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Influence of europium on structure modification of TiO_2 thin films prepared by high energy magnetron sputtering process

Damian Wojcieszak[1], Michal Mazur[1], Des Gibson[2], Grzegorz Zatryb[3], Danuta Kaczmarek[1], Jan Misiewicz[3]

[1]Wroclaw University of Technology, Faculty of Microsystem Electronics and Photonics, Janiszewskiego 11/17, 50-372 Wroclaw, Poland

[2]Institute of Thin Films, Sensors & Imaging, University of the West of Scotland, Scottish Universities Physics Alliance, High Street, Paisley PA1 2BE, United Kingdom

[3]Institute of Physics, Wroclaw University of Technology, Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland

(e-mail of corresponding author: damian.wojcieszak@pwr.edu.pl)

Abstract: In this work the modification of structural properties of TiO_2 thin films by doping with europium was described. Thin films were prepared by high energy magnetron sputtering process. Application of such deposition type resulted in receiving of undoped titanium dioxide films with nanocrystalline rutile structure directly after deposition (without additional annealing). It was found that the properties of coatings prepared by high energy process can be modified by doping with europium. The influence of Eu on the microstructure of TiO_2 was determined based on the results of X-ray diffraction, transmission electron microscopy, Raman spectroscopy and photoluminescence measurements. It was found that 0.2 at. % and 0.4 at. % of the dopant was sufficient to receive titania films with the anatase form. The type of TiO_2 structure was confirmed with the aid of Raman spectroscopy and by TEM observations. However, the amount of Eu-dopant had direct impact on PL intensity as well as the number of defect states in the film.

Keywords: thin film, titanium dioxide, europium, microstructure, high energy sputtering, photoluminescence

Introduction

Titanium dioxide is a well known material due to its many advantages such as high transparency, non-toxicity, high stability (chemical, thermal and mechanical), high photocatalytic activity, etc. [1-5]. TiO_2 may occur in three different crystalline forms - brookite, anatase and rutile, but only the last two have practical application [1, 2]. Films with the anatase structure are used as active layers in sensors [6] or as self-cleaning coatings [7], while the rutile structure is more desired for protective coatings [8] or in construction of optical filters [9]. Properties of TiO_2 can be modified by the change of deposition parameters [10, 11], doping [12-15] or post-process treatment (eg. annealing) [16, 17]. Especially, the change of deposition parameters is the most interesting for industry (no need for special composition of target materials and extra steps of production process). Nowadays, very important in the coating technology is preparation of films with nanocrystalline structure. Many examples in the literature [18- 21] testify, that application of so called 'high energy' processes results in well nanocrystalline structure of the coatings. Typically, TiO_2 thin films have anatase structure directly after deposition in 'classic' sputtering process and after additional annealing in high temperature two-phase system (anatase-rutile) or pure rutile structure can be obtained [1]. According to work [18], application of lower pressure in the chamber during conventional sputtering process results in two-phase system receiving (without extra annealing). Moreover, application of low pressure and increase of supply power (increase of energy of sputtered particles) gives a chance for preparation of coatings with fine nanocrystaline rutile structure directly after deposition. Such modification has a direct impact on the increase of hardness [20]. As mentioned above, doping is also an important way for modification of TiO_2 properties. According to the

literature [22-28] and our previous works [29-35] doping with lanthanides (eg. Eu, Tb or Nb) has a significant impact on the microstructure and other properties of titania films as well as their application area. In this work the effect of Eu-dopant on the structural properties of TiO_2 thin films was described. Europium is a well known rare-earth material, often used in order to obtain luminescence. In dependence from its oxidation state (2+, 3+) the maximum of PL spectrum can be located in region equivalent for green or red light [36]. This work contains a relation between 'high energy' process, doping with europium and the microstructure of TiO_2 coatings.

Experimental part

TiO_2 and TiO_2:Eu thin films were prepared by magnetron sputtering method. Applied process can be called as 'high energy' sputtering. Detailed description of this method was described elsewhere [20, 37, 38]. During deposition process metallic Ti and Ti-Eu discs with diameter of 30 mm were sputtered for 180 min in pure oxygen atmosphere with the gas flow of 16 sccm, what resulted in $8 \cdot 10^{-3}$ mbar pressure in the working chamber. The distance between all sputtered targets and the substrates (SiO_2, Si) was 160 mm. The thickness of as-deposited coatings was ca. 250 nm.

