

# N-Doped Photocatalytic Titania Thin Films on Active Polymer Substrates

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Active polymer substrates have found their way in the semiconductor industry as a base layer for flexible electronics, as well as in sensor and actuator applications. The optimum performance of these systems may be affected by dirt adsorbed on its surface, which can also originate mechanisms for the degradation of the polymer. Titanium dioxide (titania) semiconductor photocatalytic thin films have been deposited by unbalanced reactive magnetron sputtering on one of the most applied and investigated electroactive polymer: poly(vinylidene fluoride), PVDF. In order to increase the photocatalytic efficiency of the titania coatings, a reduction of the semiconductor band-gap has been attempted by using a nitrogen doping. 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 Photoelectron Spectroscopy provided valuable information about the cation-anion binding within the semiconductor lattice. The photocatalytic performance of the titania films have been characterized by decomposing an organic dye illuminated with combined UV/visible light.

**Keywords:** Photocatalytic, Electroactive Polymer, Titanium Dioxide, Poly(Vinylidene Fluoride), Sputtering.

## 1. INTRODUCTION

By tailoring a specific coating one might inevitably bear in mind the protection of the underlying substrate, processing the coating as an active surface against: corrosion, wear, abrasion, amongst other nuisances, or in the case of titanium dioxide, pollution adsorption. The titanium dioxide (titania) self-cleaning effect has been broadly explored since it is a well known photocatalyst used in the coatings industry due its efficiency in dissociating organic pollutants upon ultra-violet (UV) irradiation.<sup>1-4</sup> Polymer substrates have found their way in the semiconductor industry as a base layer for flexible electronics, as well as in sensor and actuator applications.<sup>5-6</sup> The optimum performance of these systems may be affected by dirt adsorbed on its surface, which can also originate mechanisms for the degradation of the polymer.<sup>7</sup> In this work, these polymer substrates act synergistically with the overlying coating in order to actively promote a higher

efficiency in photocatalysis. This effect has been achieved by depositing titania thin films by unbalanced reactive magnetron sputtering on poly(vinylidene fluoride), PVDF, substrates, in its  $\alpha$  (non electroactive) and  $\beta$  (electroactive) phases. The latter phase has been obtained by uniaxially stretching the  $\alpha$ -phase material<sup>5</sup> and has been deposited in a poled and non-poled form. The main effect of the poling process, necessary in order to optimize the electroactive properties of PVDF in its  $\beta$ -phase, is the alignment of the randomly organized dipolar moments against an applied electric field.<sup>5</sup> PVDF in the beta phase is an electroactive polymer with many applications as sensor and actuator. Furthermore, alpha PVDF is also used in wires, cables and tubes. The possibility of a photocatalytic (self-cleaning) performance will improve many of these applications and open possibilities for new ones. Enhancing the photocatalytic efficiency of titania has become a major concern for the authors, bearing in mind industrial applications for general purpose plastics.

The photocatalytic behavior of the titania coatings was determined by combined ultra-violet irradiation and

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absorption measurements of a particular dye (Red 41, acting as an organic pollutant). The observed photo-decomposition of the dye was measured in the UV/visible spectrum by the decrease of the maximum absorbance of the dye with irradiation time. In order to increase the efficiency in terms of absorption of visible light, a doping of the titania lattice has been attempted by incorporating nitrogen atoms. X-ray Photoelectron Spectroscopy and Heavy-Ion Elastic Recoil Detection Analysis enabled the determination of the doping level of nitrogen in the titania lattice and the nature of the anionic–cationic binding inside the semiconductors. Subsequently these chemical properties have been correlated with the enhancement of the photocatalytic behavior.

