

The Influence of Ni doping on the Surface Wettability of TiO₂ Thin Films

C. ADOMNITEI^a, N. CORNEI^a, D. LUCA^a, I. SANDU^b, V. VASILACHE^b, M. DOBROMIR^a, D. MARDARE^a

^aAlexandru Ioan Cuza" University, Faculty of Physics, 11 Carol I Blvd., 700506 Iasi Romania

^aARHEOINVEST Interdisciplinary Platform, "Alexandru Ioan Cuza" University of Iasi, 22 Blvd. Carol I, 700506, Iasi, Romania

Titanium dioxide (TiO₂) materials are well known for their good photocatalytic properties under UV irradiation. Doping is one of the most important methods used to improve these properties. In this paper, we study if Ni impurities in certain concentrations (from 1 at.% to 10 at.%) conduct to higher hydrophilic TiO₂ surfaces and, as a consequence, to better photocatalytic properties. The films, deposited by spray pyrolysis method on ITO/glass substrates, are amorphous, and they become polycrystalline, with the presence of the anatase phase, by heat-treatment in air. Ni enters in the TiO₂ matrix, as confirmed by X-ray Photoelectron Spectroscopy and by Energy-Dispersive X-Ray Spectroscopy. From the optical transmittance and reflectance measurements, the optical band gap was derived, and we found out that it increases by increasing the Ni content. The hydrophilic properties of all the films were investigated, and a comparison was made as a function of Ni doping.

(Received December 23, 2014; accepted May 7, 2015)

Keywords: Titania, Ni doped TiO₂, Spray pyrolysis, Hydrophilicity, XPS, SEM-EDX, XRD

1. Introduction

Nowadays, concern for the development of less polluting alternative technologies has increased all over the world, since the human confronts with sever global problems that affects our living. Photocatalysis is a hopeful method that can clean our environment [1,2]. Photocatalytic materials degrade the pollutants by using only the solar radiation, and titania is a promising such a material due to its high oxidation potential and chemical stability in unfriendly environment. It is worth to mention that it is non-toxic and less expensive than its counterparts.

In this paper, we study if introducing Ni impurities in the titania matrix, by using a large range of Ni concentrations, from 1 at.% to 10 at.%, we may improve the hydrophilicity of TiO₂ thin films and, as a consequence, their photocatalytic properties. Testing the hydrophilic properties constitutes a much simpler way to obtain information on their photocatalytic activity, a firmation confirmed by our recent studies [3].

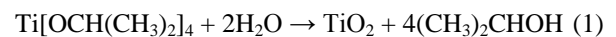
2. Experimental Part

Undoped and Ni-doped TiO₂ thin films were deposited by the spray pyrolysis technique, which it is known to present advantages like: low costs, operating at atmospheric pressure, well controlled stoichiometry, depositing films over large surface area [3-5]. We have used ITO (indium tin oxide)/glass substrates heated at 100°C, the other deposition conditions being presented elsewhere [6].

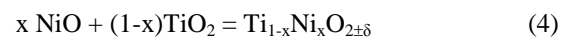
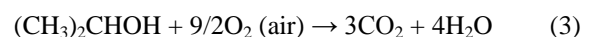
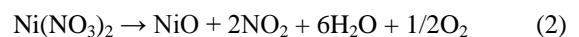
The solution used to obtain the undoped TiO₂ thin films consists in a mixture of titanium(IV) isopropoxide

(TTIP, 99.99%, Merck), ethanol (EtOH, 96 %) and acetylacetone (AcAc, 99.99 %, Merck). The solutions with the increasing Ni content were prepared to contain different amounts of Ni: 0, 1, 3, 7 and 10 at. %, and was obtained by adding to the previous mixture, increasing amounts of Ni(NO₃)₂•6H₂O (0.1 mol/L). The preparation of starting solutions was made after the following recipe: an amount of 0.758 mL TTIP (0.967 g/cm³ density) was dissolved in 25 mL absolute EtOH (0.1 mol/L), followed by the addition of 0.532 mL AcAc (0.97 g/cm³ density) used as stabilizer. The molar ratio between TTIP and AcAc was 1:2 [7]. For doping, different amounts of nickel nitrate Ni(NO₃)₂ was added, and the mixture was vigorously stirred to dissolve the formed precipitate.

