Materials Science-Poland, 31(1), 2013, pp. 71-79
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-012-0066-4

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Structural and surface properties of TiO_2 thin films doped with neodymium deposited by reactive magnetron sputtering*

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Thin films were deposited using modified, high energy magnetron sputtering method from Ti-Nd mosaic targets. The amount of neodymium dopant incorporated into two sets of thin films was estimated to be 0.8 and 8.5 at.%, by means of energy dispersive spectroscopy. On the basis of x-ray diffraction method, the type of crystalline structure and crystallites size were evaluated directly after the deposition process and after additional post-process annealing at 800 °C temperature. The influence of annealing on the surface properties was evaluated with the aid of atomic force microscopy. Uniformity of the dopant distribution in titanium dioxide matrix was examined with the aid of secondary ion mass spectroscopy. Additionally, using atomic force microscope, diversification and roughness of the surface was determined. Chemical bonds energy at the surface of TiO_2:Nd thin films was investigated by x-ray photoelectron spectroscopy method. Wettability measurements were performed to determine contact angles, critical surface tensions and surface free energy of prepared coatings. On the basis of performed investigations it was found, that both factors, the amount of neodymium dopant and the post-process annealing, fundamentally influenced the physicochemical properties of prepared thin films.

Keywords: *TiO_2; neodymium; physicochemical properties; magnetron sputtering*

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1. Introduction

Titanium dioxide (TiO_2) is known as a material with exceptionally good optical, mechanical and thermal properties, which contributes to its wide application in various fields of engineering. TiO_2 properties depend, among others, on the type of its crystallographic structure and surface topography.

Incorporation of different elements into titanium dioxide matrix can diametrically change its properties [1, 2]. In the recent years, titanium dioxide doped with various lanthanides has attracted much attention due to its particular properties. For instance it was found that doping with lanthanides can cause densification of TiO_2 matrix structure [3–8]. Also doping can increase selected functionality of the TiO_2. For example, photocatalytic activity for water splitting [9–12] or certain photoluminescent [9, 13, 14], ferroelectric [9, 15, 16] or piezoelectric [9, 17] properties of TiO_2 matrix can be improved.

Various techniques have been used for deposition of the compounds of TiO_2 doped with neodymium, like spray pyrolisis [18, 19], metalorganic deposition combined with spin-coating [18, 20], pulsed laser ablation [18, 21, 22], polymeric complex method [18, 23] and different modifications of sol-gel [15, 18, 24, 25]. However, in the current state of the art, magnetron sputtering has not been used as a deposition technique. In this work, we have used reactive magnetron sputtering for the preparation of TiO_2 thin films doped with different amounts of neodymium. This method is commonly used for deposition of thin oxide films in industrial applications. Magnetron sputtering makes possible to control the structure and stoichiometry of deposited films. Various types of materials *e.g.* dielectric, semiconducting or metallic can be sputtered to prepare thin films. Modification and a proper selection of

*This paper was presented at the 12th Seminar Surface and Thin-Film-Structures – SemPiSC, Szklarska Poreba 2012.

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sputtering parameters can result in thin films with nanocrystalline, dense structure, which in turn ensure extraordinary properties.

In this paper results of investigation of physicochemical properties of TiO_2 thin films doped with neodymium and prepared by reactive magnetron sputtering have been presented.

2. Experimental details

The TiO_2:Nd thin films were prepared by the HERMS method from metallic Ti-Nd mosaic targets [26, 27]. The sputtering process was carried out at low pressure, in reactive atmosphere using high purity oxygen as a working gas. Applying a special spacer between the target and water-cooled magnetron provided higher temperature at the target surface [26].

The atomic percent of neodymium in the prepared thin films was determined using Hitachi S-4700N scanning electron microscope equipped with energy dispersive spectrometer (Noran Vantage). The amount of Nd in two sets of prepared thin films were 0.8 at.% and 8.5 at. %. The thickness measured with Taylor Hobson Tally Surf CCI Lite optical profiler was 120 nm and 480 nm for thin films doped with 0.8 at. % and 8.5 at. % of Nd, respectively. The obtained values were related to the duration of the thin film deposition process, which was equal to 30 min and 120 min, respectively.

