Polish Journal of Chemical Technology, 14, 3, 1 — 7, 10.2478/v10026-012-0077-2

Photocatalytic properties of transparent TiO_2 coatings doped with neodymium

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In this work photocatalytic properties of TiO_2 thin films doped with 8.51 at. % of Nd were described. The self-cleaning phenomenon of thin films was discussed together with the structural, optical and surface properties of prepared thin films. Transparent coatings based on titanium dioxide were manufactured by high-energy reactive magnetron sputtering process. Incorporation of Nd during sputtering process results in amorphous behavior, without a significant influence on transparency and colour as compared to the undoped TiO_2-rutile matrix. Nevertheless, doping with neodymium doubles the photocatalytic activity of the matrix due to higher quantity of photo-generated charge carriers and more efficient mechanism of energy transfer.

Keywords: TiO_2, neodymium, photocatalysis, wettability, surface properties.

INTRODUCTION

Transparent thin films based on titanium dioxide are widely applied in coating industry, because TiO_2 is being used for preparation of hydrophobic or hydrophilic films, self-cleaning coatings, optical filters or protective films[1–5]. The properties of TiO_2 can be modified by selection of deposition parameters, doping with different elements or post-process treatment (i.e. annealing)[1–6]. By doping with rare earth elements thin films, which exhibit photoluminescence or have high photocatalytic activity can be manufactured[7–9]. Neodymium is often applied dopant for TiO_2 due to its photoluminescence properties in near-IR range[10]. Moreover, it is also an important material in the field of lasers technology. Nd^{3+}-doped materials are one of the most versatile laser host materials[11]. Similarly like Eu^{3+} or Tb^{3+}, incorporation of Nd^{3+} ions results in the increase of TiO_2 photocatalytic activity due to a higher number of energy levels which can take part in energy transfer mechanism. Our previous works have shown that incorporation of RE-dopant into nanocrystalline TiO_2 thin film increases their photocatalytic activity more than two times, without a meaningful decrease of its high transparency[12].

In this work the influence of neodymium on photocatalytic properties of TiO_2 thin films are discussed. A self-cleaning phenomenon of thin films based on TiO_2 is a consequence of photo-generation of electron – hole pairs under UV-Vis light exposure. The induced charge carriers are transferred to different positions on the surface to react with donors or acceptors[13]. Electrons, which have a strong reducing power, are easily trapped by O_2 (acceptors) in order to produce superoxides O_2^- (radical anions). The holes are trapped by organic pollutants (donors) and oxidize them. The phenomena of separation, recombination, capture and transfer of photo-induced carriers are conditioning the photocatalytic activity of thin film[13]. Incorporation of the equivalent amount of the dopant, especially from rare earth (RE) group, results in receiving coatings with high photocatalytic activity and exhibit other phenomena. Doping TiO_2 thin films with Eu, Tb or Nd results in structure modification (receiving of different phase, densification), increases the temperature of phase transformation, retains high transparency of the matrix, increases photocatalytic properties and may cause photoluminescence effect[10, 14]. A significant effect of RE-doping on the properties of TiO_2 matrix is due to a participation in energy transfer of photo-induced charge carriers[15].

In the present paper the results of photocatalytic experiment together with structural, optical and surface properties (adsorption, wettability) of transparent TiO_2:Nd thin films are discussed.

EXPERIMENTAL

Thin films were manufactured by a high energy reactive magnetron sputtering process[16]. For deposition metallic Ti and Ti-Nd targets were sputtered under the low oxygen pressure (0.1 Pa). Thin films were deposited on SiO_2 and Si substrates. The thickness of the films was about 400 nm. The atomic concentration of Nd-dopant in the film was determined by Energy Dispersive Spectroscopy. The results have shown that in TiO_2:Nd thin film was 8.51 at. % of neodymium.

The structure (crystalline form and crystallites size) of as-deposited films was determined by X-Ray Diffraction (XRD). For measurements Dron-2 powder diffractometer was used. The average size of crystallites (D) was calculated based on XRD patterns according to the Scherrer formula[17]. The structural characterization was extended by surface diversification analysis obtained from atomic force microscope (AFM). The topography was investigated in contact mode, in an ambient air by Veeco PicoForce microscope. WSxM ver. 4.0 software was used to transform the received data points into the images of the surface[18].

