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Research Article

Correlation of Photocatalysis and Photoluminescence Effect in Relation to the Surface Properties of TiO_2:Tb Thin Films

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In this paper structural, optical, photoluminescence, and photocatalytic properties of TiO_2 and TiO_2:(2.6 at. % Tb) thin films have been compared. Thin films were prepared by high-energy reactive magnetron sputtering process, which enables obtaining highly nanocrystalline rutile structure of deposited films. Crystallites sizes were 8.7 nm and 6.6 nm for TiO_2 and TiO_2:Tb, respectively. Surface of prepared thin films was homogenous with small roughness of ca. 7.2 and 2.1 nm in case of TiO_2 and TiO_2:Tb samples, respectively. Optical properties measurements have shown that the incorporation of Tb into TiO_2 matrix has not changed significantly the thin films transparency. It also enables obtaining photoluminescence effect in wide range from 350 to 800 nm, what is unique phenomenon in case of TiO_2 with rutile structure. Moreover, it has been found that the incorporation of 2.6 at. % of Tb has increased the photocatalytic activity more than two times as compared to undoped TiO_2. Additionally, for the first time in the current state of the art, the relationship between photoluminescence effect, photocatalytic activity, and surface properties of TiO_2:Tb thin films has been theoretically explained.

1. Introduction

In the recent years there has been a continuous increase of the application possibilities of various metal oxide thin films with certain properties. Thin films play a key role in the development of innovative technologies, for example, in ophthalmic or protective coatings. One of the most important coating materials is titanium dioxide (TiO_2). It is caused by its many advantages like high transparency, high refraction index, thermal, chemical, and mechanical stability, and high photocatalytic activity [1–6].

Proper selection of technological process parameters can influence the TiO_2 crystal structure (brookite, anatase, rutile, or amorphous) and the crystallites sizes. Depending on the type of the crystal structure titanium dioxide may exhibit different properties, for example, optical, electrical, and chemical. Also doping the TiO_2 with various materials influences its structural, optical, and electrical properties [7–9]. Moreover, the properties of thin films based on titanium dioxide can be further modified by the application of postprocess annealing [10–12]. The changes are then caused mainly by the increase in the crystallites sizes and as a result of the structure phase transformation, which usually takes place in elevated temperature.

Some desired properties of titanium dioxide can be obtained by doping with rare earth elements (REs). The application of the Res especially enables obtaining the photoluminescence effect. In practice, such materials can be used, for example, as light emitters in displays or in medical diagnostics. During the past two decades, a dynamic increase in interest of doping such oxides like SiO_2, ZrO_2, SnO_2, ZnO, and TiO_2 with lanthanides has been observed [9, 12–23]. In the present paper TiO_2 doped with terbium (Tb) has been described. Terbium is an f-electron element with the oxidation states of +3 and +4. The doping of oxides with terbium gives a broad photoluminescence spectrum with the maximum emission at the wavelength range corresponding to green light. However, there are rare examples in literature resources of light emission observed from terbium-doped TiO_2 thin films [24]

Incorporation of lanthanides into TiO_2 matrix also allows the modification of surface properties, what is crucial in

photocatalysis processes. Photoinduced carriers formed in the matrix can undergo the recombination process, which reduce the photocatalytic activity. Carriers can be also intercepted by the trapping centers, which allows to avoid the recombination, or take part in reaction of pollutants decomposition and form oxidizing compounds. According to Liqiang et al. [25], photocatalytic activity of TiO_2 depends directly on amount of generated carriers, but its efficiency is determined by process of separation, recombination, capture, and transfer of carriers to the surface. It results from the fact that all oxidizing and reducing processes take place at the surface of TiO_2 [4, 26, 27]. Only pollutants, which are in contact with TiO_2 crystallites, can be decomposed. Significant factor in photocatalytic reaction is oxygen amount adsorbed at TiO_2 surface, because it inhibits the carriers recombination [28]. Also holes play significant role, because reaction based on those kinds of carriers is characterized by high quantum efficiency, particularly in oxidizing reaction of TiO_2 surface [28]. Active oxygen, hydroxide radicals, and hydrogen peroxide are the most reactive species formed in photocatalysis process.