## 2. EXPERIMENTAL PROCEDURE

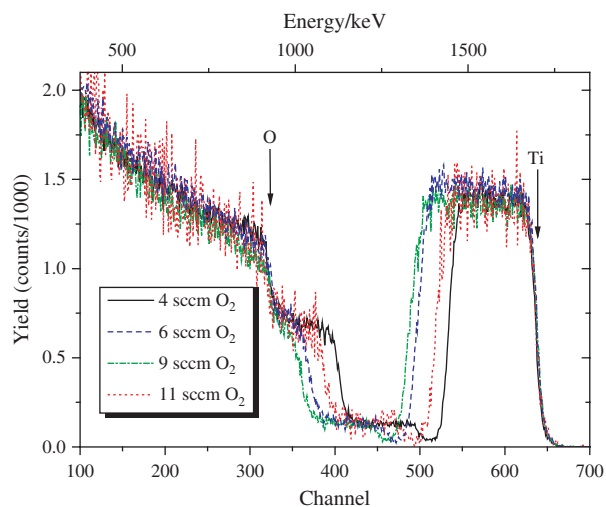
Titania thin films have been deposited at room temperature on  $\sim 30 \mu\text{m}$  thick poly(vinylidene fluoride) 14 mm  $\times$  10 mm strips, prepared after the method similar to the one presented in,<sup>5</sup> by unbalanced pulsed d.c. reactive magnetron sputtering, from a high purity Ti target in an Ar/O<sub>2</sub> atmosphere. The argon flow rate was set at 60 sccm (working gas), while the oxygen reactive gas flow rate was initially varied from 4 to 11 sccm, for the optimization of the best conditions (8 sccm). For the case of nitrogen doping, the N<sub>2</sub>:O<sub>2</sub> (85:15) gas mixture was varied between 1.5 and 4 sccm. A turbo molecular pump was used to achieve a base pressure of  $\sim 10^{-4}$  Pa (before introducing the gas mixture). No external substrate heating was used during the deposition, in order to prevent polymer structural damage, while the cathode current and substrate bias voltage was set to 0.2 A and  $-60$  V, respectively. Both the magnetron and substrate bias were powered by pulsed d.c. sources. For the magnetron, a unipolar power supply with 50 kHz pulses and a 50% duty cycle was used. For the substrate holder bias polarization, a bipolar power source with 100 kHz pulses and 50% duty cycle was employed. By using d.c. pulsed power supplies the advantages are three-fold: there is less chance of target poisoning, since the reactive gas (oxygen and nitrogen) consumption is optimized by regulating the pulse frequency; the deposition rate is increased due to better target performance; the ionization of argon is enhanced near the substrate holder due to the alternating attraction of either electrons or Ar<sup>+</sup> ions, providing a more efficient ionic bombardment of the substrate and enhancing the nucleation density of the growing film. The target-to-substrate distance was kept constant at 70 mm and the thickness of the deposited titania films was  $\sim 300$  nm. The photocatalytic properties of the titania thin films rely on the inter-band transitions induced by the UV light illumination of the surface. For UV light with a higher energy than the titania band-gap ( $\sim 3.2$  eV for anatase), electron-hole pairs are generated and diffuse to the surface. The diffusion of these charges promotes

through redox mechanisms the radical/ion generation that, in turn, will decompose organic compounds adsorbed on the catalyst surface.<sup>2</sup> In order to study the photocatalytic performance of the titania films, an organic dye (Red 41—used as organic pollutant) with a concentration of  $1.05 \times 10^{-5}$  M was prepared by dilution in water. The titania films were immersed in this solution in an open-top quartz cell with the irradiation perpendicular to the surface. No oxygen was artificially introduced in the solution during the irradiation experiments. A 150 W xenon discharge lamp was used as the UV source. A UV-broadband filter (UG11) was mounted between the lamp and cell in order to select the spectral range between 280–380 nm. The total irradiance was measured to be  $\sim 2$  mW/cm<sup>2</sup>. After the irradiation experiments, performed for a particular period of time, the solution concentration was monitored using a Shimadzu UV-2501 spectrophotometer, by recording the maximum absorbance of the Red 41 dye between 510 and 540 nm. Previous irradiation tests of the same dye in the absence of the titania catalyst proved that its decomposition decays less than 3% after a 6 hour exposure in the same conditions as the ordinary photocatalysis tests.