Distribution of titanium, oxygen and neodymium in as-deposited films was investigated by Secondary Ion Mass Spectroscopy (SIMS). The applied SIMS system

was equipped with an ion gun (Physical Electronics 06-350E) and a quadruple mass spectrometer (Balzers QMA-410). During the measurement thin films were etched by 3keV Ar^+ beam under 45° angle and positive ions were counted.

The chemical states of the elements on the surface were evaluated by X-Ray Photoelectron Spectroscopy. The XPS experiments were performed in an ultra high vacuum conditions using Mg Kα (1253.6 eV) beam. The photoelectrons were collected at the 45° take-off-angle and analyzed by a concentric hemispherical analyzer. The data were collected in the 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.

The optical properties of as-deposited TiO_2 and TiO_2:Nd films were determined by the optical transmission measurements. The measurements were carried out in the visible light range using deuterium and halogen lamps, and OceanOptics spectrophotometer.

The influence of neodymium on the wettability of TiO_2 films was investigated by water contact angle measurements. Thin films were examined by Theta Lite workstation from Attension. For tests water drops (14 μl) of the distilled water were applied on films surface.

The photocatalytic activity of the manufactured films was determined based on the results of phenol decomposition. Photocatalytic reactions were conducted by 5 hours under UV-VIS light (6 x 20 W Phillips lamps with intensity: UV 183 W/m^2, VIS 167 W/m^2). The concentration of phenol was 10 mg/L and the samples were immersed in 100 ml of solution. The concentration of phenol in water solution was inspected after each hour by absorbance measurements using the UV-VIS spectrometer. The percent decrement of phenol was determined using a standard curve for phenol λ_{max} = 270 nm. According to the simplified Langmuir – Hinshelwood equation (for the solutions with low initial concentration c_o): $c_t = c_0 \cdot \exp(-A_{crr} \cdot t)$, where c_t is the concentration after time t (hours), corrected reaction rate A_{crr} was calculated[19–21]. Besides, the received results allowed the determination of the photocatalytic activity, which can be expressed as $\left(\frac{c/c_o}{p}\right)\cdot 100\%$, where p is the area of the film (cm^2).

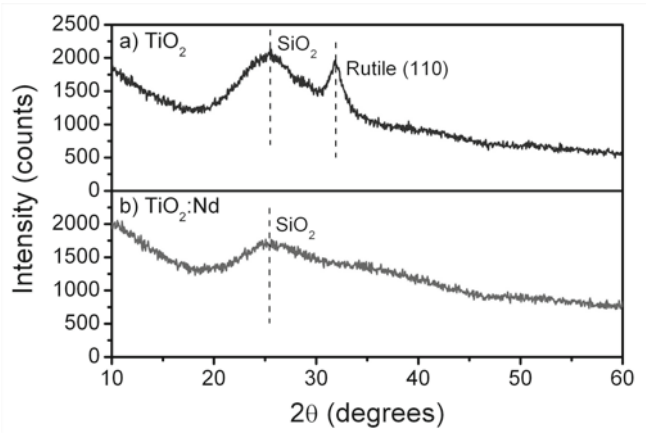

Figure 1. XRD-patterns of a) TiO_2 and b) TiO_2:Nd thin films as-deposited on SiO_2 substrates

RESULTS

The crystal structure of thin films was determined by X-ray diffraction measurements. The XRD-patterns of manufactured films are presented in Figure 1. The results have shown that as-deposited TiO_2 matrix had the rutile structure with crystallites size of 8.7 nm. Doping TiO_2 with 8.51 at. % of neodymium results in non-crystalline film. This can also be observed on the AFM images (Figure 2). Incorporation of neodymium into the film gave the smooth surface with very small roughness (*RMS* = 0.14 nm), which is characteristic of the amorphous film[9]. In the case of the undoped TiO_2 nanocrystalline structure with homogenous grains can be observed. The roughness of TiO_2 was about 1.75 nm.