For the purpose of the present work, thin films have been manufactured by magnetron sputtering method. In industrial application, sputtering processes are commonly used for deposition of thin oxide films [29–34]. These methods allow for deposition of films on the basis of infusible materials in relatively simple and cost-effective way. Additionally, magnetron sputtering gives the opportunity to control structure and stoichiometry of manufactured thin films. Huge advantage of this process is the possibility of deposition of dielectric, semiconductor, and metal films on large surfaces with different shapes. Proper selection of the magnetron sputtering process parameters enables the densification of thin-film crystal structure. The use of the modified process can result in nanocrystalline structure of deposited films with crystallites sizes varied from few to several nanometers [35, 36]. Densification of the structure is obtained by an increase in the sputtered species energy, that condenses at the substrate surface. This can be obtained by, for example, decrease of working gas pressure, increase in magnetron powering conditions, and application of voltage bias to the substrate.

In this paper, the influence of 2.6 at. % of Tb dopant on structural, optical, and photocatalytic properties of TiO_2 has been presented. Due to the lack of such description in the current state of the art, novel theoretical explanation of the relationship of photoluminescence effect and photocatalytic activity and the surface properties of TiO_2 doped with terbium has been presented.

2. Experimental

Titanium dioxide thin films doped with terbium have been deposited by high-energy reactive magnetron sputtering process (HERMS) [36–38]. Thin films were deposited in pure oxygen plasma (without argon as a working gas) by sputtering of metallic titanium target. Doping was obtained by sputtering of Ti-Tb mosaic target. Several sets of TiO_2 thin films doped with different amount of terbium were prepared. Samples consisted of 2.6 at. % of Tb were selected for further investigation due to simultaneous existence of photoluminescence and photocatalytic effects. Thickness of TiO_2 and TiO_2:Tb thin films was equal to 377 nm and 585 nm, respectively. The amount of the terbium dopant has been analyzed using energy-dispersive spectrometer.

X-ray diffraction (XRD) measurements were performed with the aid of Dron-2 powder diffractometer with Fe-filtered Co Kα radiation. Average crystallite sizes were determined using the standard Sheerer formula. Surface morphology of deposited samples was examined by atomic force microscope UHV VT AFM/STM Omicron operating in contact mode.

Optical properties of TiO_2:Tb thin films were investigated on the basis of transmission spectra. Transmission is the basic parameter defining the transparency level of the thin films and is defined as the ratio of light passing through the sample to the light incident the sample.

Emission properties of TiO_2:Tb thin films deposited on silica substrates were investigated by the photoluminescence (PL) method. For photoluminescence measurements UV argon laser with the excitation wavelength of 302 nm was used. Thin films were measured at room temperature.

The influence of terbium doping on photocatalytic properties of nanocrystalline TiO_2 thin films was estimated based on phenol decomposition reaction. The experimental setup consisted of a UV-Vis light source (6×20 W Phillips lamps with intensity of UV and Vis radiation: 183 W/m^2 and 167 W/m^2, resp.) and cylindrical reservoir which contained 100 mL of solution with the phenol concentration of 10 mg/L. To avoid the heating of the solution, the reaction temperature was controlled by circulation of water through the jacket at constant temperature of ca. 15°C. All experiments were carried out under agitation with a magnetic stirrer operating at 500 rpm in order to provide a good mixing of the suspension. No external oxygen supply was used. The phenol concentration was calculated from the absorption peak at 270 nm by means of a calibration curve. After 30 minutes of premixing at constant temperature, lights were switched on to initiate the reaction. To determine the change of the phenol concentration, samples of phenol solutions were withdrawn regularly every 60 minutes for 5 hours from the reactor. The final transparent solution was poured into a quartz cuvette and analyzed by UV-Vis spectrophotometer, in the wavelength range of 200–700 nm.

3. Results

As it was mentioned above, doping with lanthanides can result in modification of structural properties of TiO_2 thin films in a wide range. The significant role plays the amount of the dopant incorporated into titanium dioxide matrix. By selection of the dopant amount the specified crystal structure of TiO_2 directly after deposition process can be obtained. In Figure 1 results of XRD measurements of undoped TiO_2 and TiO_2:Tb deposited on silica substrates have been presented.