The surface morphology and elemental composition of TiO_2 and TiO_2:Eu thin films was investigated with the aid of a FESEM FEI Nova NanoSEM 230 scanning electron microscope equipped with EDS spectrometer (EDAX Genesis). Structural properties of the films were determined based on the results of the X-Ray Diffraction (XRD) method. For the measurements, Siemens 5005 (Siemens, Germany) powder diffractometer with Cu Kα X-ray employing Bragg-Brentano reflecting geometry parafocusing optics was used. The step size was equal to 0.02° in 2θ range, while time-per-step was 5 s. The average crystallite sizes was calculated using Debye-Scherer's formula from the full width at half maximum (FWHM).

The crystal structure of TiO_2:Eu thin films was also characterized by a TECNAI G^2 FEG Super-Twin (200 kV) transmission and scanning electron microscope fitted with a high angle annular dark field (HAADF) detector. Transmission electron microscope was equipped with both side-entry wide angle SIS and on-axis bottom mounted Gatan 2K CCD cameras. For TEM analysis thin foils were prepared using a focused ion beam (FIB Quanta 3D system) equipped with an Omniprobe lift-out system. The photoluminescence measurements were performed at the room temperature using an excitation source operating at 266 nm and 400 nm high-pass filter. The PL signal was measured by Ocean Optics HR4000 spectrophotometer.

Results and discussion

Influence of europium on the structure of titanium dioxide was examined by SEM measurements. For the analysis undoped TiO_2 and TiO_2:Eu thin films with 0.2 at. % and 0.4 at. %. of the dopant were used. Material composition was determined by x-ray microanalysis. In the Fig. 1 SEM images of as-deposited films surface are shown. As it can be seen all of them were homogenous. For both TiO_2:Eu films (at magnification of x200k) grains in size from a dozen to a few hundred nanometers can be observed (Fig. 1b,c). The grains in TiO_2:(0.2 at. % Eu) were about four times greater as-compared to TiO_2:(0.4 at. % Eu) film. Moreover, it is worth to emphasize that SEM images of undoped titanium dioxide (Fig. 1a) indicate that this film had fine-grained structure, built from the smallest grains than both TiO_2:Eu films.