The homogeneity of films composition was investigated by secondary ion mass spectroscopy (SIMS). The SIMS profiles of TiO_2 and TiO_2:Nd films as-deposited on silicon substrates are shown in Figure 3. The results have revealed that distribution of titanium, oxygen and neodymium atoms was constant in the entire volume of manufactured films. Especially, the constant concentra-

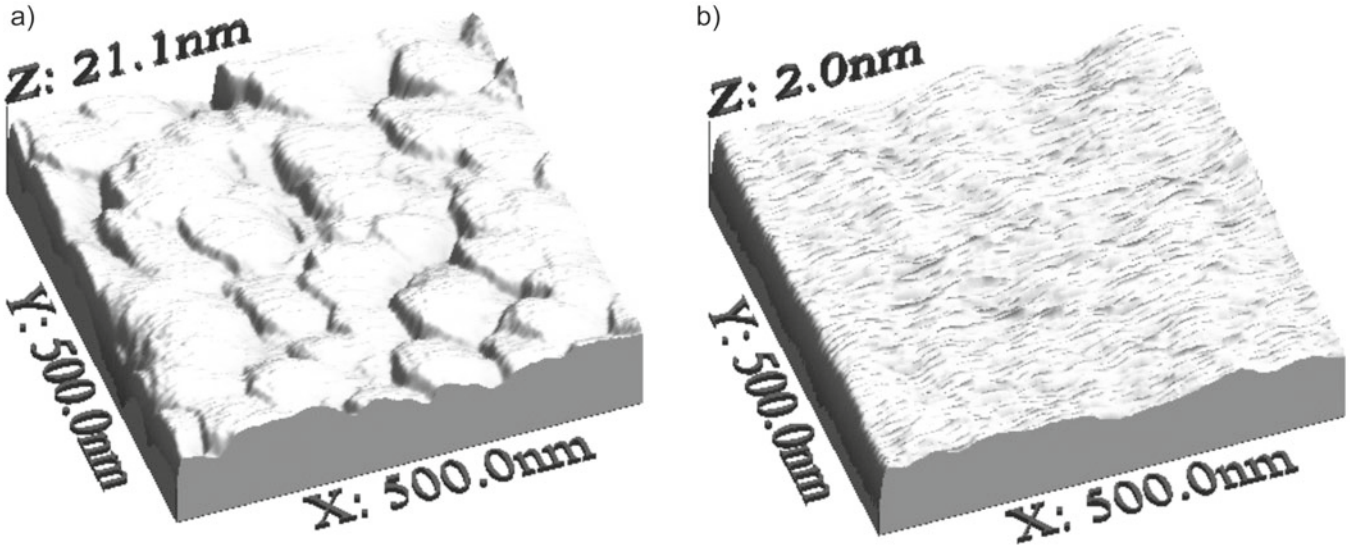

Figure 2. AFM images of a) TiO_2 and b) TiO_2:Nd thin films surface

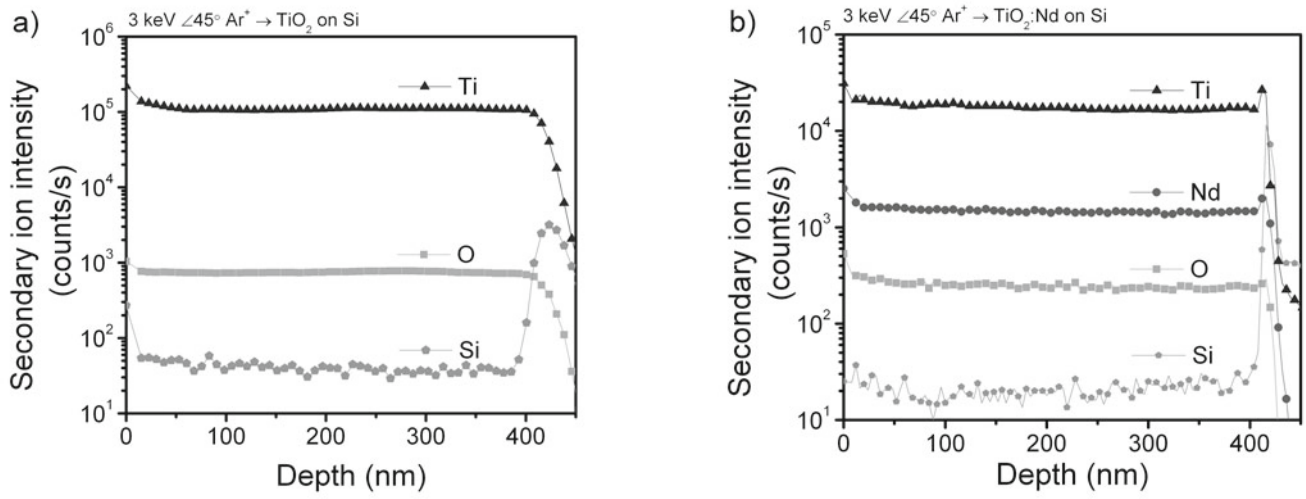

Figure 3. Secondary ion mass spectroscopy results of a) TiO_2 and b) TiO_2:Nd thin films as-deposited on Si (100) substrates

tion of Nd-dopant indicates homogenous distribution which will give equal properties on the whole surface of TiO_2:Nd film.

The influence of Nd-doping on the transmission characteristics of TiO_2 thin films is presented in Figure 4. Transmission measurements revealed high transparency of as-deposited films in visible light range. Transmission T_λ of undoped matrix was about 72%, while for Nd-doped film T_λ was 76%. Doping TiO_2 with neodymium results also in absorption edge λ_{cutoff} shift into the shorter wavelength range (from 338 nm to 318 nm). Based on transmission characteristics the optical absorption α and optical band gap E_g^{opt} for indirect allowed transitions have been calculated[22]. The analysis of optical measurements have revealed that doping with neodymium results in an increase of the optical band gap E_g^{opt} from 3.08 eV to 3.42 eV for the undoped film and the doped one, respectively. From an application point of view excellent optical properties of TiO_2:Nd in comparison with TiO_2 film testifies that Nd-doped films might be interesting, especially as a functional film for optical coatings.