Broad peaks in the XRD patterns have shown that both thin films had nanocrystalline structure. Undoped TiO_2 have rutile structure with crystallites sizes of 8.7 nm. Doping with 2.6 at. % of terbium the TiO_2 matrix resulted in 25% decrease

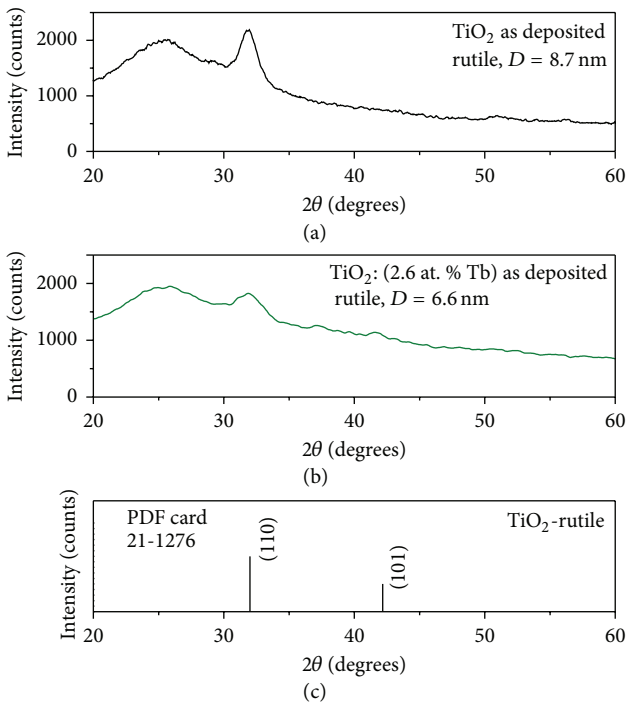

FIGURE 1: XRD measurements results of (a) undoped TiO_2 thin film, (b) TiO_2:Tb thin film, and (c) standard patterns for TiO_2-rutile structure. D: crystallite size.

of crystallites sizes to 6.6 nm; however, the structure was still the rutile [37, 39, 40]. No diffraction peaks of Tb or Tb-O compounds have been found. These indicate that Tb (or its compounds) particles were too small to be detected by XRD or that Tb ions were incorporated into TiO_2 nanocrystals. Taking into account the ionic radius of Tb^{3+} the latter is less probable. It is more reasonable to assume that Tb dopant is localized at the surface of TiO_2 nanocrystals.

Structure densification is clearly seen on AFM images presented in Figure 2. Despite nanocrystalline structure, as-deposited thin films are very homogenous with small surface roughness. Root mean square (RMS) value is 3 times lower in case of terbium-doped titanium dioxide in comparison to undoped matrix. It was 7.2 and 2.1 for TiO_2 and TiO_2:Tb thin films, respectively. Symmetrical shape of grains size histogram in Z direction testifies about homogenous distribution of grains in deposited thin films.

Influence of terbium doping on transparency of TiO_2 thin films was determined on the basis of transmission characteristics presented in Figure 3(a). Visible minima and maxima are connected with light interferences. Measurements have shown that the incorporation of Tb into TiO_2 matrix with the rutile structure has not changed significantly the transparency of the thin films. Moreover, doping has shifted the cutoff wavelength through longer wavelengths.

Transmission measurements results allow for estimation of absorption coefficient, and on this basis the width of optical energy gap (E_g^{opt}) has been determined. Characteristics, which were used to define optical energy gap, are presented in Figure 3(b). Results have shown that lower E_g^{opt} value was obtained for TiO_2:Tb and was equal to 2.96 eV.