Rutherford Backscattering Spectroscopy (RBS) studies were performed with a 2.0 MeV He<sup>+</sup> beam, at normal incidence, to characterize the thickness and composition of the samples. 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 (Cl<sup>7+</sup>) 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.<sup>8</sup> X-ray photoelectron spectroscopy (XPS) is a very surface sensitive technique, since the sampling depth is lower than 5 nm. The experiments were carried out using Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). The C1 s binding energy due to surface adventitious carbon ( $E_b = 284.6$  eV) has been taken as reference level. For the scanning electron microscopy analysis a FEI Nova 200 FEG-SEM was used in high vacuum mode.

## 3. RESULTS AND DISCUSSION

In order to determine the composition and thickness of the titania samples, Rutherford Backscattering Spectroscopy (RBS) experiments were performed for a set of samples with varying oxygen flow rate (from 4 to 11 sccm) during deposition. From Figure 1 one can see that as the oxygen flow rate is increased from 4 to 9 sccm, the thickness of the thin film increases. However, for the extremely high oxygen partial pressure (11 sccm), a target poisoning by an oxide layer occurs leading to a decrease in the deposition rate and consequently in the thickness of the films. This behavior has been already reported by the authors.<sup>9</sup> From RBS refinement analysis, the atomic composition of TiO<sub>2</sub>



**Fig. 1.** RBS spectra for four titania samples deposited with varying oxygen flow rates, from 4 to 11 sccm. Inset arrows indicate the yields of titanium and oxygen levels.

is relatively stable with varying oxygen flow rate, being the films constituted by  $\sim 30$  at.% of titanium and 69 at.% of oxygen, hence being slightly over-stoichiometric in terms of oxygen content. HI-ERDA analysis enabled the determination of the level of atomic percentage of nitrogen doping in the titania lattice, with varying reactive nitrogen gas flow rate during deposition. For a reactive flow rate of  $N_2:O_2$  of 1.5 sccm the atomic percentage of N-doping is 0.72%, and increases up to a maximum of 1.19% for a 3 sccm  $N_2:O_2$  flow rate. However, above 3 sccm  $N_2:O_2$  flow rate the cathode target surface becomes poisoned and thus the deposition rate and N-doping level is reduced. This data is reported in Table I, along with the film thickness (in atoms/cm<sup>2</sup>). The errors were determined with a Bayesian inference procedure that reflects the statistical errors of the data as well as other sources of experimental error such as the charge measurement.<sup>10</sup> In Figures 2(a and b) one can see for a particular titania sample with the highest level of N-doping (sample NTiO13 from Table I) the HI-ERDA elemental scattered profiles and the atomic composition as a function of film thickness, respectively. The depth profile was determined with the NDF code by fitting simultaneously the HI-ERDA and RBS spectra (not shown) in a self-consistent way.<sup>8</sup> Traces of carbon and hydrogen have been found on both the surface and interface film/substrate due to ultrasonic bath cleaning of the substrate with ethanol prior to deposition.

Previous Raman spectroscopy experiments<sup>11</sup> revealed that the as-deposited coatings on PVDF polymer substrates are mostly amorphous; however evidence of anatase and rutile nano-crystalline phases were found. The XPS survey spectra given in Figure 3 yields evidence on the atomic species within the close surface. The photo-electrons and Auger peaks reveal the presence of titanium, oxygen and surface adventitious carbon. The low amount of nitrogen

**Table I.** Determination of the atomic composition of the N-doped titania thin films, by means of combined refinement of the RBS and HI-ERDA spectroscopic data.