X-ray diffraction (XRD) method was applied for structural investigations of the thin films. The patterns were recorded at room temperature using DRON-2 powder diffractometer, with Co Kα radiation. Surface morphology was examined with atomic force microscope (AFM) UHV AFM Omicron operating in the contact-mode, in ultra high vacuum with a contact silicon probe of tetrahedral tip shape. For analysis of experimental data WSxM ver. 5.0 software was used [28]. In order to determine the neodymium distribution in the depth profile of thin films and the ratio of Ti^+/Nd^+ and Nd^+/O^+ ions, the secondary ion mass spectroscopy (SIMS) has been used. SIMS experiments were conducted using an SAJW-05 instrument, equipped with quadruple-based mass spectrometer (Balzers QMA-410). A Physical Electronics ion gun with Ar^+ primary beam of about 100 µm in diameter and with 3 keV ion energy at 0.6 µA of beam current, rastered on 1.5 mm $\times$ 1 mm area, was used. Selected parameters assured a low sputter rate and a high secondary signal during SIMS measurement.

X-Ray Photoelectron Spectroscopy (XPS) was used to determine the chemical states of the elements on the surface. The experiments were performed with Specs Phoibos 100 MCD-5 hemispherical analyzer in ultra high vacuum conditions, using Specs XR-50 X-ray source with Mg Kα (1253.6 eV) beam. Photoelectrons were collected at 45° take-off-angle and analyzed using a concentric hemispherical analyzer. Data were collected in a range equivalent to Ti2p, O1s and Nd4d states. All the spectra were calibrated with respect to the binding energy of adventitious C1s peak at 284.8 eV.

Wettability measurements were performed to characterize the surface properties of the thin films. The contact angle (θ) was used to correlate the thermodynamic properties of thin film surface. Using Young's equation [29], a liquid-solid-vapour system can be characterized. The total surface free energy of measured thin films is the sum of its dispersive and polar component. In Zisman approach, a series of homologous liquids with different surface tensions is used and a graph of $\cos\theta$ *vs.* γ is determined [30, 31]. Critical surface tension equals the surface tension at which the plotted line intersects 1.0. It is often interpreted as the highest value of surface tension of a liquid, which will completely wet the solid surface. The measurements of contact angle and surface free energy were carried out with Attension Theta Lite tensiometer. Contact angle measurements were performed according to the sessile drop method [31] and the liquids used in experiments were water, ethylene glycol and ethanol.

3. Results and discussion

XRD measurements have revealed that TiO_2 thin films doped with neodymium, directly after deposition, are amorphous. After additional annealing at 800 °C for 2 hours, anatase phase in the thin film of TiO_2:Nd (0.8 at. %) and rutile phase in the thin film of TiO_2:Nd (8.5 at. %) have occurred. Crystallites sizes were calculated using Scherrer's formula

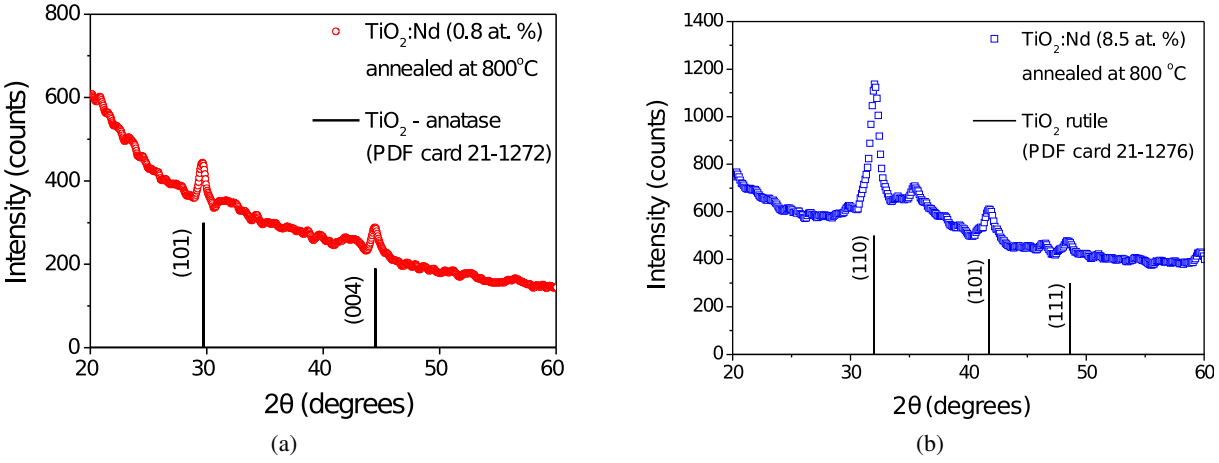


Fig. 1. XRD patterns of annealed TiO_2 thin films doped with: a) 0.8 at. % of Nd, b) 8.5 at. % of Nd. Standard patterns are from refs. [33, 34].