As the result of TiO_2 matrix excitation with ultraviolet illumination, the photoluminescence spectrum in wide emission range, from 350 to 800 nm, has been observed (Figure 4). This spectrum is the superposition of six emission lines of various wavelengths, which corresponds to radiative recombination of carriers from different energy levels. Characteristic emission lines of Tb^{3+} ions, which occur at the wavelength of: 418 nm, 431 nm, 491 nm, 545 nm, and 619, correspond to electron transitions between $^5D_3$–$^7F_5$, $^5D_3$–$^7F_4$, $^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$, and $^5D_4$–$^7F_3$ levels, respectively. Moreover, light emission at 370 nm is connected with defect states transitions of titanium dioxide. Photoluminescence of terbium ions in TiO_2 matrix with rutile structure is unique phenomenon. Sheng et al. [24] have confirmed that such unique phenomenon was obtained only by authors of current paper.

Kinetics of photocatalytic decomposition of organic compounds at the TiO_2 surface is usually consistent with Langmuire-Hinshelwood relationship [27, 41, 42]:

$$r = -\frac{dc}{dt} = \frac{kKc}{1 + Kc}, \tag{1}$$

where r is oxidizing rate, c is solution concentration, t is exposure time, k is reaction rate constant, and K is absorption coefficient.

For solutions with low initial concentration c_o (at 10^{-3} mol level) the above equation can be simplified as follows [14, 28, 41]:

$$\ln\left(\frac{c_o}{c}\right) = k \cdot K \cdot t = k_{\text{RRC}} \cdot t \tag{2}$$

or

$$c_t = c_o \cdot \exp\left(-k_{\text{RRC}} t\right), \tag{3}$$

where k_{RRC} is corrected reaction rate constant and c_t is solution concentration after time t.

The value of corrected reaction rate constant can be determined from slope of $\ln(c/c_o)$ characteristic in the function of light exposure t.

Results of phenol decomposition have shown that investigated thin films were photocatalytic. Photocatalytic activity was determined under the exposure to UV light based on dependence of $\ln(c/c_o)$ in time function. Measurement results for TiO_2 and TiO_2: (2.6 at. % Tb) thin films have been shown in Figure 5. Those results were used to calculate phenol decomposition as thin film's photocatalytic activity, which can be defined as

$$\frac{(c/c_o)}{p} \cdot 100\%, \tag{4}$$

where p is area of thin film.

By the reason of small sample size of approximately 1 cm^2, the phenol decomposition was estimated as %/cm^2. It has been found that the incorporation of 2.6 at. % of Tb has increased the photocatalytic activity more than two times as

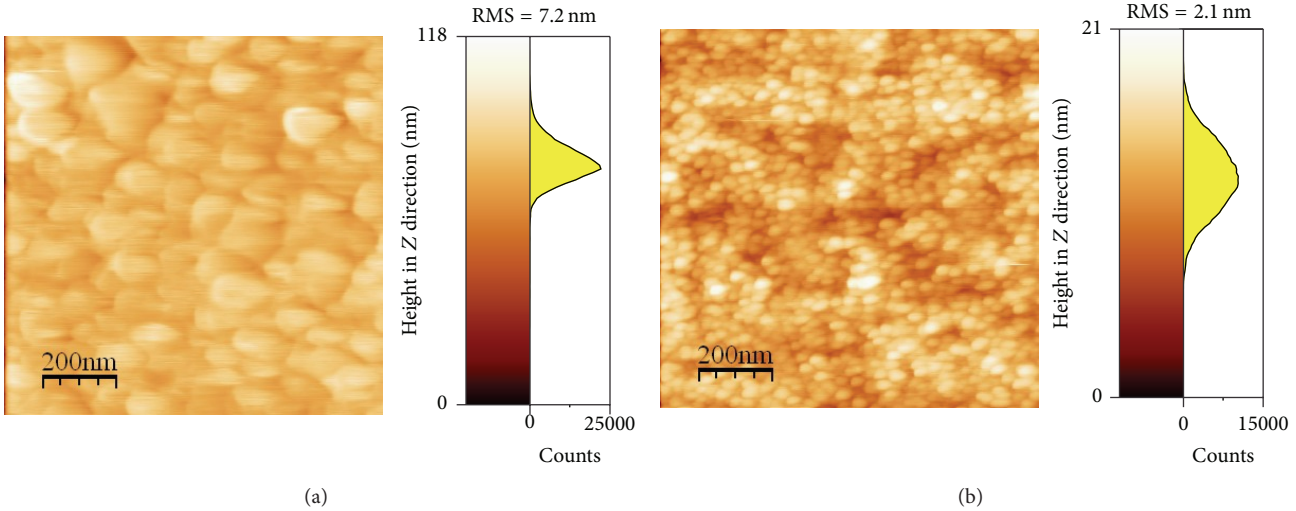

FIGURE 2: AFM images of (a) TiO_2 thin film and (b) TiO_2:Tb thin film with height distribution of grains size in Z direction and surface roughness determined by RMS factor.