Sample	$N_2:O_2$ (sccm)	Thickness (10 <sup>15</sup> at./cm)	Ti (at.%)	N (at.%)	O (at.%)
NTiO10	1.5	3621(150)	30.2(3)	<b>0.72(5)</b>	69.1(3)
NTiO11	2.5	3588(150)	29.6(3)	<b>0.94(6)</b>	69.4(3)
NTiO13	3	4230(170)	30.3(3)	<b>1.19(6)</b>	68.5(3)
NTiO14	4	3869(160)	29.5(3)	0.74(5)	69.8(3)

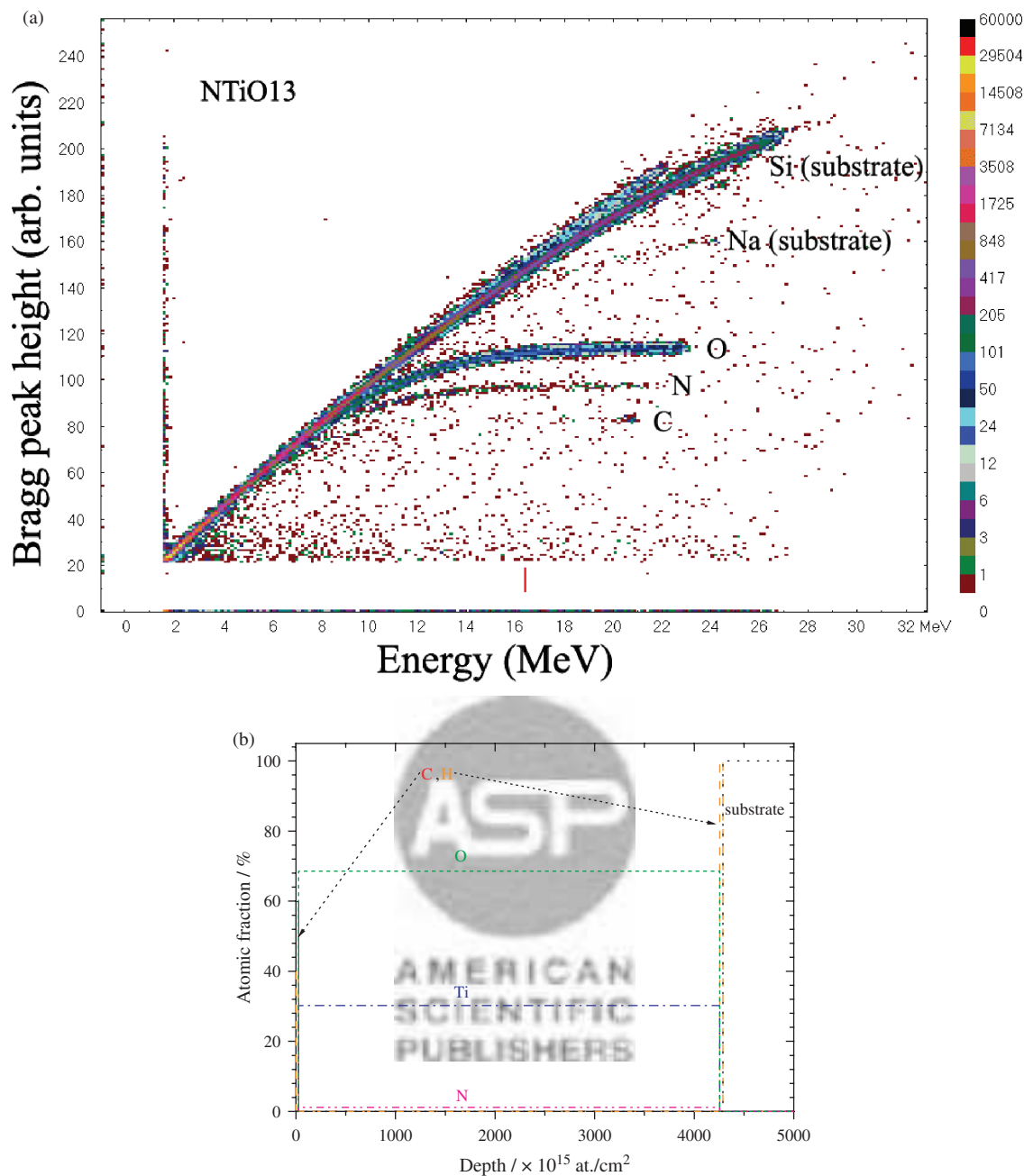
*Note:* The bold values represents the level of atomic percentage of nitrogen doping in the titania thin films prior to target poisoning and loss of deposition rate and photocatalytic improvement.