[32] and were equal to 6 nm and 12 nm for the TiO_2 doped with 0.8 at. % and 8.5 at. % of neodymium, respectively. However, Signal-to-Noise ratio (S/N) of registered XRD patterns was rather poor, therefore the crystallites dimensions can be overestimated. The amount of 0.8 at. % of Nd makes possible to obtain a crystalline structure which after annealing at the temperature of at least 800 °C transforms into anatase phase, while the incorporation of 8.5 at. % of Nd, followed by annealing, results in rutile phase in the thin film. The XRD patterns of annealed thin films are presented in Fig. 1.

Surface morphology of TiO_2 thin films doped with neodymium, investigated with the AFM, has been presented in Fig. 2. The structure is densely packed and the surface is homogenous in case of all measured thin films. For TiO_2:Nd (0.8 at. %) post-process annealing caused an increase in the grain size of the thin film. In case of as deposited TiO_2:Nd (8.5 at. %) no grains are visible in the AFM image and the surface is the flattest among all measured thin films. Additional annealing of the sample caused the growth of the grains and the surface is less homogenous and more diversified.

Surface roughness (RMS – root mean square) has been determined from the AFM images. In case of TiO_2:Nd (0.8 at. %) the surface is homogenous with a roughness of about 2.89 and 3.10 nm for as deposited and annealed at 800 °C thin films, respectively. The least roughness of 0.18 nm was observed for as deposited TiO_2:Nd (8.5 at. %) thin film, while the annealing increased the RMS value to ca. 10.66 nm. The distribution of grain size in Z direction in TiO_2 thin films doped with neodymium has been shown in Fig. 3. In both cases, annealing of the samples increased the diversity of thin films surface. As deposited and annealed TiO_2:Nd (0.8 at. %) thin film have similar roughness and surface texture. However, additional annealing of TiO_2:Nd (8.5 at. %) caused a significant increase of surface roughness and grain size.

SIMS method allowed us to determine the homogenous distribution of elements in the investigated thin films. SIMS depth profiles recorded for TiO_2:Nd (0.8 at. %) and TiO_2:Nd (8.5 at. %) thin films are presented in Fig. 4. The depth profiles are represented by the distribution of positively charged atomic species of Ti^+, Nd^+ and O^+ plotted against the sputter time (cycles). The differences in sputter time in case of investigated thin films resulted from various thicknesses of the samples. Therefore, the thinner layer is TiO_2:Nd (0.8 at. %), which corresponds to the measured thickness of 120 nm.

In Fig. 5 the depth profiles of atomic species ratios of Nd^+/Ti^+ and Nd^+/O^+ are presented. At the X axes of the charts, the thickness of measured samples is given. The distribution of neodymium in both thin films is homogenous. Concentration of Nd is about ten times higher in case of TiO_2:Nd (8.5 at. %) than for TiO_2:Nd (0.8 at. %), which