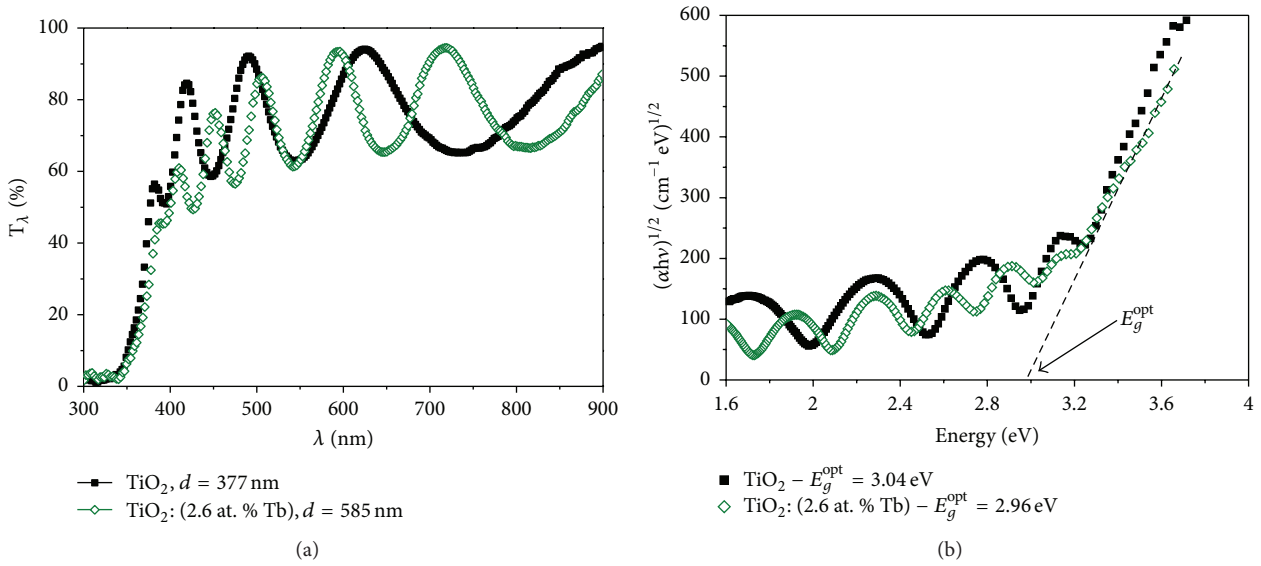

FIGURE 3: Optical properties of TiO_2 and TiO_2:Tb: (a) transmission characteristics and (b) Tauc plots for allowed indirect transitions. d: thin film thickness.

compared to undoped TiO_2 matrix. After five hours TiO_2 doped with terbium has decomposed ca. 4.7% of phenol, while, in the same time, undoped TiO_2 has decomposed just 2.2% of phenol. Such results are unique in case of TiO_2 with the rutile structure. Corrected reaction rate constant was also two times higher for TiO_2:Tb in comparison to TiO_2 thin film.

4. Discussion

Nanocrystalline TiO_2 thin film doped with Tb exhibits photoluminescence properties and increased photocatalytic activity in comparison to undoped nanocrystalline TiO_2 thin film with rutile structure. From the state of the art it is well known that materials with nanocrystalline structure composed of crystallites in size of less than 10 nm exhibit higher photoluminescence or photocatalytic activity as compared to materials with larger crystallites [43–45]. In case of materials with such nanocrystalline structure, the influence of quantum size effect on luminescence properties was first described by Bhargawa et al. [46]. According to the literature [43–45], both specific energy levels and the decrease of energy band gap in nanocrystalline oxide matrix can be observed as size of the crystallites is in the range from 2 to 10 nm. Size of the crystallites has an essential influence on series of different properties of metal oxides connected with the degree of the surface area development. Similarly, as in case of photoluminescence, also photocatalytic activity of the thin

