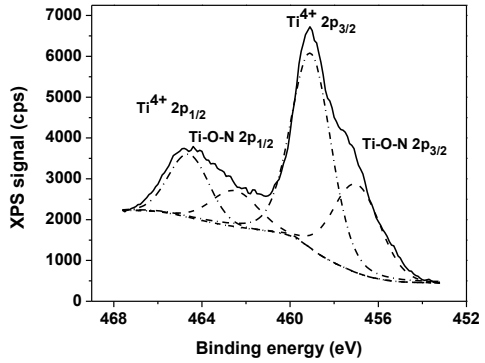


Fig. 3. The deconvolution of the Ti 2p high resolution spectrum of the sample S2.

The O 1*s* spectra of the as-deposited samples (Fig. 4) were deconvoluted into a main component at 530 eV, corresponding to Ti^{4+}-O bonds [11], and a secondary one at 531.3 eV.

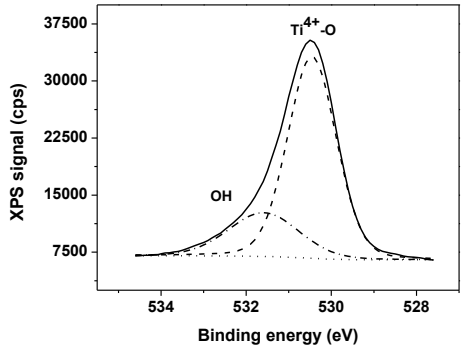


Fig. 4. The deconvolution of the O 1s high resolution spectrum of the sample S2.

The origin of this peak is still debated, some authors ascribing it to adsorbed OH groups [4].

The N 1*s* XPS spectra feature two well-resolved peaks, one at *BE* = 397 eV and a second one at *BE* = 400 eV (Fig. 5). The low-energy peak is currently associated with the Ti-N bond (the so-called β-N state) and its area increases with the increase of N concentration. The second one is associated with terminally bonded nitrogen in the so-called γ-N state (N-N, N-C, N-O) [3, 13].

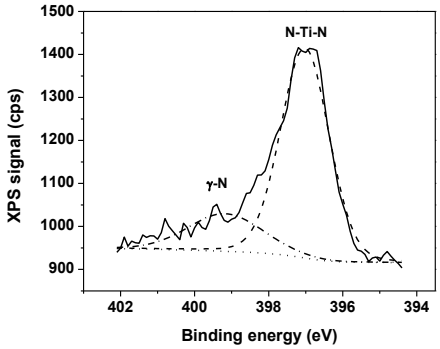


Fig. 5. The deconvolution of the N 1s high resolution spectrum of the sample S2.

The Raman spectrum taken for sample S2 is shown in Fig. 6. This spectrum presents four visible peaks around 157, 208, 416 and 617 cm^{-1}. The bands detected at 157, 208 and 416 cm^{-1} can be assigned to anatase phase, while the presence of the bands located at 617 cm^{-1} seems to demonstrate the coexistence with a rutile phase [10, 14]. Both Raman characteristic features are blue shifted. This slowly shift to higher frequencies can be caused by strain, defects and non-stoichiometry in the film induced by the growing process [15]. No other peaks characteristic to TiN were detected. Future work will be performed in order to establish how doping with nitrogen influence the phase structure of TiO_2 thin films.

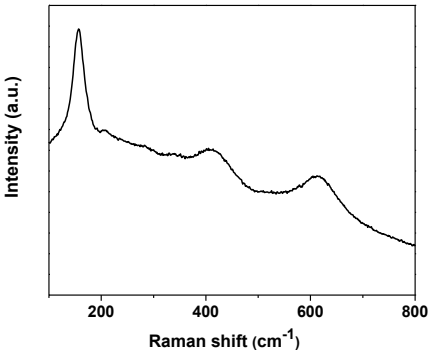


Fig. 6. Raman spectrum of the S2 sample.