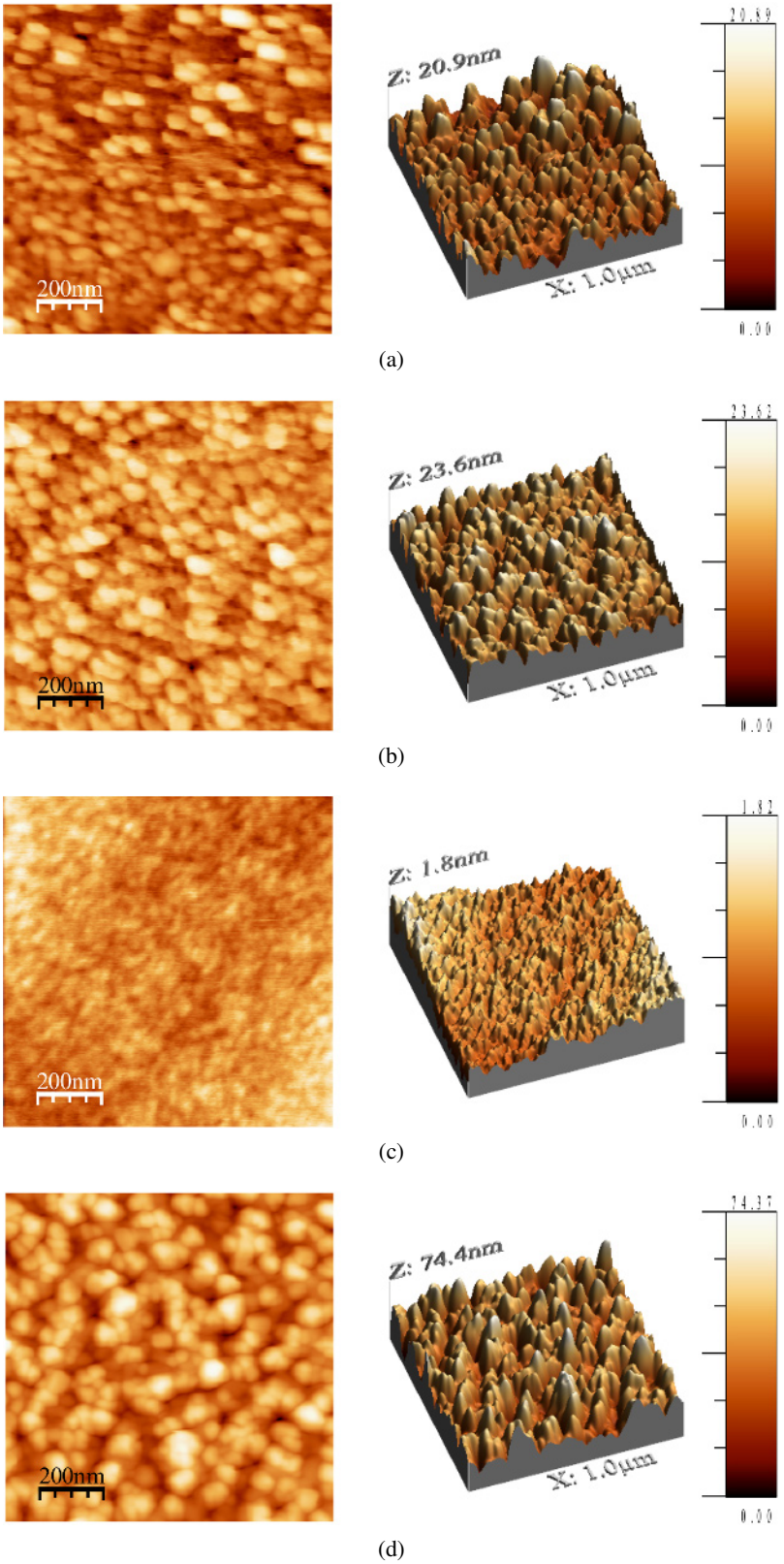


Fig. 2. AFM surface images of: a) as deposited TiO_2:Nd (0.8 at. %) thin film, b) annealed TiO_2:Nd (0.8 at. %) thin film, c) TiO_2:Nd (8.5 at. %) thin film, d) annealed TiO_2:Nd (8.5 at. %) thin film.

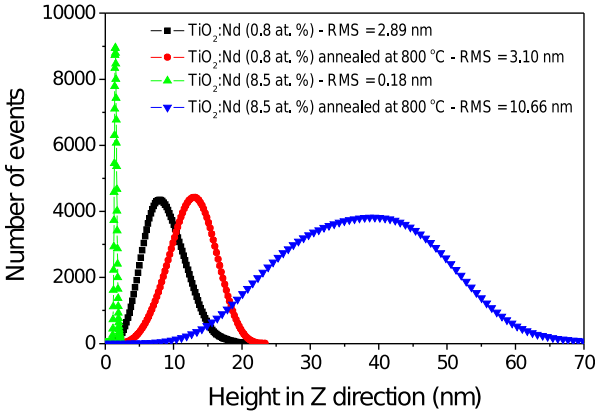


Fig. 3. The distribution of grain size in *Z* direction of TiO_2 thin films doped with neodymium.