The results of phenol decomposition reactions on the surface of thin films during UV-Vis light exposure were used to determine their photocatalytic activities. The photocatalytic activity of the undoped and Nd-doped TiO_2 thin films are compared in Figure 5. The results have shown that Nd-doping doubles the photocatalytic activity of TiO_2 matrix. After 5 hours of UV-light exposure the TiO_2:Nd film decomposed 4.7% of phenol while the undoped matrix decomposed 2.2%. Based on the received results the corrected rate of phenol decomposition reaction A_{crr} was calculated for both films. For non-crystalline TiO_2:Nd film the value of A_{crr} was 0.93 [%/(cm^2)] per 1 hour, while in the case of nanocrystalline titanium dioxide A_{crr} was 0.45 [%/(cm^2)].

The wettability and the surface state of as-deposited films have been investigated by contact angle measurements and X-ray photoelectron spectroscopy. The images of water drops on the surface of TiO_2 and TiO_2:Nd thin films are presented in Figure 6. In the case of nanocrystalline matrix the contact angle value was about 70.5° which means that TiO_2 film was hydrophilic (Figure 6a). Doping with neodymium results in the increase of contact angle up to 93.2° and receiving the hydrophobic non-crystalline film.

Analysis of neodymium influence on surface state of TiO_2 films was determined based on the X-ray photoelectron spectroscopy. The spectra recorded in the regions equivalent to Ti2p, O1s and Nd4d states for TiO_2 and

