



Incorporation of N in TiO₂ films grown by DC-reactive magnetron sputtering

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ABSTRACT

Photocatalytic properties of TiO₂ are expected to play an important role on emerging technologies based on OH radicals to destroy harmful nonbiodegradable organic and inorganic contaminants in water. The drawback is the wide band gap of TiO₂ (3.2 eV) limiting its use to the UV part of electromagnetic spectrum under sunlight. Therefore, modifications of TiO₂ are needed to tune the gap in order to allow an efficient use of the entire solar spectrum. One possibility is N-doping of TiO₂ to make the photocatalytic activity possible under visible light and more suitable for water treatment.

In our study nitrogen-doped TiO₂ (TiO_{2-x}N_x) films were deposited by DC-reactive magnetron sputtering using a dual-magnetron co-deposition apparatus on unheated glass and silicon substrates using a pure titanium target. The depth profile of nitrogen was measured with heavy ion elastic recoil detection analysis combined with Rutherford backscattering spectrometry (RBS) and correlated with the optical and structural properties obtained by UV–VIS spectroscopy and X-ray diffraction (XRD).

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1. Introduction

Titanium dioxide is a photocatalyst compound with a large application in the coating industry due its efficiency in dissociating organic pollutants under ultra-violet (UV) irradiation [1–3]. Among the TiO₂ phases, anatase has proven to be the most promising semiconductor photocatalyst for widespread environmental applications because it is chemically stable, nontoxic and consumes only light. However, the photocatalysis property emerges only for UV radiation with energy above 3.2 eV, the band-gap of the anatase crystalline phase of TiO₂. This poses a limitation to the use of solar light as a sustainable energy source for TiO₂ activation because only 5% of the incoming solar energy on the earth's surface is in the UV range. To overcome this constraint we must tune the band gap by doping. Some years ago, doping with nonmetal atoms such as N, S, and C into the TiO₂ lattice were reported, and show that the absorption edge shifts to lower energies and increase the visible absorption [4,5]. In particular the work by Asahi et al. [4] has renewed a great interest in N-doped TiO₂ as a visible light photocatalyst. A variety of methods such as sputtering, ion implantation, chemical vapor deposition, sol–gel, oxidation of TiN, and decomposition of N-containing metal organic precursors have been utilized to prepare N–TiO₂ [6–9].

This work reports the effect of the nitrogen doping on the growth, structure, crystallinity and optical properties of TiO₂ thin films deposited by DC reactive magnetron sputtering. Rutherford Backscattering Spectroscopy was used in order to assess the composition of the titania thin films, whereas Heavy Ion Elastic Recoil Detection Analysis provided the evaluation of the doping level of nitrogen. X-ray diffraction provided valuable information about the crystallinity of the films while UV/VIS absorption allows band-gap energy assessment.

2. Experimental details

Nitrogen-doped TiO₂ films were deposited by DC-reactive magnetron sputtering on glass and silicon substrates at room temperature in a custom made system. A titanium disc (99.99% purity) having 64.5 mm of diameter and 4 mm of thickness was used as sputtering target. The gases in the system were 99.99% pure Ar, O₂ and N₂, and partial pressures of these gases were separately controlled by mass flow controllers. Prior to the deposition, the glass substrates were cleaned successively in acetone, isopropanol and deionized water for 5 min each step and dried with nitrogen gas to remove any organic contaminant. The total pressure, P_T , during the deposition was kept constant at 0.8 Pa. The partial pressure of nitrogen P_{N_2} was varied between 0.008 and 0.04 Pa (i.e. 1%, 2% and 5% of P_T) while the partial pressure of oxygen was set at 0.08 Pa (10% of P_T). The sputtering power was kept at 1000 W and the deposition times were 80 min. The target-to-substrate distance was kept constant at 100 mm. The as-sputtered films