The ellipsometric measurements included the determination of the Δ and Ψ parameters versus incidence angle, α (see Fig. 7). From the measured ellipsometric parameters, the values of *n* and *k* have been calculated using the following equation [16]:

$$(n+jk)^2 = \sin^2\alpha\left[1+\tan^2\alpha\left(\frac{1-\tan\Psi e^{j\Delta}}{1+\tan\Psi e^{j\Delta}}\right)\right] \quad (1)$$

were θ is the incidence light angle.

The determination of n and k was done using the principal incidence angle method $(\Delta = \pi/2)$. According to this method the equation (1) becomes [16]:

$$(n+jk)^2 = \sin^2\alpha_p\left[1+\tan^2\alpha_p\left(\cos 4\Psi_p + j\sin 4\Psi_p\right)\right] \quad (2)$$

The refractive index of TiO_2 thin films, n, has been reported previously to decrease, with the increase of the wavelength, between 2.7 and 2.0 in the visible range, the values depending on the elemental composition, film crystalline structure and density, surface roughness etc. [17, 18-20]. A similar behavior was found for the values of the extinction coefficient, k. Results in agreement with the ones reported in the literature have been found in our experiments. For the used wavelength (λ = 632.8 nm), the values of n and k were determined to be 2.5 and 0.19, respectively. The values of the refractive index of our samples are characteristic for thin films presenting the anatase crystalline phase.

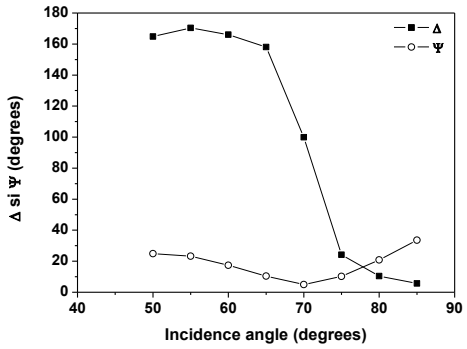
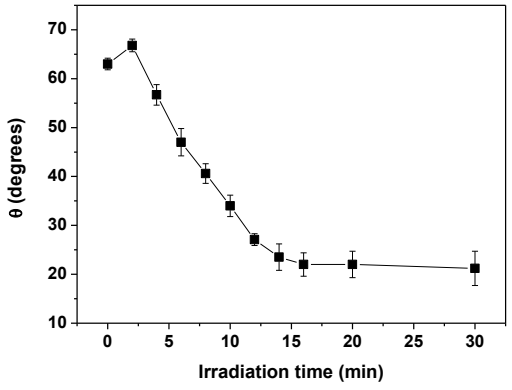


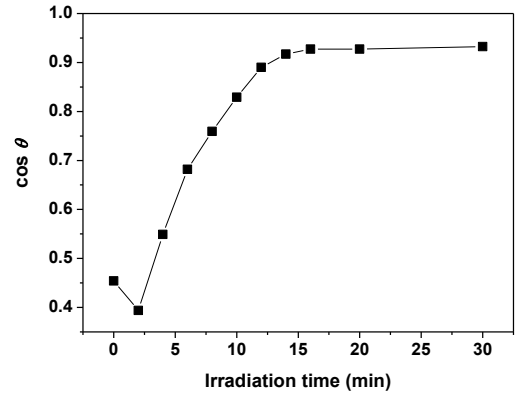
Fig. 7. The experimental results concerning the dependence of Δ and Ψ versus α.

The hydrophilic behavior of the N-doped TiO_2 thin films were investigated by means of contact angle measurements between the distilled water and film's surface under UV irradiation condition [21]. In Fig. 8 is presented the time evolution of the contact angle, θ, and of cos θ.

As can be observed from the Fig. 8.a after 30 min irradiation time the contact angle reaches a saturation value around 20°. This suggests that the samples do not present the superhydrophilic conversion process probably due to non-stoichiometry nature of the obtained samples as shown by the XPS measurements.