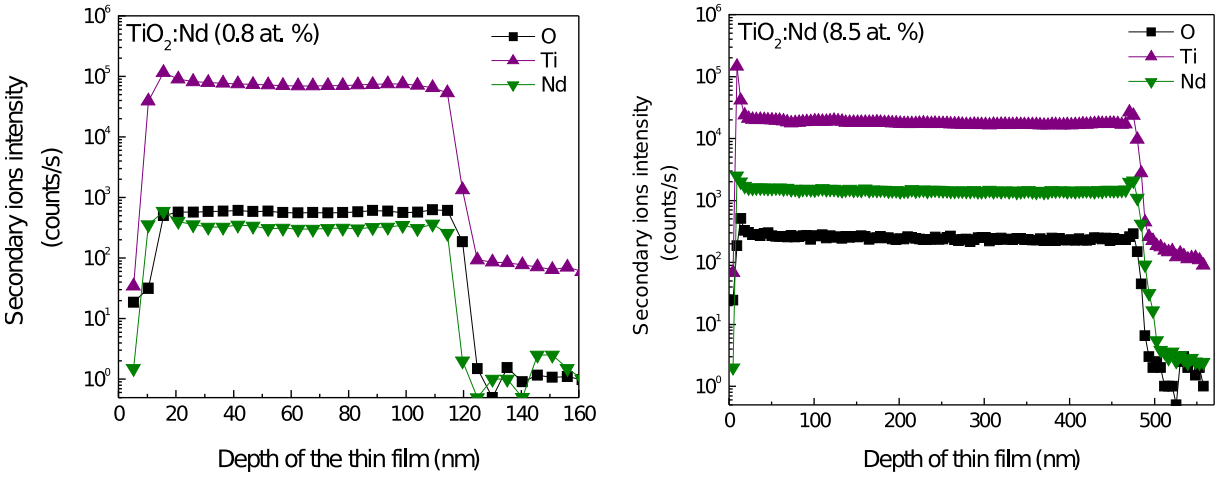
corresponds very well to the results obtained with the energy dispersive spectrometer.

Analysis of neodymium influence on surface states of TiO_2 films was determined on the basis of X-ray photoelectron spectroscopy. The spectra recorded in the regions equivalent to Ti2p, O1s and Nd4d states for TiO_2:Nd films doped with 0.8 and 8.5 at. % are shown in Fig. 6. Ti2p states doublet peak can be observed (Fig. 6a,b) in both cases. The distance between the positions of $Ti2p_{1/2}$ and $Ti2p_{3/2}$ peaks, defined as ΔBE, amounts to 5.6 eV for TiO_2:(0.8 at. % Nd). The position of the doublet peak and the value of ΔBE testify the presence of Ti^{4+} which creates TiO_2. In case of TiO_2:(8.5 % at. Nd) film we can observe insignificant shift of the peaks position and increase of ΔBE (to 5.8 eV) which results from doping with higher amount of Nd [35]. XPS measurements allow also the analysis of oxygen states and determination of surface adsorption of hydroxyl species and water molecules. According to the literature [36, 37], adsorption of hydroxyl groups (OH^-) and water molecules (H_2O) on the surface of titanium dioxide can be observed in the XPS spectrum in O1s region. On the basis of multi-peak analysis, the percentage contribution of OH^- groups and H_2O molecules to the signal from oxygen (O^{2-}) near surface can be estimated. In the XPS investigation of O1s states the peaks of oxygen (O^{2-}), hydroxyl groups ($OH^-_{(ads)}$) and water ($H_2O_{(ads)}$) adsorbed on the surface of thin films were detected (Fig. 6c,d).The total level of OH^- and H_2O_{ads} was higher for the film with lower Nd dopant content. The analyses of XPS spectra in the range equivalent to Nd4d state (Fig. 6e,f) have shown that in both cases neodymium occurs in Nd^{3+} oxidation state. This suggests the formation of Nd_2O_3 between the crystallites of TiO_2.