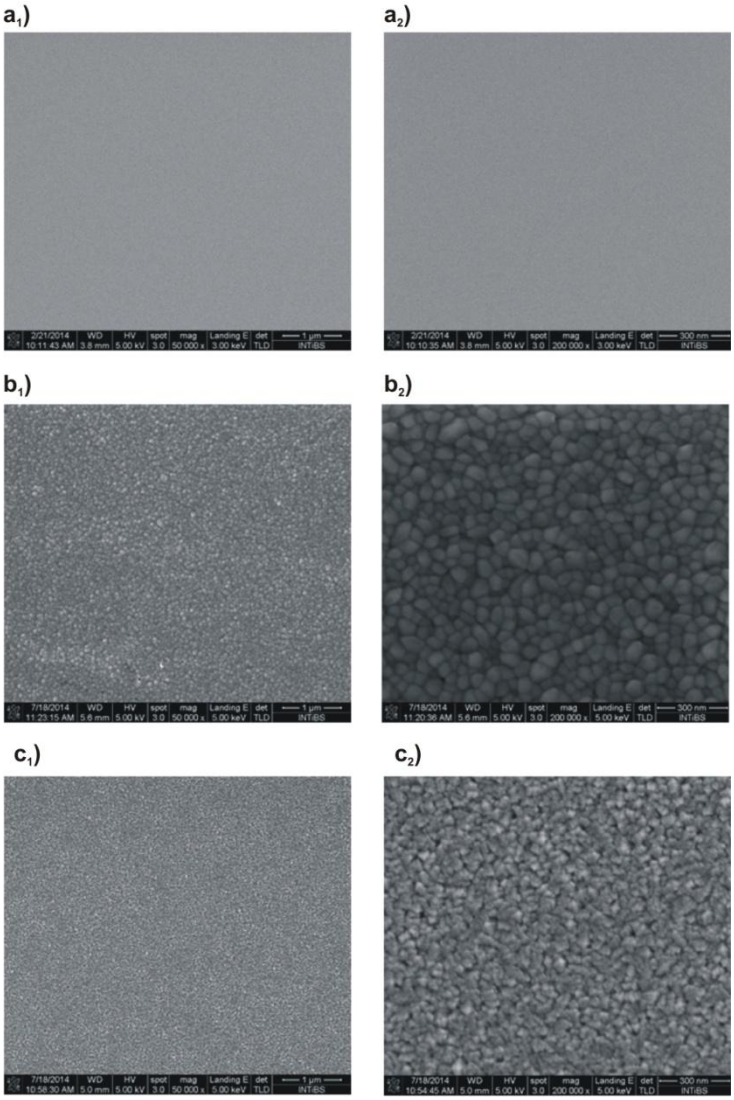

Fig. 1. SEM images of: a) TiO_2, b) TiO_2:(0.2 at. % Eu), c) TiO_2:(0.4 at. % Eu) thin films

The influence of europium on the microstructure of titanium dioxide was examined by x-ray diffraction. The XRD patterns are shown in Fig. 2 and results are summarized in Table 1. It was found that all examined films had crystalline nature. The structure of undoped TiO_2 was dominated by the rutile phase (Fig. 2a). The average size of crystallites (*D*) was 7.1 nm and it corresponds to (110) crystal plane [39]. In the case of the coatings with europium significant effect of this dopant on the titania structure can be observed. In contrast to the undoped film, TiO_2:(0.2 at. % Eu) had the anatase form. Presence of peaks on the XRD pattern at 2θ = 25.26^o and 55.03^o corresponds to (101) and (211) crystal planes of anatase, respectively (Fig.

2b) [40]. This film was built from crystallites in size of 18.8 nm ÷21.7 nm, which is ca. 3-times higher as-compared to undoped titania. The intensity of reflections from both anatase planes testify about the vast majority of crystallites related to (101) plane (D = 21.7 nm). Greater amount of the dopant in the film results in well crystalline anatase structure. XRD peaks located at 2θ = 25.37°, 37.34° and 48.26° correspond to (101), (103) and (200) crystal planes of the TiO_2 - anatase form, respectively (Fig. 2c) [40]. The most intensive reflection comes from (103) plane, so the vast majority of crystallites in average size of 28.3 nm was dominant in the TiO_2:(0.4 at. % Eu) film. The contribution of crystallites in size of 23.1 nm was also significant, due to high intensity of reflection from (101) plane. This film was also built from crystallites in size of ca. 15.6 nm - related to (200) crystal plane, but its volume was relatively low. The XRD results indicate on occurrence of tensile stress in the structure of TiO_2 and TiO_2:(0.2 at. % Eu) thin films due to positive value of Δd, which is a relative difference between measured (d) and standard interplanar distance (d_{PDF}) ($\Delta d = [d - d_{PDF}]/d_{PDF}$) (Table. 1). In the case of the coating with 0.4 at. % of Eu the situation is different and the values of Δd parameter have a negative sign, which may point to compressive stress.