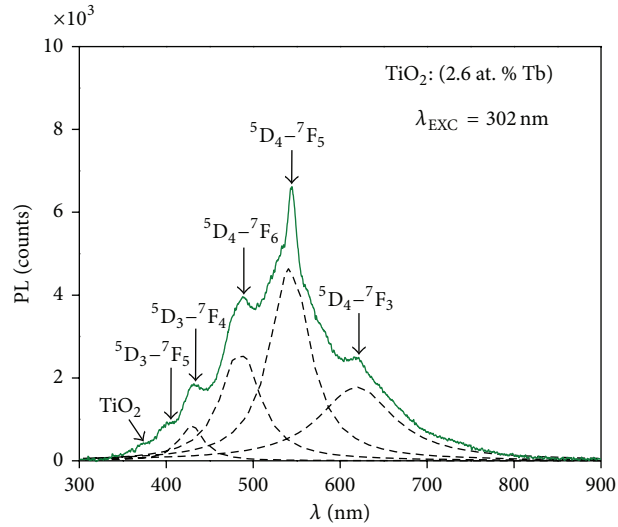

Figure 4: TiO_2:Tb thin film photoluminescence spectrum under the excitation of Ar laser.

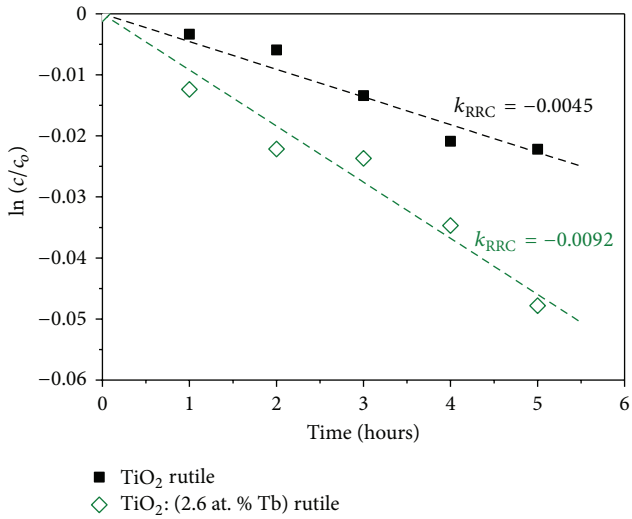

Figure 5: Photocatalytic activity of TiO_2 and TiO_2:Tb thin films with rutile structure exposed to UV light time function based on dependence of $\ln(c/c_o)$.

films based on TiO_2 is the highest for matrix composed of crystallites in size that ranges from 5 to 10 nm [42, 43, 47].

In current state of the art only one article [25] can be found, which tries to describe mutual relationship between the photocatalysis and the photoluminescence. The key factor for conjunction of photoluminescence effect and the decomposition of pollutants, which proceeds at the surface of material, is the oxygen vacancies concentration [25]. These defects are the trapping centers, which inhibit recombination and simultaneously enables on efficient joining electrons with oxygen. Moreover, they are active centers for surface absorption of water particles and OH^- groups, which are necessary for carrying out of the photocatalytic reaction.

One of the main limits for these both effects is relatively low total quantum efficiency connected with high level of recombination of the electron-hole pairs generated at the TiO_2 surface [25]. Therefore, increasing of light emission intensity or photocatalytic activity of thin films based on TiO_2 can be obtained by, for example, decrease of crystallites size [48, 49] or by doping [8, 50, 51]. It is because, for nanomaterials, diffusion rate is much larger than recombination rate. The most often, thin films with high photocatalytic activity exhibit weak photoluminescence effect, which is connected with low carriers recombination efficiency [52, 53]. However, in the current state of the art there are also examples of materials characterized by strong photoluminescence effect and high photocatalytic activity [54, 55]. It indicates that these results are inconsistent, and explanation of reasons of such different interpretations needs much more detailed analysis of carriers: excitation and recombination mechanisms. For TiO_2:(2.6% at. % Tb) strong photoluminescence and high photocatalytic activity have been found simultaneously; hence, it is necessary to elaborate on the model, which takes into consideration the relationship between these two phenomena.