requires a zoom displayed in the inset of Figure 3. As it would be expected, the peak area is clearly enhanced with increasing N-doping level. Moreover the 1.19 at % N sample evidences an additional contribution. This peak located at  $\sim 396$  eV is attributed in the literature to oxygen substitution with nitrogen ( $\beta$ -N) in the titania lattice, while the peak at  $\sim 399.5$  eV is related to chemisorbed nitrogen ( $\gamma$ -N<sub>2</sub>).<sup>12,13</sup> Hence, from this overall analysis, proof is given that doping of the titania lattice with nitrogen as a substitution of oxygen is possible when the reactive gases flow rate of nitrogen is sufficient.

In order to verify which type of PVDF phase substrate would actively, and synergistically with the top N-doped titania coating, promote an enhancement of photocatalysis, UV irradiation tests were performed by immersing a titania film in a very highly resistant dye (Red 41), acting as a pollutant. The concentration of the dye ( $c$ ) was monitored as a function of time by the Beer Lambert's law:  $A = l\epsilon c$ , where  $A$  is the absorption of the dye,  $l$  is the optical length of the quartz cell in which the catalyst is immersed in the dye and  $\epsilon$  is the molar absorbance coefficient. Since  $l$  and  $\epsilon$  are constant, the ratio of absorption decay is proportional to the concentration decay (being  $c_0$  the initial concentration of the dye). The speed of the dye composition degradation can be calculated from the first order decay rate equation ( $k$ ):

$$\ln\left(\frac{c}{c_0}\right) = -kt \quad (1)$$

From irradiation tests shown in Figure 4 one can see that the  $\beta$ -PVDF poled substrates actively promote higher photocatalytic efficiency together with the N-doped titania thin films. Conversely, it is worse when deposited in the non-polar  $\alpha$ -PVDF substrates. The explanation for this resides in the charge density within the polymer surface and the polar nature of the polymeric molecular chains: in increasing order of photocatalytic performance, the  $\alpha$ -phase is formed by non-polar chains with a trans-gauche conformation, the unpoled  $\beta$ -phase, on the other hand, is composed by polar all-trans conformation polymeric chains. The dipoles are arranged in a disordered way, but polar nano and micro regions are present in the polymer surface. The poled  $\beta$ -phase shows preferential orientation of

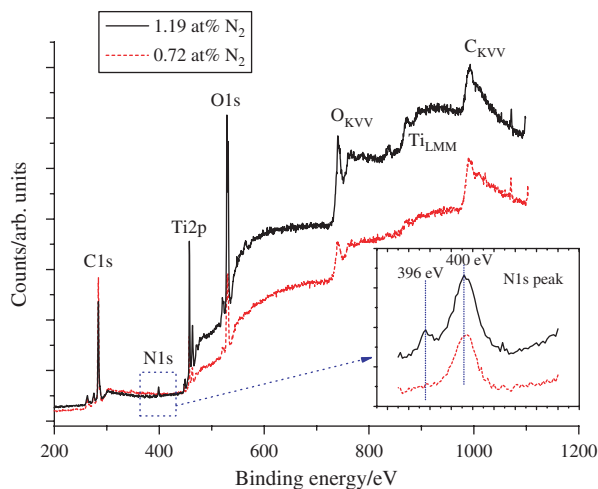


**Fig. 2.** HI-ERDA (a) experimental profiles and (b) calculated composition as a function of film thickness for the elements constituting the titania coating with the highest level of atomic% nitrogen doping (sample NTiO13 from Table I).

the dipolar moments and therefore a well defined surface charge.<sup>14</sup> Hence, as the surface electric charge is increased within the PVDF substrate, depending on phase and poling state, the photo-oxidation and reduction mechanisms on the dye are enhanced, since there is a larger carrier density and mobility, thus providing a pathway for a more efficient photocatalysis. The overall photocatalytic activity is far from being outstanding: after 6 hours of UV-irradiation the dye decomposition is  $\sim 10\%$ , which implies that further work must be endured in order to deposit self-cleaning TiO<sub>2</sub> thin films on polymer substrates at room temperature.