(a)



(b)

Fig. 8. Contact angle (a) and cos θ (b) dependence on UV irradiation time.

5. Conclusions

N-doped TiO_2 thin films deposited on glass substrate by pulsed laser deposition using as TiO_2 target were investigated.

The XPS measurements revealed the presence of the Ti-N bonds. The atomic concentration of the nitrogen in the as-deposited thin films decreases due to target poisoning with oxygen during deposition time.

The investigated films present a coexistence of the anatase and rutile TiO_2 crystalline phases, as revealed by the Raman spectroscopy measurements. Nitrogen incorporation does not affect films crystallinity.

The optical constants of the nitrogen-doped TiO_2 thin films have been derived from ellipsometry measurements. They have been related to chemical and structural characteristics of materials.

Acknowledgements

The financial support from the Romanian Ministry of Education, Research and Innovation through the projects POSDRU/89/1.5/S/49944 and POSDRU/89/1.5/S/55216 are acknowledged.

References

[1] A. Fujishima, X. Zhang, D. A. Tryk, Surf. Sci. Rep. **63**, 515 (2008).
[2] T. L. Thompson, J. T. Yates, Chem. Rev. **106**, 4428 (2006).
[3] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science **293**, 269 (2001).
[4] Y. Nakano, T. Morikawa, T. Ohwhi, Y. Taga, Chem. Phys. **339**, 20 (2007).
[5] D. Heřman, J. Šicha, J. Musil, Vacuum **81**, 285 (2006).
[6] B. Farkas, J. Budai, I. Kabalci, P. Heszler, Z. Geretovszky, Appl. Surf. Sci. **254**, 3484 (2008).
[7] M. Batzill, E. H. Morales, U. Diebold, Chem. Phys. **339**, 36 (2007).
[8] S. Livraghi, M. R. Chierotti, E. Giamello, G. Magnacca, M. C. Paganini, G. Cappelletti, C. L. Bianchi, J. Phys. Chem. **C 112**, 17244 (2008).
[9] E. Gyorgy, G. Socol, E. Axente, I. N. Mihailescu, C. Ducu, S. Ciuca, Appl. Surf. Sci. **247**, 429 (2005).
[10] P. Liu, W. Cai, M. Fang, Z. Li, H. Zeng, J. Hu1, X. Luo, W. Jing, Nanotechnology **20**, 285707 (2009).
[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.
[12] Y. Cheng, Y. F. Zheng, Surf. Coat. Tech. **201**, 6869 (2007).
[13] N. C. Saha, H. G. Tompkins, J. Appl. Phys. **72**, 3072 (1992).
[14] C.-H. Yang, Z.-Q. Ma, Appl. Opt. **51**, 5438 (2012).
[15] M. J. Šćepanović, M. Grujić-Brojčin, Z. D. Dohčević-Mitrović, Z. V. Popović, Sci. Sinter. **41**, 67 (2009).
[16] R. M. A. Azzam, N. M. Bashara, Ellipsometry and polarized light, North-Holland Physics Publishing, Amsterdam, The Netherlands, 1986.
[17] P. G. Wu, C. H. Ma, J. K. Shang, Appl. Phys. A **81**, 1411 (2005).
[18] H. Xie, F. L. Ng, X. T. Zeng, Thin Solid Films **517**, 5066 (2009).
[19] L. – J. Meng, V. Teixeira, H. N. Cui, F. Placido, Z. Xu, M. P. Dos Santos, Appl. Surf. Sci. **252,** 7970 (2006).
[20] J. Yao, Z. Fan, Y. Jin, Y. Zhao, H. He, J. Shao, Thin Solid Films **516**, 1237 (2008).
[21] A. Manole V. Dascaleanu, M. Dobromir, D. Luca, Surf. Interface Anal. **42**, 947 (2010).

*Corresponding author: alina.v.manole@gmail.com