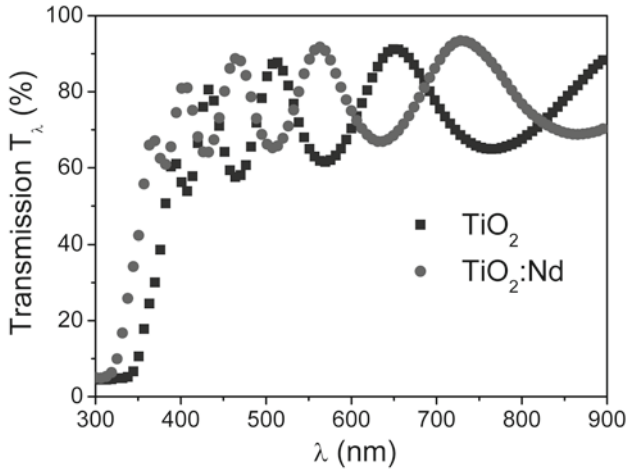

Figure 4. Transmission characteristics of TiO_2 and TiO_2:Nd thin films as-deposited on SiO_2 substrates

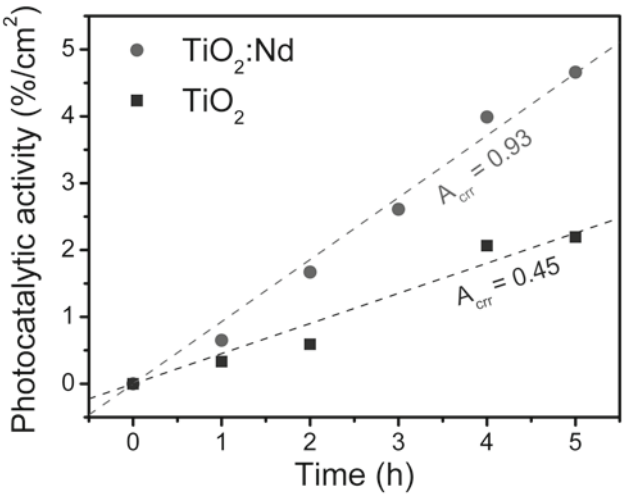

Figure 5. Influence of neodymium on photocatalytic activity of TiO_2 thin films based on phenol decomposition under UV-Vis light exposure

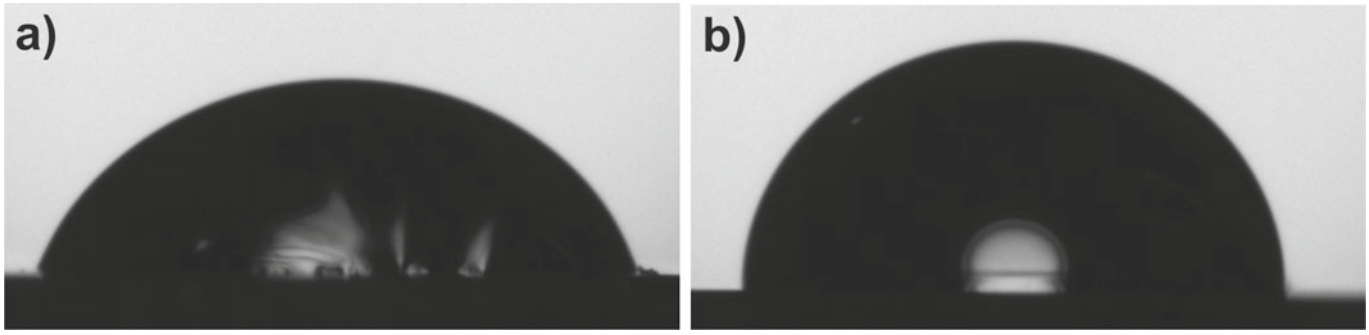

Figure 6. Images of water drops on the surface of a) hydrophilic TiO_2 and b) hydrophobic TiO_2:Nd thin films

TiO_2:Nd are shown in Figure 7. Ti2p states doublet peak can be observed (Figure 7a,b) in both cases. The distance between the positions of $Ti2p_{1/2}$ and $Ti2p_{3/2}$ peaks defined as ΔBE was about 5.6 eV for undoped TiO_2, which is the same according to the reference data[23]. The position of the doublet and the value of ΔBE testify about the presence of Ti^{4+} which creates TiO_2. In the case of TiO_2:Nd film we can observe an insignificant shift of peaks position and an increase of ΔBE (to 5.8 eV) which can be a result of Nd-doping[24]. The XPS