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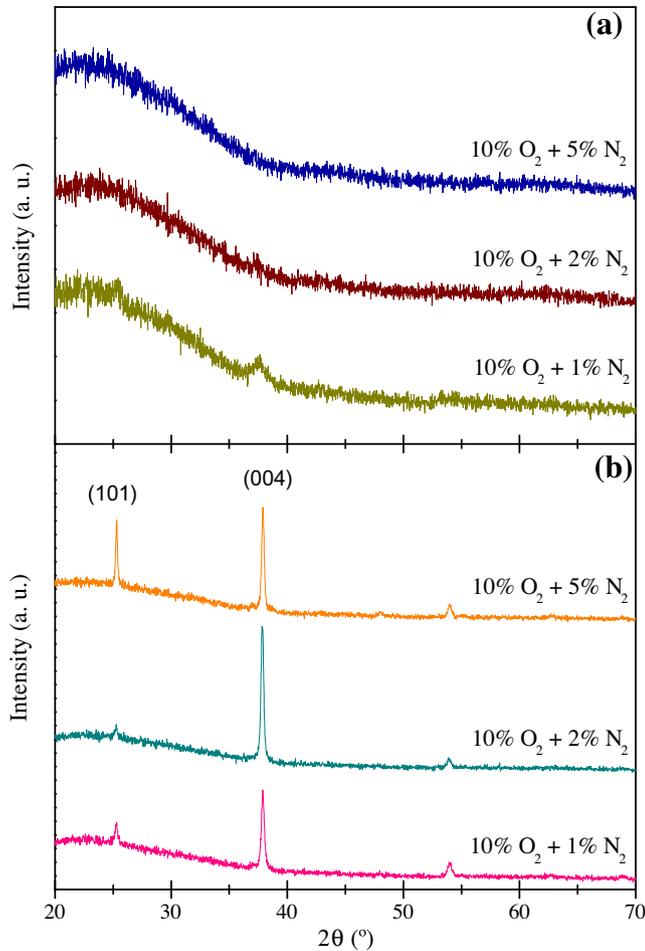


Fig. 1. XRD patterns of the N-doped TiO₂ films deposited at $P = 1000$ W for a fixed oxygen percentage (10%) and at different percentage of nitrogen (1%, 2% and 5% N₂) in Ar/O₂/N₂ mixture (a) as-deposited and (b) annealed 4 h at 400 °C.

were thermal annealed in N₂ atmosphere at 400 °C for 4 h in a tubular furnace in order to improve crystalline growth.

The structural characterization of the films was carried out by X-ray diffraction (XRD) using a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using the CuK line. To characterize the thickness and composition of the samples, Rutherford Backscattering Spectroscopy (RBS) studies were performed with 2 MeV ⁴He⁺ beam. In order to increase the sensitivity to nitrogen EBS was used with 1.4 MeV ¹H⁺. The backscattered particles were detected at 140° (standard) and 180° (annular), using silicon surface barrier detectors, with resolutions of 13 and close to 18 keV, respectively. For the Heavy-Ion Elastic Recoil Detection Analysis (HI-ERDA) chlorine ions (Cl⁷⁺) with 35 MeV were used. The angle of incidence was 15° and the recoils were detected at 31.1°, except hydrogen, detected at 38°. The NDF code was used for the subsequent structural simulation refinement analysis [10]. The optical absorption properties of the films were measured with a Shimadzu UV b – 2101PC UV/VIS spectrophotometer at room temperature within the wavelength range 300–900 nm.