Explanation of relationship between photoluminescence effect and photocatalysis phenomenon needs the complex analysis of different types of recombination, which occurs in titanium dioxide [25, 56–59]. In such material, electrons and holes are generated under the photoexcitation. Photoexcited electrons transit to the conduction band and fill the energy levels, which correspond to excitation energy. These carriers can easily recombine and return to valence band in different ways, and their energy can be emitted as photons or phonons. Excited electrons can transit directly to valence band with release of energy in the form of light emission. This type of direct transitions can take place also in case of electrons with higher energy than E_g; however, transfer of carriers proceeds then directly from levels situated above the bottom edge of conduction band. The recombination process can also occur via sublevels in energy band gap (defect states of the matrix) and it is an indirect radiative transition.

In case of photoluminescence effect, which is present as the result of direct radiative recombination, lower recombination of generated carriers causes the decrease of light emission intensity. However, this process simultaneously increases the photocatalytic activity of the semiconductor [53]. Whereas, in case of indirect radiative recombination, the relation between photoluminescence effect intensity and photocatalytic activity depends on the type of the incorporated dopant. According to Liqiang et al. [25], lower recombination cause smaller photoluminescence intensity and higher photocatalytic activity of semiconductor. Although, sometimes also the increase of defects amount and oxygen vacancies at the thin film surface allow to obtain higher intensity of photoluminescence and photocatalytic activity [25]. Such relations can be applied for analysis of TiO_2 thin films doped with rare earth elements, in which emission levels are below defect states of the matrix. For prepared TiO_2:(2.6 at. % Tb) thin film, none of the abovementioned explanations can be accepted as a basis for analysis of relation between photoluminescence and photocatalysis phenomena. Therefore, it was necessary to elaborate on individual model, which takes into consideration properties of prepared thin films and mechanisms occurring during both discussed processes.

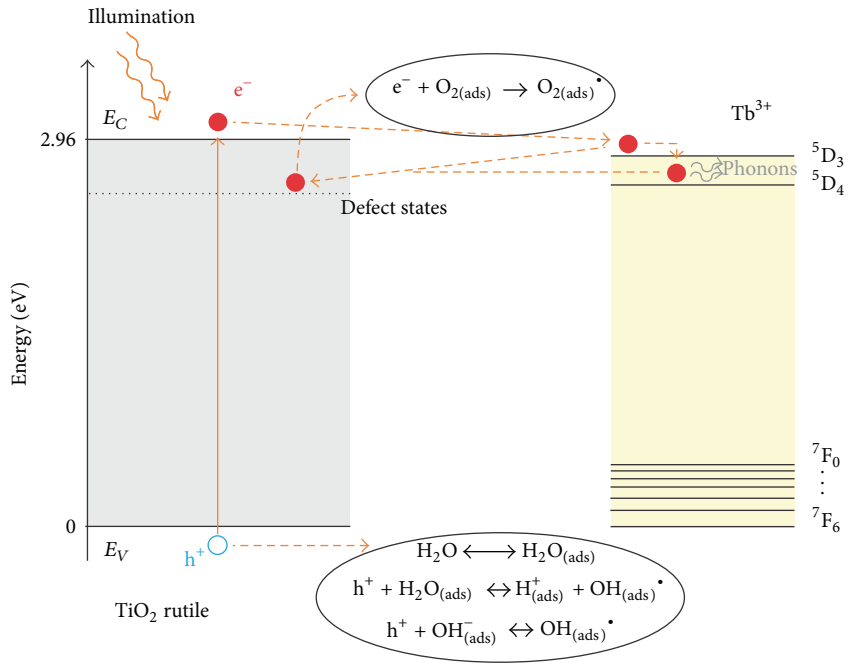

Figure 6: The scheme of processes proceeding at the TiO_2:Tb surface with rutile structure. Designations: E_c, E_v, energy of the bottom edge of the conduction band and the top of the valence band, respectively; e^-, electron; h^+, hole; O_2, oxygen; $O_2^{\bullet}$, oxygen radical; H_2O, water; H^+, hydrogen; OH^-, hydroxide group; $OH^{\bullet}$, hydroxide radical; (ads), surface adsorption.