In Table 1, the results of contact angle investigation, carried out with water, ethylene glycol and ethanol for TiO_2:Nd thin films with different amounts of neodymium have been presented. A higher contact angle was determined for thin film doped with 8.5 at. % of Nd, which can be connected with its very low surface roughness of *ca.* 0.18 nm. Both thin films revealed hydrophilic behavior, with water contact angles of 74.9° and 84.3° for TiO_2:Nd (0.8 at. %) and TiO_2:Nd (8.5 at. %), respectively. In case of other liquids, a higher contact angle was obtained for TiO_2:Nd (8.5 at. %). The highest contact angles for both thin films have been recorded for water, which is a polar liquid with much higher surface energy than ethylene glycol or ethanol. The lowest values of contact angles were obtained for ethanol, which simultaneously has the lowest surface energy.

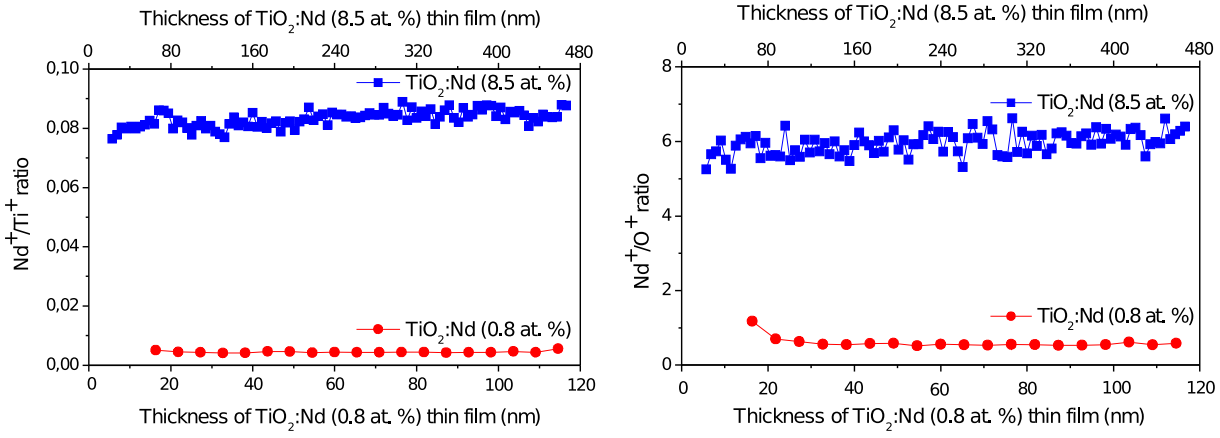
In Fig. 7 Zisman plot and critical surface tensions of TiO_2 thin films doped with different amounts of neodymium have been presented. The values of critical surface tension have been calculated using Zisman approach. The investigation has shown, that a change of the dopant amount incorporated into TiO_2 matrix has not changed the thin film's critical surface tension significantly. The results have been compared in Table 2.

Surface free energy of TiO_2 thin films doped with neodymium was determined using geometric mean approach. The values have been estimated according to Fowkes approach [38], using Owens and Wendt equations. The surface free energy is about 20 % higher in case of TiO_2 thin film doped with 0.8 at. % of Nd in comparison to thin film doped with 8.5 at. % of Nd. This indicates that the surface of TiO_2:Nd (8.5 at. %) film is a little less wettable. In the geometric approach, the dispersive part is the main component of the total surface free energy of this film, while for TiO_2:Nd (0.8 at. %) thin film, the polar component is the main part of the total surface free energy.



(a) (b)

Fig. 4. SIMS depth profiles of atomic species taken with 3 keV Ar+ beam for: a) TiO_2:Nd (0.8 at. %), b) TiO_2:Nd (8.5 at. %).



(a) (b)

Fig. 5. Depth profiles of atomic species ratio of: a) Nd^+/Ti^+ and b) Nd^+/O^+.

4. Conclusions

Titanium dioxide thin films doped with 0.8 and 8.5 at. % of neodymium were prepared by reactive magnetron sputtering method.

As deposited TiO_2 thin films doped with Nd reveal amorphous behavior, while additional annealing at 800 °C results in a transformation of the structure phase into anatase or rutile in case of TiO_2:Nd (0.8 at. %) and TiO_2:Nd (8.5 at. %), respectively. The annealed thin films are highly nanocrystalline with crystallites size of 6 nm and 12 nm for anatase and rutile phase. SIMS investigations confirmed that the distribution of Ti^+, Nd^+ and O^+ atomic species are homogenous.