3. Results and discussion

3.1. Structural characterization

The as deposited films at room temperature are amorphous or poorly crystallized. This is evident from the XRD spectra shown

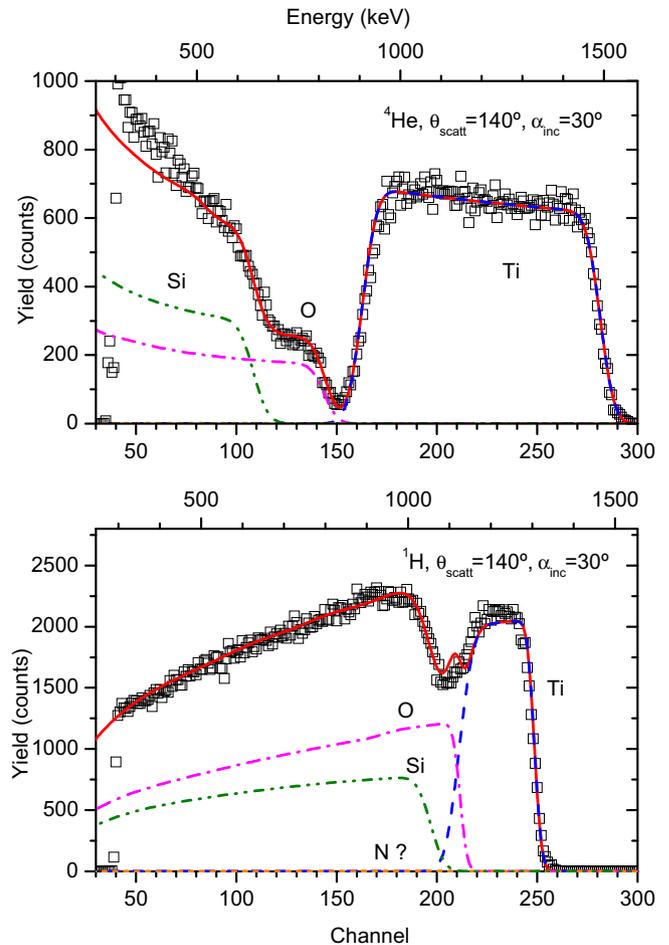


Fig. 2. IBA spectra obtained from a TiO₂ film deposited in Si: (bottom) 1.4 MeV H⁺ beam EBS spectrum, identifying the profiles of Ti, O, and Si; (top) 2 MeV ⁴He⁺ beam RBS spectrum of the same film. The presence of nitrogen is below the detection limit of these techniques.

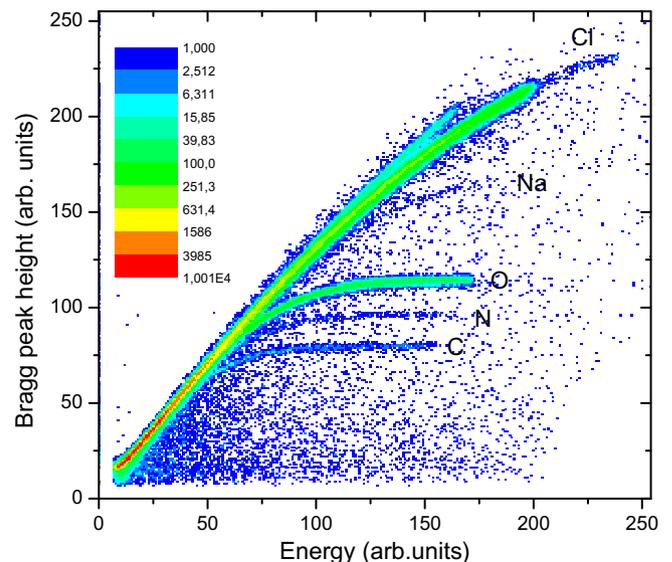


Fig. 3. HI-ERDA 2D spectrum of a film deposited in the same conditions of film shown in Fig. 1 but on glass substrate (Na is a contamination from the glass).

Table 1

Summary of the thickness (x) and composition of the annealed N-doped TiO₂ films deposited at $P = 1000$ W for a fixed oxygen percentage (10%) and at different percentage of nitrogen (1%, 2% and 5% N₂) in Ar/O₂/N₂ mixture.