TTIP was hydrolyzed due to the amount of water present in ethanol and in the nickel nitrate:



The reactions that take place on the substrate during the deposition process are:



where $\text{Ti}_{1-x}\text{Ni}_x\text{O}_{2\pm\delta}$ is the chemical composition of the obtained films (from the starting solutions for films synthesis), with the atomic percentage of nickel: $x = 1$ at. %, 3 at. %, 7 at. %, 10 at. %.

The resulting thin films were labeled as: S0, S1, S2, S3 and S4. S0 refers to the undoped films, and S1 ÷ S4 to the Ni doped films with increasing content.

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

The as-deposited thin films were compacted by thermal treatment in air, by placing the samples in the middle of an open furnace (Barnstead Type F21130-33). The heating rate was 2 °C/min, and it was followed by an annealing for 60 min at 400 °C, and then a cooling down to room temperature.

The X-ray Photoelectron Spectra (XPS) were recorded to obtain information on the surface elemental composition and chemical state of the atomic species in the studied samples. In this purpose, a Physical Electronics PHI 5000 VersaProbe instrument, equipped with a monochromated Al $\text{K}\alpha$ X-ray source (1486.6 eV) was used. The morphology of the surface was investigated by scanning electron microscopy (SEM), by using a SEM VEGA II LSH scanning electron microscope, coupled with an EDX QUANTAX QX2 detector. The optical transmittance and reflectance were recorded in the wavelength range 300 - 1000 nm using a double beam spectrophotometer Specord UV-VIS, Carl Zeiss Jena.

The investigation of the surface hydrophilicity was performed by contact angle measurements at room temperature, under 75 % environment humidity conditions. Details are given in ref. [3].

3. Results and discussion

The as deposited films were amorphous as indicated by XRD analysis. The heat treatment drives to the appearance of the anatase phase, with the presence of A(101), A(004) and A(200) peaks (Fig. 1). It is worth to mention that the main peak A(101), appears only in the low doped film S1. The average crystallite size values of the heat-treated films calculated with the Debye-Scherrer formula are under 14 nm, and do not essentially differ (see Table 1).

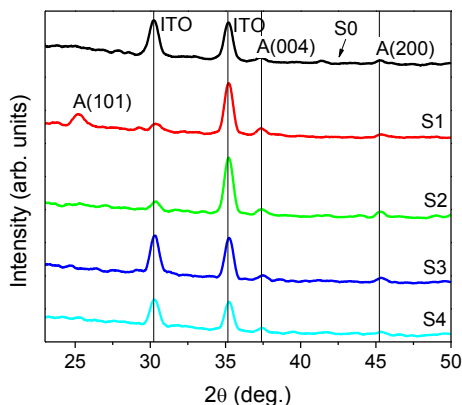


Fig. 1. XRD patterns for the undoped and Ni doped TiO_2 samples

The Ti 2p XPS spectra demonstrates the existence of Ti^{4+} state, with two peaks located at the binding energy (BE) of 459.4 eV and 465.05 eV, corresponding to the $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$ (Fig. 2).

Table 1. Ni atomic concentration ratio in the starting solutions; anatase average crystallite size ($D_{A(101)}$) and $D_{A(004)}$); the optical band gap (E_g)

	(Ni) _{sol.} (at.%)	$D_{A(101)}$ (nm)	$D_{A(004)}$ (nm)	E_g (eV)
S0	0	-	11.59	3.37
S1	1	9.36	12.54	3.19
S2	3	-	11.51	3.15
S3	7	-	12.73	3.28
S4	10	-	13.80	3.24

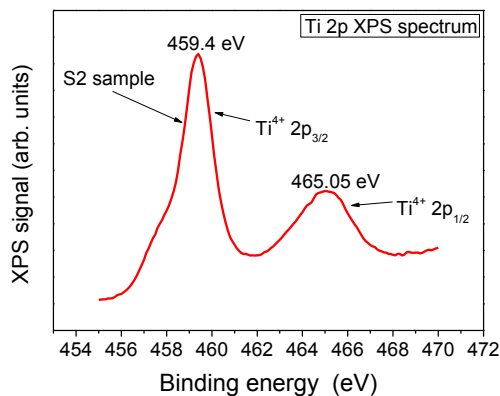


Fig. 2 Ti 2p XPS spectrum

The O 1s spectra are almost the same for all the samples. A representative O 1s spectrum for the S2 sample is given in the Fig. 3. The spectra were deconvoluted in two main components: one at the value of 530.9 eV, corresponding to lattice oxygen, and a secondary one at 531.9 eV, due to hydroxyl groups adsorbed at the surface. The ratio area of the two components is almost the same for all the TiO_2/Ni samples (equal to 79/21).