The abovementioned processes proceed at the titanium dioxide nanograin surface with rutile structure. Under the exposure to light, generated electrons in matrix pass from the valence to conduction band and take part in reaction with oxygen adsorbed at the film surface, creating oxygen radicals ($O_2^{\bullet}$) [28]. On the other hand, holes from valence band take part in reaction with water and hydroxide groups (OH^-) adsorbed at the surface. Consequently hydroxide radicals ($OH^{\bullet}$) are formed [28]. Moreover, electrons trapped by the matrix's defect states also can take part in process of oxygen radicals formation, which is caused by considerably shorter time of diffusion than recombination in case of nanograins. In the following stages, at the surface of nanocrystalline film, the decomposition of contaminations proceeds with the participation of oxygen ($O_2^{\bullet}$) and hydroxide ($OH^{\bullet}$) radicals. Final products of these reactions are CO_2 and H_2O.

Doping TiO_2 matrix with 2.6 at. % of terbium allows obtaining thin film with photoluminescence properties, which exhibits two times higher photocatalytic activity as compared to undoped titanium dioxide. The incorporation of terbium dopant causes increase in the number of energy levels to which electrons generated in TiO_2 matrix can be transferred. Therefore, photocatalytic rate increases and favorably influences thin film activity. In Figure 6 scheme of processes proceeding at the TiO_2:Tb surface with the rutile structure is presented.

In case of photocatalysis process, presence of terbium at the surface causes changes of the surface energy parameters. Both terbium ions on +3 and +4 oxidation states can accept and return electrons. Presence of these ions facilitates the transfer of carriers, which is necessary in photocatalysis reaction.

Briefly, based on structural and optical properties analysis of the TiO_2:Tb thin films, it was found that the incorporation of terbium dopant during high-energy reactive magnetron sputtering process allowed for preparing of homogenous, densely packed films, which were composed of crystallites in size of 6.6 nm. Such small crystallites sizes and significantly higher degree of order of film structure (in comparison to undoped titanium dioxide) favorably influence both discussed phenomena by the increasing of active area. Smaller crystallites size causes that the range of transition to make for electrons is also smaller [25, 42, 43]. Therefore, the probability of carrier transfer between the TiO_2 crystallites and Tb ions localized at the surface is large. Except nanocrystalline structure, the key role for both phenomena plays amount of the dopant, which should be incorporated into TiO_2 matrix in high-energy deposition process. It is necessary to incorporate the sufficient amount of the dopant to obtain the suitable number of the ions at the +3 oxidation state.

5. Conclusions

In present paper analysis of the influence of 2.6 at. % terbium dopant on the TiO_2:Tb thin films properties has been outlined. Thin films deposited in high-energy reactive magnetron sputtering process were homogenous and densely packed. TiO_2:Tb film had rutile structure with crystallites size of 6.6 nm.

Investigations of photocatalytic properties have shown that doping with terbium favorably influence the increase

of TiO_2 matrix surface activity. Moreover, based on optical properties analysis, it was found that terbium did not deteriorate the high transparency of TiO_2, but influence the position shift of cutoff wavelength and width of optical band gap. The incorporation of terbium allowed for obtaining photoluminescence effect of Tb^{3+} in TiO_2 matrix with the rutile structure, which is unique and has not been reported yet by other authors. TiO_2:Tb after 5 hours of the photocatalytic activity investigation has decomposed two times more phenol as compared to undoped TiO_2.

Results of investigations have shown that, to increase the photocatalytic activity of TiO_2:Tb thin films the presence of Tb^{3+} at the surface of TiO_2 nanocrystals is necessary. The addition of terbium to TiO_2 matrix caused that additional energy levels have appeared and favorably influenced energy transfer mechanism. Thanks to terbium doping of titanium dioxide, it was possible to obtain effective photoinduced carriers transfer mechanism, which is necessary requirement for the presence of both phenomena: photocatalysis and photoluminescence.

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