However, we have obtained a decomposition of the same dye 25 times faster using titania-deposited glass substrates, with subsequent thermal annealing at 500 °C—which is impossible for polymer substrates. PVDF is chemically very stable and therefore photo-decomposition of the polymer will not occur upon the UV irradiation experiments. This stability is in fact a general characteristic of most fluorinated polymers.<sup>15</sup>

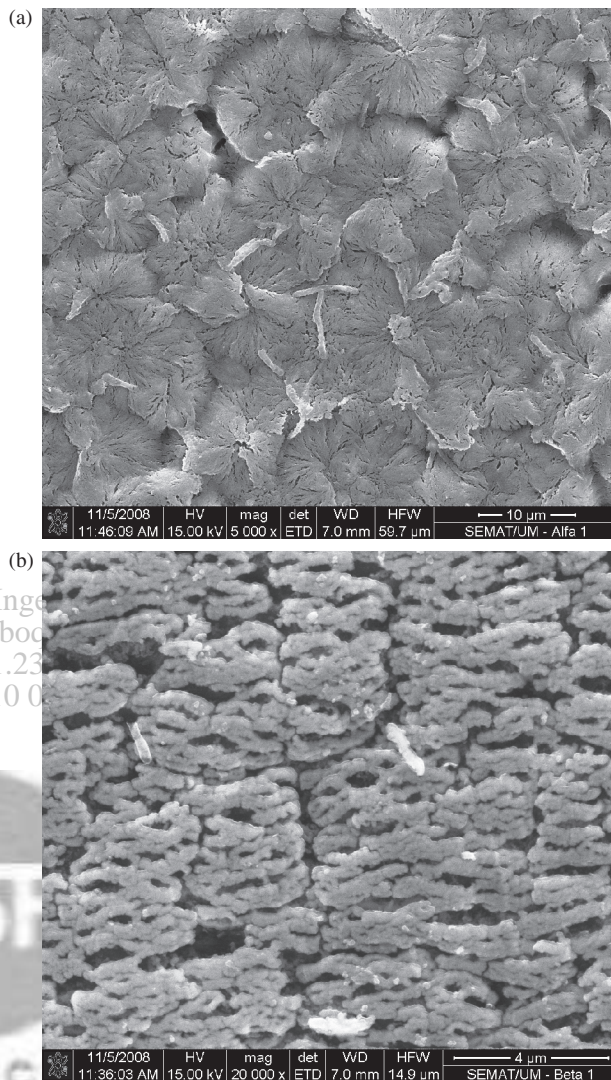
In Figure 5 we can observe scanning electron microscopy (SEM) images of titania thin films deposited on (a)  $\alpha$ -PVDF and (b)  $\beta$ -PVDF (poled) substrates. The



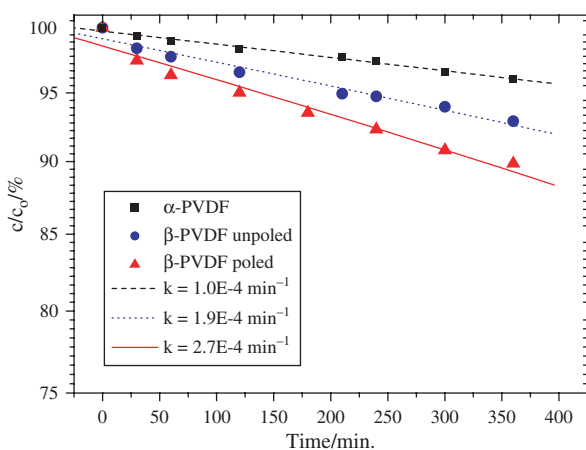
**Fig. 3.** Survey XPS spectra profiles for NTiO10 and NTiO13 samples (refer to Table I). Inset: XPS spectra characteristic of the N1s core level.

characteristic isotropic spherules of the  $\alpha$ -phase are replicated with the titania layer deposition. In the same way, for the anisotropic  $\beta$ -phase polymer, the titania crystalline grains coalesce in the crests of the longitudinal polymer chains, surrendering a larger surface area for the deposited thin film, thus providing evidence for the higher dye adsorption and subsequent higher photocatalytic yield that has been reported in the last paragraph.