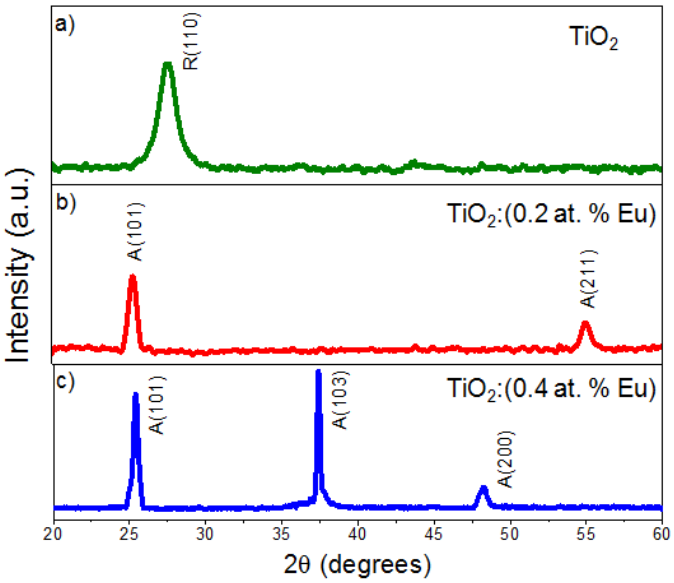

Fig. 2. XRD patterns of a) TiO_2, b) TiO_2:(0.2 at. % Eu) and c) TiO_2:(0.4 at. % Eu) thin films

Table 1. Structural parameters of TiO_2 and TiO_2:(0.2 and 0.4 at. % Eu) thin films based on XRD

Thin film		Crystal plane (hkl)	Phase	2θ (degrees)	*D* (nm)	*d* (nm)	d_{PDF} (nm)	*Δd* (%)
TiO_2		(110)	rutile	27.60	7.1	0.3229	0.3247	+0.55
TiO_2:Eu	0.2 at. %	(101)	anatase	25.26	21.7	0.3523	0.3520	+0.09
		(211)		55.03	18.8	0.1667	0.1687	+1.16
	0.4 at. %	(101)	anatase	25.37	23.1	0.3507	0.3520	-0.37
		(103)		37.34	28.3	0.2404	0.2431	-1.11
		(200)		48.26	15.6	0.1884	0.1892	-0.42

Designations: *D* – average crystallites size, *d* – interplanar distance, d_{PDF} – standard interplanar distance, *Δd* – relative difference between *d* and d_{PDF}, where $\Delta d=[d-d_{PDF}]/d_{PDF}$ (%)

Influence of Eu-dopant on the microstructure of TiO_2 thin films was also investigated with the aid of Raman spectroscopy (Fig. 3). In the case of undoped titania matrix peaks in the spectrum at 144, 240, 445, 610 and 825 cm^{-1} correspond to five Raman active modes: B_{1g}^{R}, multi-photon process, E_g^{R}, A_{1g}^{R} and B_{2g}^{R} (Fig. 3a), which are typical for the rutile structure [41, 42]. Presence of any other structural form of titania was not found. Moreover, the weak intensity of peaks at the spectrum might be attributed to the fine crystalline structure of undoped TiO_2 coating as-deposited in 'high energy' process. As regards to the films doped with europium, the results of Raman studies are fully in line with the XRD measurements. For both TiO_2:Eu films at 141, 194, 396, 515 and 639 cm^{-1} are exclusive peaks characteristic for the anatase structure (Fig. 3b). These modes ($1A_{1g}^{A} + 2B_{1g}^{A} + 3E_g^{A}$) can be assigned only to

TiO_2 - anatase and there is a lack of the rutile phase [41, 42]. Moreover, intensities of peaks related to anatase modes indicate on less crystalline structure of the film with higher amount of Eu-dopant (Fig. 3b). For this reason, increase of europium amount in the titania thin film has a negative impact on its microstructure.