AFM measurements revealed that the structure is densely packed and the surface is homogenous in case of all thin films. For as deposited TiO_2:Nd (8.5 at. %) thin film no grains were visible in the image, however additional annealing caused the growth of the grains and the surface was more diversified. For all measured thin films additional annealing caused an increase of the surface roughness.

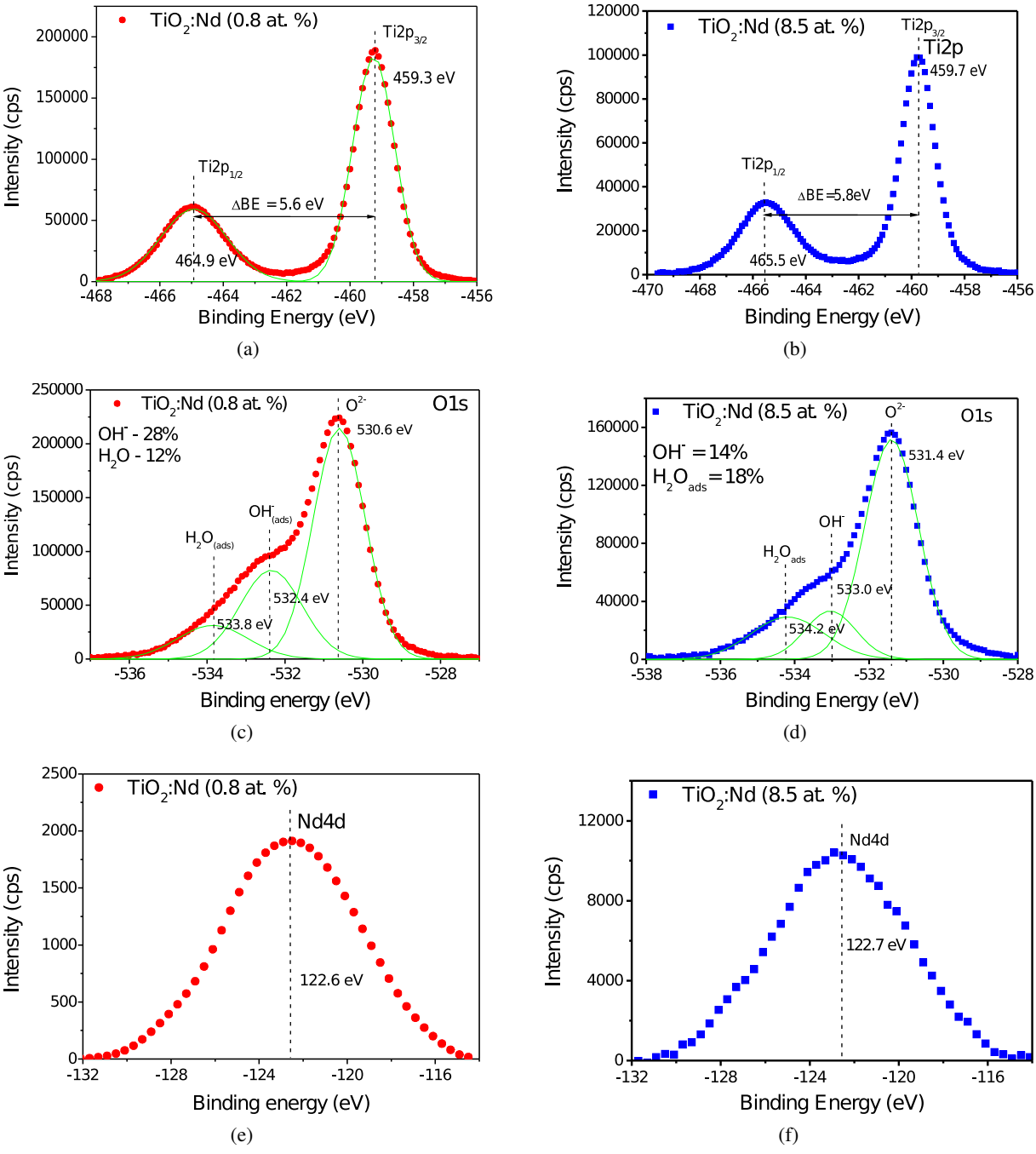


Fig. 6. XPS spectra recorded in regions equivalent to Ti2p, O1s and Nd4d states for TiO_2:Nd thin films doped with 0,8 at. % and 8,5 at. %.