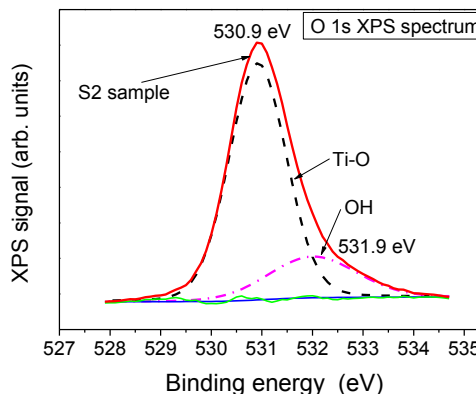


Fig. 3 O 1s XPS spectrum

The Ni 2p XPS spectra of all the doped films demonstrate the presence of Ni^{2+} state, with binding

energy values of 871.5 eV (corresponding to Ni²⁺ 2p_{1/2} state) and 854.06 eV (corresponding to Ni²⁺ 2p_{3/2} state) (Fig. 4). Ni could easily enter in TiO₂ matrix by substitution, without causing important lattice distortion, due to the similarity of the ionic radii of Ni²⁺ with that of Ti⁴⁺ [8,9].

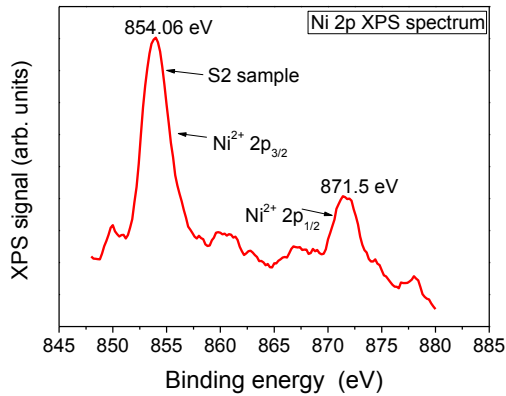


Fig. 4 Ni 2p XPS spectrum

The elemental atomic percentages are given in Table 2. Comparing with our previous studies [3,6], where the films retained a smaller amount of dopant (Nb, or Mo respectively), compared to the amounts from the solution synthesis report, this situation appear here only at higher Ni concentrations, namely for the samples S3 and S4. So, we may consider that Ni was incorporated into TiO₂ matrix up to a certain saturation value, or it is irregular distributed on the films surface.

Table 2. Ni atomic concentration ratio in the starting solutions; Ni, Ti, O atomic concentrations from XPS

	(Ni) _{sol.} (at.%)	(Ni) _{XPS} (at.%)	(Ti) _{XPS} (at.%)	(O) _{XPS} (at.%)
S1	1	0.9	33.7	65.4
S2	3	2.4	34.6	63.0
S3	7	3.0	34.4	65.4
S4	10	3.9	35.4	60.8

From Table 2 one could see that the ratio O/Ti varies from 1.7 to 1.9, showing that the doped samples are slightly suboxidized.

The presence of Ni atoms in the TiO₂ matrix is confirmed also by EDX analysis (See Table 3).

Table 3. Elemental composition from SEM-EDX analysis at the surface of S2 sample

Element	Weight [%]	Atomic [%]	Error [%]
Nickel	0.80	1.45	0.06
Titanium	2.50	5.51	0.12
Indium	11.43	2.29	2.80
Silicon	25.78	21.14	1.30
Tin	8.39	1.20	5.37
Oxygen	51.10	68.41	67.94
	100.00	100.00	

Compact structures are revealed by SEM images (Fig. 5).

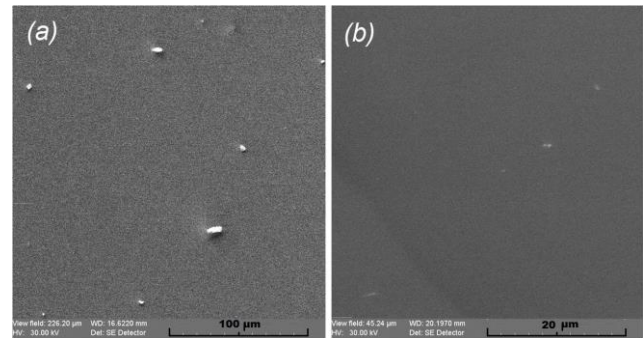


Fig. 5. SEM images of the S2 sample at different scales.