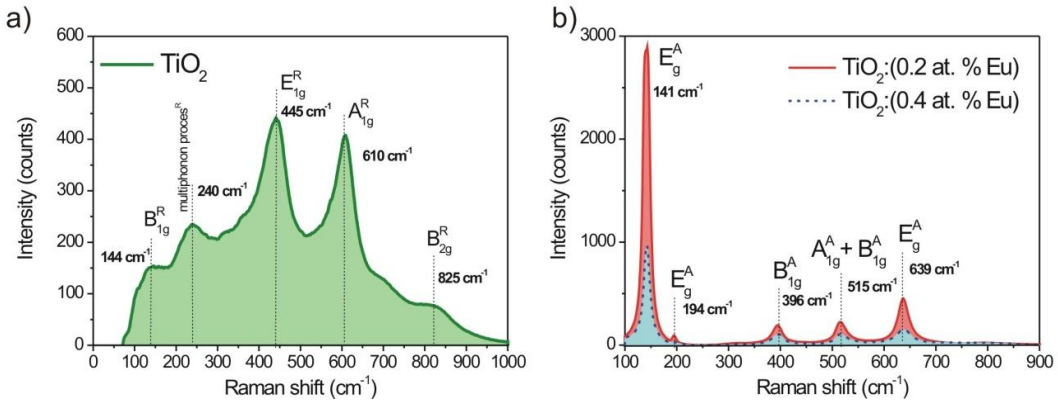

Fig. 3. Raman spectra of a) undoped TiO_2 and b) TiO_2:Eu thin films

Effect of Eu-dopant on the microstructure of TiO_2 films was also observed in the results of optical studies. It was found that for both TiO_2:Eu coatings the photoluminescence (PL) phenomenon occurs (Fig. 4). This is a direct proof of europium presence in the structure of prepared films, due to the lack of such information from XRD or Raman studies (related to low amount of the dopant). In the case of TiO_2:(0.2 at. % Eu) film strong PL-signal associated with radiative recombination of photo-generated electrons in TiO_2 via energy levels of Eu^{3+} and Eu^{2+} ions can be seen (Fig. 4a). The maximum of light emission at a wavelength of about 620 nm (red color) corresponds to Eu^{3+} ions and is typical for most films doped with this rare element [36, 43-45]. We can observed also a peak split effect (two PL maxima at 615 nm and 622 nm, corresponding to $^5D_0$–$^7F_2$ transitions) due to nanocrystalline surrounding of Eu^{3+} ions [44]. Besides, at the PL - spectrum also four other emission lines (at 575 nm, 598 nm, 660 nm and 715 nm) related to the electron transitions between $^5D_0$ and $^7F_{0,1,3,4}$ levels of ions Eu^{3+} can be seen. As mentioned above, in this spectrum (Fig. 4a) also intensive and broad PL – peak

(at λ = 515 nm) related to Eu^{2+} ions can be highlighted. This radiative recombination is responsible for the emission of green light [36]. In turn, Fig. 4b presents the photoluminescence spectrum of TiO_2 thin film doped with 0.4 at. % of europium. As it can be seen, this coating also exhibit PL-effect, but the intensity of light emission is much lower as-compared to the film with 0.2 at. % of the dopant. Most probably, this fact is related to greater efficiency of non-radiative recombination process via defect states of the titania matrix [44]. Weak and broad PL - peak in the range of 400 nm ÷ 700 nm indicate on presence of europium ions at 2+ and 3+ state. However, the light emission effect related to Eu^{2+} ions (with a maximum at ca. 515 nm) has a dominant character. In the PL-spectrum also a peak at a wavelength of 620 nm corresponding to $^5D_0$–$^7F_2$ transitions of Eu^{3+} can be identified, but its intensity is very weak.

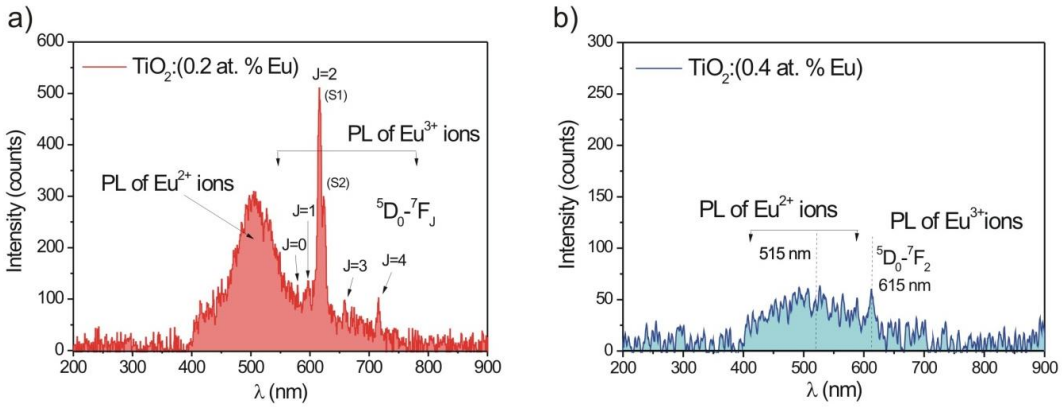

Fig. 4. Photoluminescence spectra of a) TiO_2:(0.2 at. % Eu) and b) TiO_2:(0.4 at. % Eu) thin films