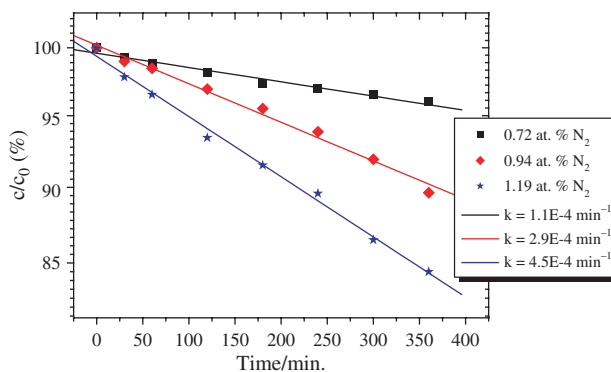
In order to see the effect of the nitrogen doping on the photocatalytic properties of the titania thin films, similar irradiation experiments were carried out for different levels of nitrogen doping, using the same reference substrate. These results are shown in Figure 6 and from this analysis we conclude that the highest level of N-doping on the titania lattice yields a higher efficiency in degrading the Red 41 dye. When comparing 0.72 atomic% of N-doping with the higher amount of 1.19%, the first order decay rate ( $k$ ) is almost 4 times greater in the latter case, yielding



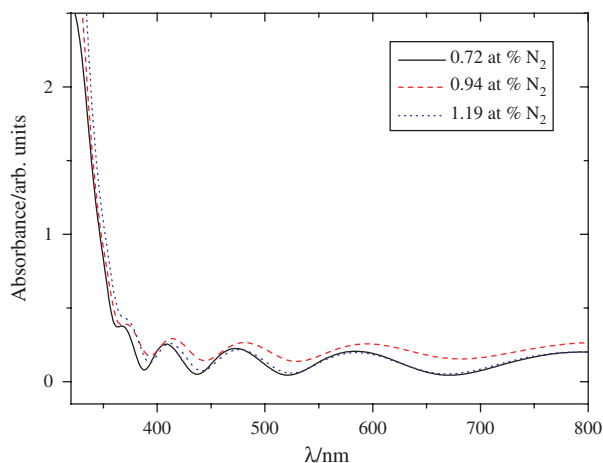
**Fig. 5.** SEM images of titania thin films deposited on (a) PVDF- $\alpha$  and (b) PVDF- $\beta$  (poled) substrates.



**Fig. 4.** Relative decrease in RED 41 dye concentration (log scale) as a function of time for titania deposited on the different PVDF electroactive polymer substrates.



**Fig. 6.** Relative decrease in RED 41 dye concentration (log scale) as a function of time for titania deposited with increasing amount of N-doping for a reference substrate.



**Fig. 7.** Absorbance spectra of different titania thin films with increasing amount of N-doping.

evidence that the nitrogen substitution in the titania semiconductor lattice results in an increase of its photocatalytic efficiency. Absorbance spectra were recorded and are displayed in Figure 7 for the different levels of N-doping. As this level of N-doping increases from 0.72 to 1.19 atomic% the absorption edge of the N-doped titania thin films shifts slightly to the visible part of the spectra, thus indicating the expected band-gap narrowing, due to the absorption of more visible light.