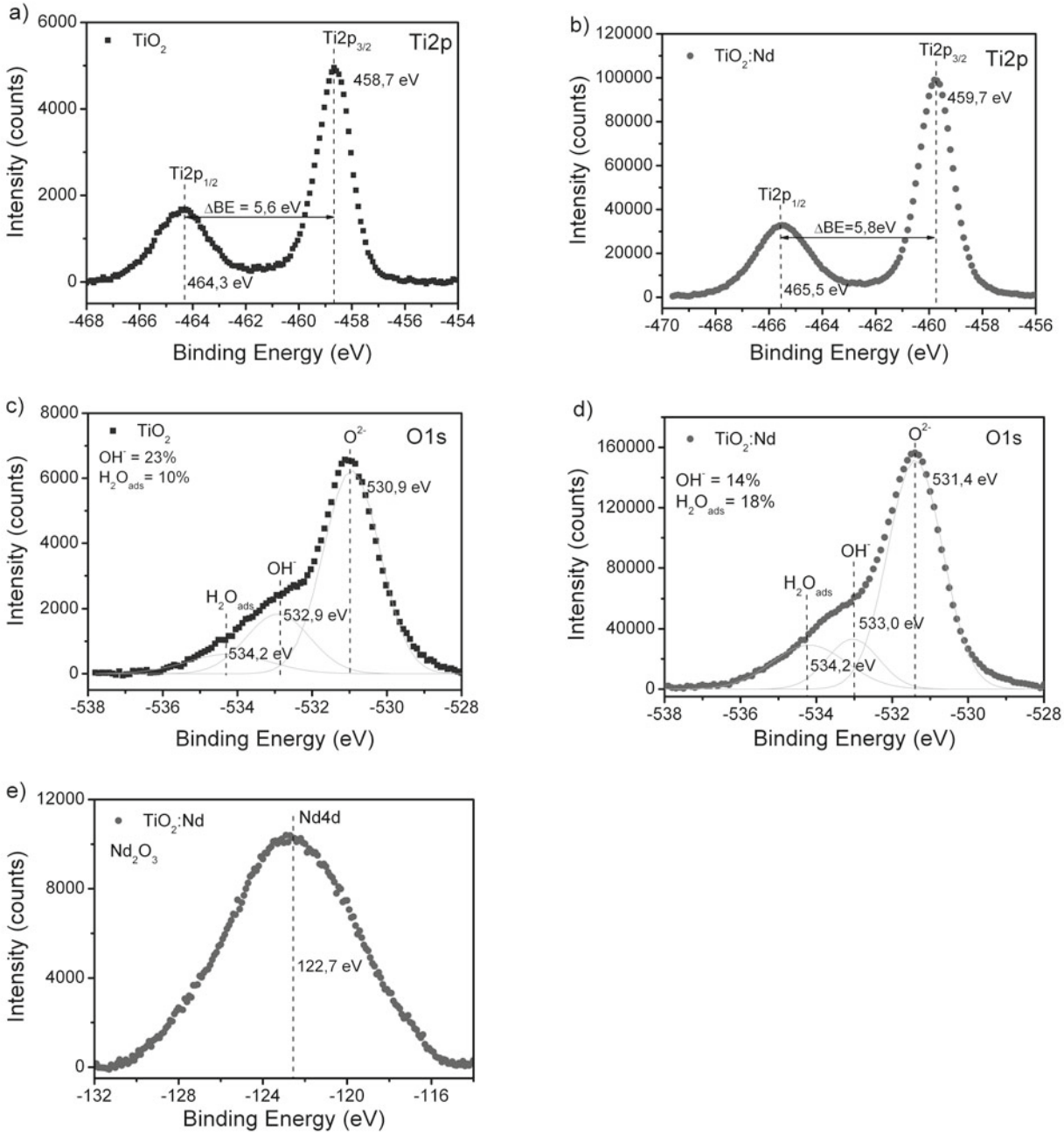

Figure 7. XPS spectra recorded in regions equivalent for Ti2p, O1s and Nd4d states for nanocrystalline TiO_2 and amorphous TiO_2:Nd thin films