XRD as well as Raman studies have left no doubts about high impact of europium on the microstructure of prepared titania films. The structure of TiO_2:Eu coatings was homogenous - there was a lack of two-phase system (anatase – rutile). Moreover, except hinder of rutile formation in high energy process both doped films were nanocrystalline and had small crystallites. However, the results of PL-measurements testify that the increase of recombination via titania defect states (decrease of PL signal) indicate on dependence

between Eu-amount and film growth mechanism (including formation of defects). For this reason, the research was conducted by means of bright field (BF TEM) and high resolution (HR TEM) observations as well as selected area electron diffraction (SAED) measurements (Fig. 5). In the case of undoped TiO_2 the BF TEM observations have shown columnar, fine nanocrystalline structure. Presence of rutile structure was confirmed by SAED measurements (inset at Fig. $5a_1$). However, the broadening of the SAED pattern and fuzzy diffraction rings testify about a share of the amorphous phase [46]. High resolution observations confirmed that undoped titania thin films consist of a fine nanocrystalline (rutile) structure. In the inset at Fig. $5a_2$ (FFT diffraction patterns) the visible fringe spacing's are equal to 3.22 Å, 3.23 Å and 4.65 Å, which correspond well with the separation between the (1 -1 0), (1 1 0) and (1 0 0) planes of the TiO_2-rutile phase, respectively. HR TEM images (Fig. $5a_2$) also confirmed presence of (1 -1 0), (1 1 0) and (1 0 0) crystal planes, but at the boundaries of rutile crystallites the amorphous area can be observed. In the case of both TiO_2:Eu thin films TEM observations also exhibit nanocrystalline character of their structure (Fig. 5b,c). Presence of the anatase form was confirmed by SAED measurements due to occurrence of rings related to (101), (105), (100), (004) and (204) crystal planes (insets at Fig. 5b,c). A light blur of diffraction rings at SAED patterns testify about the small participation of amorphous phase for both films. High resolution observations with FFT diffraction also confirmed that both Eu-doped films had anatase structure due to separation between the (101) and (011) planes (Fig. $5b_2$,c_2). Moreover, BF TEM results have shown that doping with europium resulted in receiving of titania with fibrous microstructure. Except well crystalline fibers, the voids between them also can be observed (brighter area between neighboring fibers is a void) (Fig. 5b,c). As it can be seen, the increase of Eu-amount causes formation of more voids, with a greater sizes. This fact can be directly connected with decrease of PL-intensity for the film with higher amount of Eu. Most probably, very small EuO_2 and Eu_2O_3 agglomerates were

located on the surface of TiO_2 fibers [44, 47]. For this reason increase of the voids number in TiO_2:Eu film means more defected microstructure, what results in receiving of more effective recombination via defect states of titania. This means, that doping with Eu allows on manufacturing of nanocrystalline TiO_2 thin films with anatase structure in high energy magnetron sputtering process. But to high amount of the dopant provides to formation of higher number of defects in the film structure.