#### 4. CONCLUSIONS

Titania thin films have been deposited by reactive pulsed d.c. magnetron sputtering, at room temperature, on different types of PVDF polymer substrates. These polymer substrates revealed a synergistic effect with the top titania coating with respect to the self-cleaning property. RBS and HI-ERDA combined experiments revealed the atomic composition and thickness of the nitrogen-doped titania layers, as a function of the reactive gas partial flow, indicating a slightly over-stoichiometric composition. The assessment of atomic nitrogen doping was fulfilled as well. It was found that for a 1.19 atomic percentage inclusion of nitrogen in the titania lattice there was a clear improvement on the UV-photocatalytic efficiency upon degrading a chosen dye, acting as a pollutant. From XPS measurements it was possible to conclude that nitrogen occupies substitutional oxygen sites in titania lattice, as  $\beta$ -N states whose orbitals in the band-gap should overlap with the titania states. These states promote the transfer and mobility of photoexcited charges in the surface of titania responsible for the redox mechanisms in the dye. Furthermore, absorbance spectra recording of these anionic N-doped films yielded evidence of small absorption shift to the visible part of the solar spectra, thus evidencing a band-gap

narrowing and absorption efficiency increase of combined UV-visible light for the photocatalytic enhancement. The as-deposited state of the room temperature-deposited photocatalytic thin films is predominantly amorphous, albeit previous Raman spectroscopy experiments revealed traces of nano-crystalline combined-phases of anatase and rutile.  $\beta$ -PVDF (poled) substrates provided a better and synergistic photocatalytic response as an active substrate base for the N-doped self-cleaning titania layer, indicating that the higher the surface charge density of the polymer substrate, due to chain conformation and dipolar orientation, the better photocatalytic efficiency is attainable. Additionally, the titania deposition on the anisotropic  $\beta$ -PVDF (poled) substrates yields a larger surface area for the crystalline grains, thus providing a better adsorption of the organic pollutant and subsequently a higher photocatalytic efficiency upon UV/vis irradiation experiments.

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#### References and Notes

1. A. Fujishima and K. Honda, *Nature* 238, 37 (1972).
2. M. A. Fox and M. T. Dulay, *Chem. Rev.* 93, 341 (1993).
3. M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.* 95, 69 (1995).
4. M. Kitano, M. Matsuoka, M. Ueshima, and M. Anpo, *Appl. Catal. A: General* 325, 1 (2007).
5. V. Sencadas, V. M. Moreira, S. Lanceros-Mendez, A. S. Pouzada, and R. Gregório Filho, *Mat. Sci. Forum* 514, 872 (2006).
6. A. Kumar, A. Srivastava, I. Y. Galaev, and B. Mattiasson, *Prog. Polym. Sci.* 32, 1205 (2007).
7. M. Day, J. D. Cooney, and M. MacKinnon, *Polym. Degrad. Stab.* 48, 341 (1995).
8. N. P. Barradas, S. Parascandola, B. J. Sealy, R. Grötzschel, and U. Kreissig, *Nucl. Instrum. Methods Phys. Res.* B161, 308 (2000).
9. C. J. Tavares, S. M. Marques, S. Lanceros-Méndez, V. Sencadas, V. Teixeira, J. O. Carneiro, A. J. Martins, and A. J. Fernandes, *Thin Solid Films* 516, 1434 (2008).
10. N. P. Barradas, S. A. Almeida, C. Jeynes, A. P. Knights, S. R. P. Silva, and B. J. Sealy, *Nucl. Instrum. Methods Phys. Res.* B148, 463 (1999).
11. C. J. Tavares, S. M. Marques, L. Rebouta, S. Lanceros-Méndez, V. Sencadas, C. M. Costa, E. Alves, and A. J. Fernandes, *Thin Solid Films* 517, 1161 (2008).
12. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science* 293, 269 (2001).
13. N. C. Saha and H. G. Tompkins, *J. Appl. Phys.* 72, 3072 (1992).
14. J. Serrado Nunes, A. Wu, J. Gomes, V. Sencadas, P. M. Vilarinho, and S. Lanceros-Méndez, *Applied Physics A—Materials Science & Processing* 95, 875 (2009).
15. X. Gu, C. A. Michaels, D. Nguyen, Y. C. Jean, J. W. Martin, and T. Nguyen, *Appl. Surf. Sci.* 253, 5168 (2006).

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