Sample	N ₂ (%)	x (nm)	Ti (at.%)	C (at.%)	N (at.%)	O (at.%)	Na (at.%)	H (at.%)	E_g (eV)
B01	1	550 (40)	28.04 (.01)	3.26	0.15 (.03)	54.20 (.01)	1.03 (.05)	13.32 (.01)	3.28 (.01)
B02	2	880 (50)	26.96 (.01)	2.47	0.52 (.05)	57.61 (.01)	0.70 (.05)	11.75 (.01)	3.19 (.01)
B03	5	700 (50)	26.79 (.01)	3.18	0.70 (.05)	55.95 (.01)	0.89 (0.5)	12.49 (.01)	3.17 (.01)

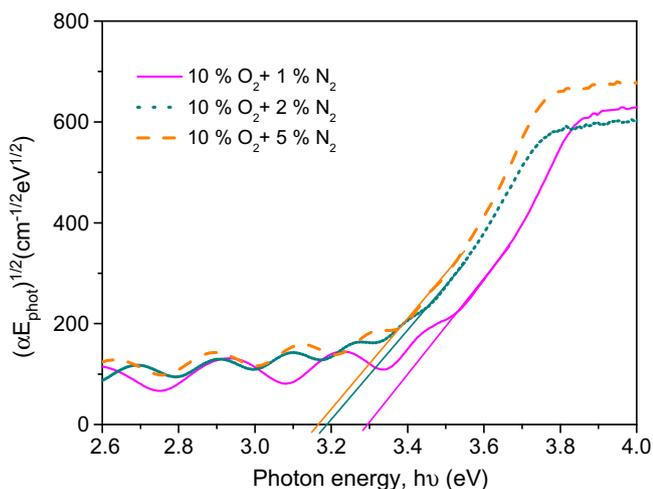


Fig. 4. Plots of $(\alpha E_{\text{phot}})^{1/2}$ vs. photon energy for the annealed N-doped TiO₂ thin films deposited at $P = 1000$ W for a fixed oxygen percentage (10%) and at different percentage of nitrogen (1%, 2% and 5% N₂) in Ar/O₂/N₂ mixture. Straight lines are the corresponding extrapolations which allow the determination of E_g .

in Fig. 1a for N-doped TiO₂ films deposited at different nitrogen concentrations with a sputtering power of 1000 W. The crystallization of the films was achieved after annealing at 400 °C during 4 h (Fig. 1b). The diffraction patterns reveal the presence of sharp peaks indicating the coalescence of the crystalline TiO₂ anatase phase with a preferential growth along the c axis. The films grown with lower N concentration are highly textured along the c -axis and when the amount of N increases other orientations start to develop. In any case the narrow diffraction peaks suggest the presence of large grains with good crystallinity. Similar variations in the preferred orientation have been also observed in the growth of anatase TiO₂ films by DC-reactive magnetron sputtering [11].

The amount of N incorporated the depth profile was measured with ion beam techniques. Fig. 2 shows the typical RBS results obtained for the films. The upper figure was measured with a ⁴He⁺ beam and allowed the measurement of the thickness and homogeneity of the films. The continuous curves are the elemental profiles extracted from the simulation results obtained using the NDF code. The EBS spectrum in the lower panel of Fig. 2 was obtained with a ¹H⁺ beam and confirms the RBS results. However in both cases there was no evidence for the presence of nitrogen. To get information on the nitrogen and hydrogen content in the films we performed HI-ERDA and a 2D raw data spectrum from one of the samples is shown in Fig. 3. Since irradiation with a heavy ion beam can lead to loss of some elements during the experiment we need to assess this effect. For that and for each experiment the data were collected and stored at regular steps, so we could observe the yield rate as the experiment progresses, for each element separately. If there is no elemental loss during the measurement, this should be the final result otherwise the NDF fit results were corrected. The results of the combined, RBS, EBS and HI-ERDA analysis are summarized in Table 1 as well as the band gap energy. We estimate that for the Ti and O the uncertainty is around 2 at.% with a

further systematic 5% (relative) coming from the accuracy with which the stopping powers are known. This gives a good stoichiometry for all the films over the entire thickness. The accuracy of N is around 10% relative. That is, 3.3 at.% can be between 3.0 and 3.6 at.%. The same applies for the C contamination found in the films coming probably from the vacuum system.