Results of XPS investigations revealed that in case of the measured thin films, Ti^{4+} species were present at the surface, which led to TiO_2 formation. All thin films adsorbed OH^- and H_2O_{ads} at the surface. For both thin films neodymium occurred in Nd^{3+} oxidation state, which indicates the formation of Nd_2O_3 oxide between the crystallites of TiO_2. Wettability measurements revealed that TiO_2 thin films doped with different amounts of Nd are hydrophilic and have very similar critical surface

Table 1. Results of contact angle measurements of TiO_2:Nd thin films.

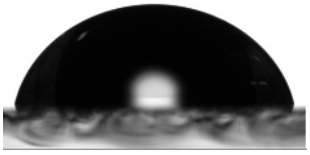
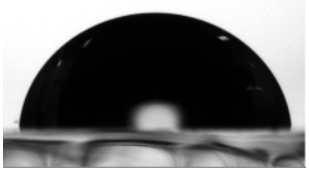
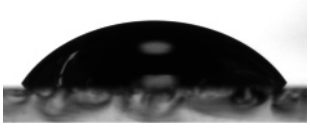
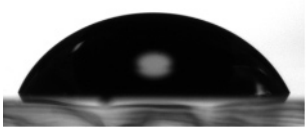
Liquid	Contact angle of measured thin films	
	TiO_2:Nd (0.8 at. %)	TiO_2:Nd (8.5 at. %)
Water	$74.9° \pm 3.5°$	$84.3° \pm 1.1°$
		
Ethylene Glycol	$56.1° \pm 2.5°$	$62.8° \pm 1.7°$
		
Ethanol	$8.9° \pm 1.9°$	$10.9° \pm 1.6°$
		

Table 2. Results of critical surface tension and surface free energy investigations of TiO_2:Nd thin films.

Thin film	Critical surface tension (mN/m)	Surface free energy (mN/m)		
		Dispersive component	Polar component	Total value
TiO_2:Nd (0.8 at. %)	20.2 ± 0.3	11.3 ± 0.2	18.1 ± 0.3	29.4 ± 0.5
TiO_2:Nd (8.5 at. %)	19.9 ± 0.5	14.7 ± 0.4	9.8 ± 0.2	24.5 ± 0.6

tension. Surface free energy was ca. 20 % higher for thin film doped with 0.8 at. % of Nd in comparison to thin film with 8.5 at. % of Nd.

Acknowledgements

Fellowship co-financed by European Union within European Social Fund. This work was financed from the sources given by the NCN in the years 2011–2013 as a development research project number N N515 4963 40 and in the years 2013–2014 as a development research project.

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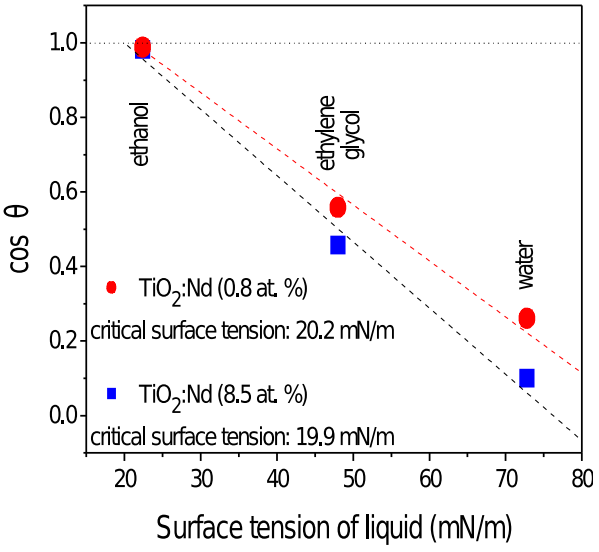

Fig. 7. Zisman plot and results of critical surface tension investigation of TiO_2 thin films doped with neodymium.

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Received: 2012-10-30
Accepted: 2012-11-16