From the optical transmittance and reflectance spectra, presented in Fig. 6, the absorption coefficient α was obtained using the relation [10]:

$$\alpha = d^{-1} \ln \left[(1 - R)^2 / T \right] \quad (5)$$

where T and R are the optical transmittance and optical reflectance at a certain wavelength and d is the thickness of the film. From the study of obtained spectra by transmission and reflection measurements, we conclude that the deposited films have a relatively high optical quality considering the deposition technique used. One can observe a relatively high transmission in the visible domain (> 70%) for the S2 and S3 samples, and a clear absorption edge.

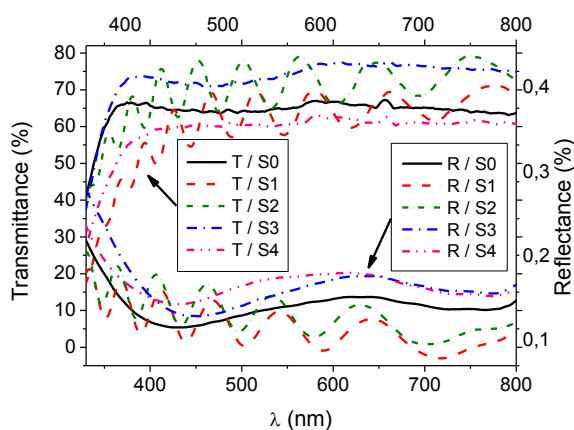


Fig. 6 Transmittance and reflectance spectra

The optical band gap values (E_g) obtained by plotting $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$), considering that the indirect allowed transition dominates over the optical absorption [11,12] (Fig. 7), are given in Table 1. A slight decrease of the optical band gap of all the Ni-doped films can be observed, compared to the undoped one. The films S0, S3 and S4 have the thickness around 200nm, while S1 and S2 are about 250nm thick, as revealed by interferometry method.

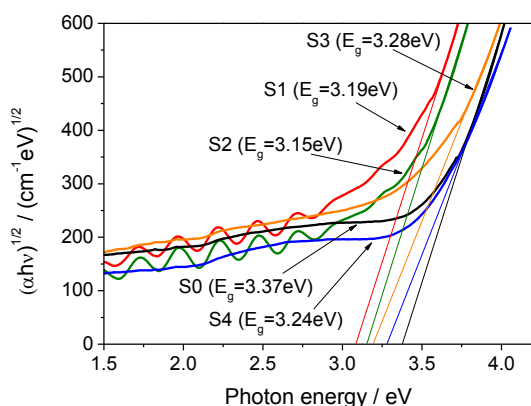


Fig. 7 The $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots

We may expect that all the films exhibit good hydrophilic properties cause we have obtained the anatase phase which, compared to rutile, presents a higher density of localised states, determining a higher concentration of surface-adsorbed hydroxyl radicals [3,13], which may be responsible for the hydrophilic conversion. But, from Fig. 8, one can see that only the undoped film, together with the one that contain the lowest Ni content (sample S1) reach the superhydrophilic state (contact angles lower than 10 deg.) with final contact angles of 3.7 deg. and 4.8 deg. respectively. The others reached the saturation of the photoactivation with contact angles that increase from 12.5 deg. till 70.5 deg. The explanation could be related to the higher optical band gap of the undoped film, that maybe increases the lifetime values of the electron-hole pairs occurring upon UV irradiation in the surface region

[3]. As concern the doped film S1, it is the only one that contain the peak A(101), peak that was present in all the films with good hydrophilic properties previous studied [3,14-16]. Since each plane has a different mixture of Ti an O atoms, it determines surface sites available for water adsorption which differ in density and type. On the other hand, as suggested in ref. [17], the metal is not hydrophilic, and this reflects in the hydrophilicity of the films with higher concentration.