3.2. Optical properties

The band gap of the films was determined assuming that the N-doped TiO₂ is an indirect semiconductor, like TiO₂, and the optical band gap E_g of the films is related with the absorption coefficient through the Tauc model [12]

$$\alpha E_{\text{phot}} = (E_{\text{phot}} - E_g)^m \quad (1)$$

where α is the absorption coefficient (in cm⁻¹), $E_{\text{phot}} = 1239/\lambda$ is the excitation energy (in eV), with the wavelength λ in nanometers and m is a parameter accounting for the different band-gap transition modes ($m = 2$ for indirect allowed) [13]. The extrapolation of the αE_{phot} product to zero value gives an absorption energy, Fig. 4, which corresponds to the E_g band gap. The results obtained are also summarized in Table 1.

The shift of the absorption edge towards the visible is an indication [4] of the energy gap narrowing. Earlier studies have reported that N-doped TiO₂ powders exhibited visible light absorption as a shoulder in the wavelength range of 400–600 nm and then suggested that the isolated N 2p narrow band formed above the O 2p valence was responsible for the visible light response [14].

4. Conclusions

The TiO₂ films deposited with a oxygen percentage (10%) and at different percentage of nitrogen (1%, 2% N₂) in Ar/O₂/N₂ mixture show a good crystalline quality after annealing at 400 °C and are highly texture along the c -axis. Increasing the N₂ concentration to 5% induces the growth of grains with other orientations. The films are stoichiometric under the accuracy of the measurements and reveal good homogeneity over the entire thickness. The amount of N incorporated scales with the pressure and the band gap E_g decreases with the nitrogen increase in the films. The smooth shift of absorption edge to the visible light region, which implies the narrowing of the band gap due to the nitrogen doping suggest the mixture of N 2p and O 2p states in our films.

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References

- [1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
- [2] M. Kitano, M. Matsuoka, M. Ueshima, Masakazu Anpo, Appl. Catal., A 325 (1) (2007) 1–14.
- [3] S. Klösek, D. Raftery, J. Phys. Chem. B 105 (2001) 2815.
- [4] R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki, Y. Taga, Science 293 (2001) 269–271.
- [5] S. Khan, M. Al-Shahry, W.B. Ingle, Science 297 (2002) 2243.

- [6] K. Kobayakawa, Y. Murakami, Y.J. Sato, *Photochem. Photobiol. A* 170 (2004) 177.
- [7] M. Morowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, *J. Phys. Chem. B* 108 (2004) 17269.
- [8] G.R. Torres, T. Lindgern, J. Lu, C. Granqvist, S. Lindquist, *J. Phys. Chem. B* 108 (2004) 5995.
- [9] C.J. Tavares, S.M. Marques, T. Viseu, V. Teixeira, J.O. Carneiro, E. Alves, N.P. Barradas, F. Munnik, T. Girardeau, J.-P. Rivière, *J. Appl. Phys.* 107 (2010) 059901.
- [10] N.P. Barradas, C. Jeynes, M.A. Harry, *Nucl. Instrum. Methods B* 136–138 (1998) 163.
- [11] S. Sérgio, M.E. Melo Jorge, M.J.P. Maneira, Y. Nunes, *Chemistry and Physics* 126 (2011) 73–81.
- [12] J. Tauc, *Amorphous and Liquid Semiconductors*, Plenum, London, 1974.
- [13] K. Eufinger, P. Poelman, H. Poelman, R. De Gryse, G.B. Marin, *J. Phys. D: Appl. Phys.* 40 (2007) 5232.
- [14] H. Irie, Y. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 107 (2003) 5483.