measurements also allow an analysis of oxygen states and determination of surface adsorption of hydroxyl species and water molecules. Results obtained for O1s states (Figure 7c,d) were separated on peaks from O^{2-} – oxygen in compound with titanium or neodymium, and OH^- and H_2O_{ads} – adsorbed on the surface. We can observe that the summarised level of OH^- and H_2O_{ads} was about 30%. In the case of amorphous TiO_2:Nd film analysis of XPS spectrum in range equivalent to Nd4d state has shown that neodymium occurs in Nd^{3+} oxidation state. This suggests formation of Nd_2O_3 between crystallites of TiO_2.

DISCUSSION

Doping of nanocrystalline TiO_2-matrix results in the amorphous phase of TiO_2:Nd film. According to the literature and our previous experiments with Tb and Eu[10,14] we suggest that Nd, like some other lanthanides, is blocking the formation of crystalline structure in a high-energy sputtering process due to its dimensions. The difference in ion radius (1.13 nm for Nd^{3+} and 0.64 nm for Ti^{4+}) means that the neodymium (III) ion unlikely effectively impregnates into the crystal lattice position in TiO_2[15]. In the case of a manufactured film XPS experiments have revealed Nd_2O_3 form in the TiO_2 matrix. Therefore, neodymium cannot be built into the TiO_2 lattice. Moreover, homogenous distribution of Nd-dopant in the film excludes formation of its bigger aggregates and testifies to the same properties in different areas on the film surface.

The photocatalytic activity of the manufactured films was determined by phenol decomposition under UV-Vis light exposure. The results have shown that both films were photocatalytically active. Incorporation of 8.51 at. % of neodymium increased the phenol decomposition rate twice.

Usually, higher activity of the Nd-doped films can be obtained due to the electronic arrangement character of neodymium with the partially filled atomic *d* or *f* shells[15]. The absorption of equivalent energy during UV-Vis light exposure results in electron excitation and transition from Nd^{3+} $4f^3$ orbital. The surrounding of Nd^{3+} can react with Nd^{4+} ions obtained from the self-sensitization process and form the positively charged neodymium clusters $(Nd_n)^{m+}$ (m>3n). Nd-clusters have empty energy levels (sub-band) below the conduction band of TiO_2. So, the electronic transition from the matrix to empty levels can occur[15]. Such transition requires less energy than the valence-conduction band in TiO_2 and it also can proceed in the visible light[25]. However, in the case of the manufactured TiO_2:Nd film occurrence of such mechanism is less probable due to its weak absorption of the light in visible range. Figure 8 presents the absorption spectra for TiO_2 and TiO_2:Nd thin films as a function of energy in comparison with the spectrum of UV-Vis lamp, which was used for photocatalysis. It should be noticed that the absorption edge for TiO_2:Nd is strongly blue-shifted relative to TiO_2-rutile. Thus the TiO_2:Nd thin film absorbs just about 40% of the light, while the undoped TiO_2 has absorbed almost all light near UV. The schematic representation of the photo-induced phenol decomposition process is shown in Figure 9. We suggest that the photo-induced electrons are being transferred to $^4F_{3/2}$ level of Nd^{3+} ions via matrix defect states (*DS*), which are being located below the conduction band of TiO_2. Electrons from neodymium energy levels or from *DS* are trapped (*EC* – electron capturing) by O_2 (acceptors) and produce superoxides $O_2^{\bullet}$ (radical anions), which participates in the formation of hydroxyl radicals $OH^{\bullet}$. During light exposure also the holes called as positively charged vacancies (h^+), are created in the TiO_2 valance band. The holes are responsible for the extraction of electrons from water and hydroxyl species to produce hydroxyl radicals ($OH^{\bullet}$), which oxidizes (decomposes) phenol molecules on the surface. A phenomenon of higher photocatalytic activity of Nd-doped film can be explained as a higher efficiency of photo-generated electrons transfer from the conduction band of TiO_2 to O_2 via *DS* or energy levels of Nd^{3+} and higher number of oxygen vacancies in *DS* near valence band of TiO_2. Both phenomena are being responsible for producing hydroxyl radicals that fulfill a key-role in the decomposition process.