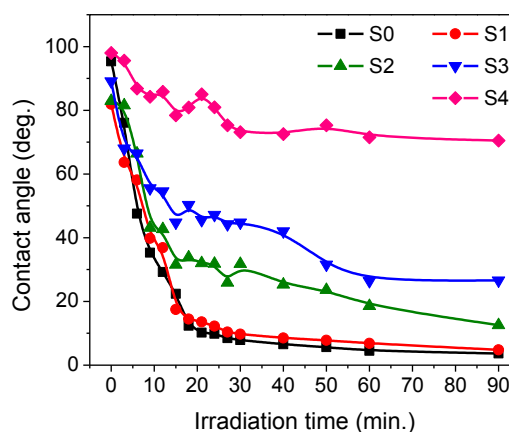


Fig. 8. Contact angle as a function of the irradiation time

4. Conclusions

Undoped and Ni-doped TiO_2 thin films were deposited on ITO substrates by the spray pyrolysis method. The as-deposited films are amorphous. By performing a heat treatment in air, the films become pure anatase. One can notice the presence of the most intense peak A(101) only in the film with the lowest Ni content. This film, together with the undoped one, shows remarkable hydrophilic properties. XPS and SEM-EDX analyzes confirm the presence of Ni embedded in TiO_2 matrix. The optical band gap is lower for all the Ni-doped films, compared to the undoped one.

Acknowledgements

One of the authors, Catalin Adomnitei, acknowledges the financial support from the strategic grant POSDRU/159/1.5/S/137750, "Project Doctoral and Postdoctoral programs support for increased competitiveness in Exact Sciences research" cofinanced by the European Social Found within the Sectorial Operational Program Human Resources Development 2007 – 2013.

References

- [1] K. Hashimoto, H. Irie, A. Fujishima, Journal of Applied Physics, **44**, 8269 (2005).

- [2] C. Orbeci, M. Totu, S. K. Tanczos, E. Vasile, A. Dinu, A. C. Nechifor, *J. Optoelectron. Adv. Mater* **7**(11-12), 822 (2013).
- [3] D. Mardare, N. Cornei, D. Luca, M. Dobromir, S. A. Irimiciuc, L. Pungă, A. Pui, C. Adomnitei, *J. Appl. Phys.*, **115**, 213501 (2014).
- [4] I. Vaiciulis, M. Girtan, A. Stanculescu, L. Leontie, F. Habelhames, S. Antohe, *Proceedings of the Romanian Academy, Series A*, **13**, 35 (2012).
- [5] M. Girtan, R. Mallet, *Proceedings of the Romanian Academy, Series A*, **15**, 146 (2014).
- [6] C. Adomnitei, D. Luca, M. Girtan, I. Sandu, V. Nica, A. V. Sandu, D. Mardare, *J. Optoelectron. Adv. Mater* **15**(5-6), 519 (2013).
- [7] I. O. Acik, A. Junolainen, V. Mikli, M. Danilson, M. Krunk, *Appl. Surf. Sci.* **256**, 1391 (2009).
- [8] R. D. Shannon, *Acta Cryst.* **32**, 751 (1976).
- [9] H. Zhang, J. I. Tianhao, L. Li, X. Qi, Y. Liu, J. Cai, H. Du, J. Sun, *Acta Phys. Chim. Sin.* **24**, 607 (2008).
- [10] T. S. Moss, *Optical Properties of Semiconductors*, Butterworths, London (1959).
- [11] D. Mardare, G. I. Rusu, *Phys. Low Dimens. Struct.*, **9/10**, 111 (2002).
- [12] L. L. Kazmerski, (Ed.) *Polycrystalline and Amorphous Thin Films and Devices*, Academic Press, New York (1980).
- [13] D. A. H. Hanaor, C. C. Sorrell, *J. Mater. Sci.* **46**, 855 (2011).
- [14] D. Mardare, A. Manole, A. Yıldız, D. Luca, *Chem. Eng. Comm.* **198**, 530 (2011).
- [15] D. Mardare, F. Iacomi, D. Luca, *Thin Solid Films* **515**, 6474 (2007).
- [16] D. Crisan, N. Dragan, M. Raileanu, M. Crisan, A. Ianculescu, D. Luca, A. Nastuta, D. Mardare, *Appl. Surf. Sci.* **257**, 4227 (2011).
- [17] S. D. Sharma, D. Singh, K. K. Saini, C. Kant, V. Sharma, S. C. Jain, C. P. Sharna, *Applied Catalysis A: General* **314**, 40 (2006).

*Corresponding author: dianam@uaic.ro