Except photo-generation and the mechanisms of carriers transferring in the film also surface adsorption level and wettability are important in the decomposition

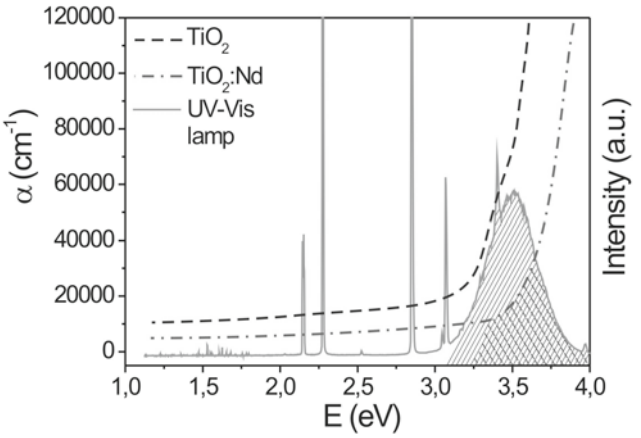

Figure 8. Absorption spectra of TiO_2 and TiO_2:Nd thin films in comparison with the spectrum of UV-Vis lamp, which was used for photocatalytic experiment

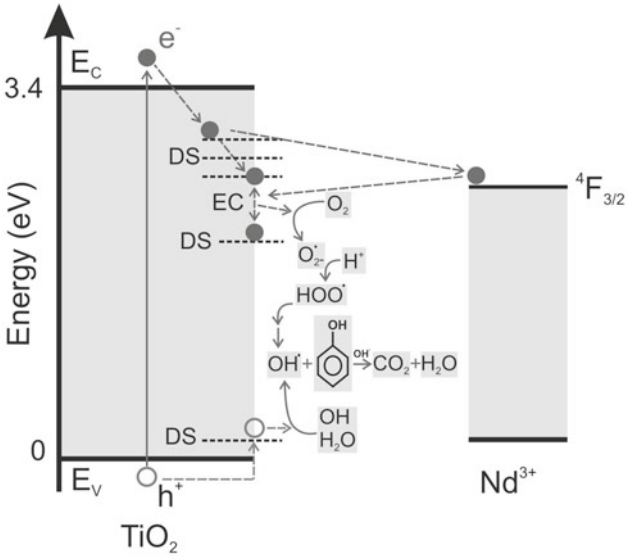

Figure 9. Schematic representation of the photo-induced phenol decomposition process

process. Analysis of surface adsorption has revealed that in both cases the total amount of OH species and H_2O_{ads} molecules was on the same level. But, it can be observed that the nanocrystalline, hydrophilic TiO_2 film attached more OH^- species due to higher surface reactivity, which is a result of a higher number of reactive places on grain edges. The TiO_2:Nd film adsorbs more H_2O molecules thanks to the hydrophobic character of the surface, which can be a consequence of the small roughness of the amorphous film.

CONCLUSIONS

In this work the photocatalytic activity in comparison with the structural, optical and surface properties of thin films was described. Thin films based on titanium dioxide were manufactured by a high-energy reactive magnetron sputtering process. The incorporation of Nd during sputtering process results in the change of TiO_2-matrix structure from the nanocrystalline rutile to the amorphous one, with an insignificant increase of high transparency in the visible light range. Doping with neodymium also produced a two-times increase of the photocatalytic activity of the matrix. The higher efficiency of the phenol decomposition process was obtained due to a higher quantity of the photo-generated charge carriers and more efficient mechanisms of energy transfer. Moreover, the incorporation of neodymium results in a significant decrease of the surface roughness which had an effect on the wettability and surface adsorption. The amorphous Nd-doped film adsorbed more H_2O molecules due to hydrophobic surface with very small roughness, while the hydrophilic surface of nanocrystalline TiO_2 matrix attached more OH^- species.

ACKNOWLEDGEMENTS

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

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