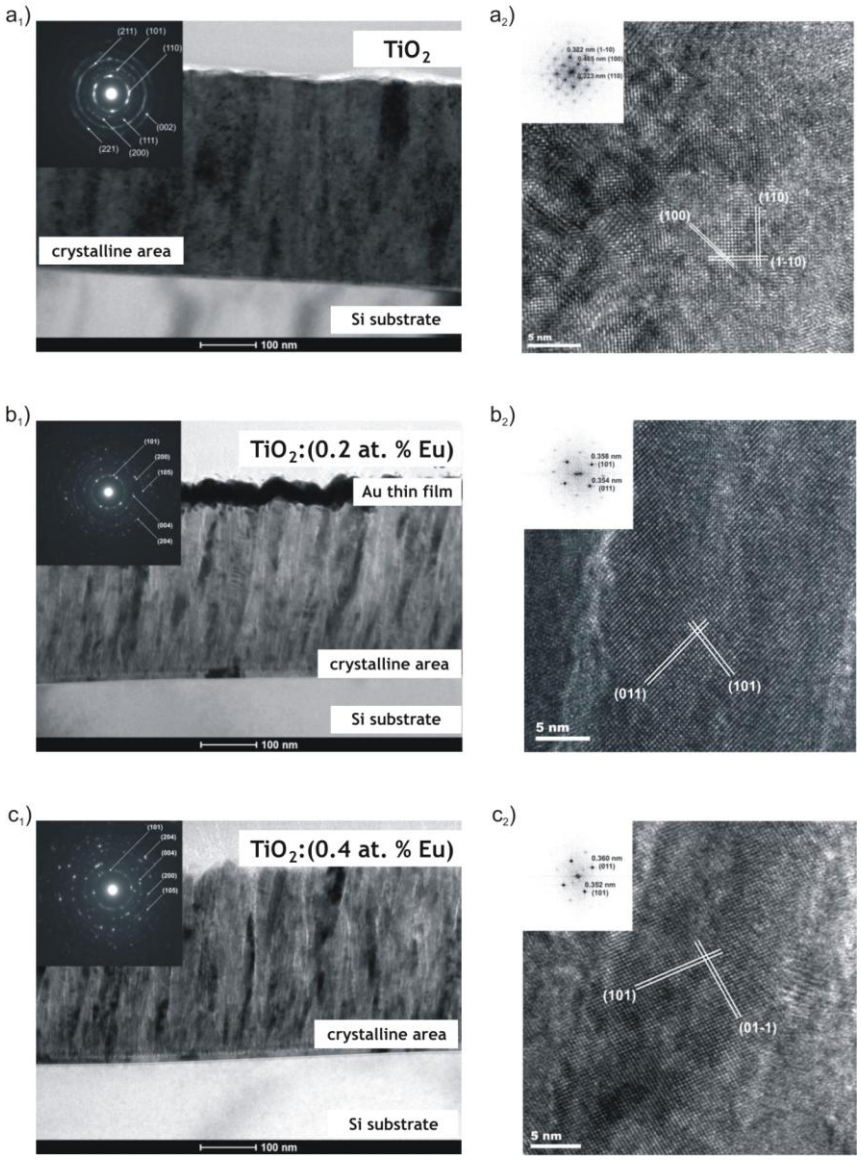

Fig. 5. Bright field TEM images of the cross-section with SAED inserts (1) and high resolution TEM images with FFT diffraction (2) of: a) TiO_2, b) TiO_2:(0.2 at. % Eu), c) TiO_2:(0.4 at. % Eu) thin films

Conclusions

In this work the influence of europium on microstructure of TiO_2 thin films was described. Nanocrystalline coatings were prepared by high energy magnetron sputtering process. Such type of sputtering gives many advantages, but its main disadvantage is a lack of anatase phase, which is more desirable for sensor technology or self-cleaning coatings, etc. For this reason, modification of structural properties of TiO_2 by doping with europium is very promising. It was found that incorporation of 0.2 at. % (as well as 0.4 at. %) of Eu into TiO_2 thin film in high energy process allows on receiving of fine nanocrystalline, anatase structure. Crystal forms of Eu-dopant were not observed in the microstructure of both TiO_2:Eu films, but presence of Eu^{2+} and Eu^{3+} ions was confirmed by PL measurements. It is worth to emphasize that such small amount of the dopant gave fibrous structure, while undoped TiO_2 had columnar character. Moreover, the amount of europium had a direct impact on the voids number as well as their sizes in the structure of titania films. These structural changes were associated with decrease of PL-intensity due to higher efficiency of non-radiative recombination via defect states of TiO_2 matrix.

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Suggested reviewers:

1. Marcin Grobelny, Motor Transport Institute, Centre for Material Testing and Mechatronics, e-mail address: marcin.grobelny@its.waw.pl
2. Professor Dieter Schmeisser, Brandenburg University of Technology, Physics and Sensors, e-mail address: dsch@b-tu.de
3. Professor Antoni W Morawski, West Pomeranian University of Technology in Szczecin, e-mail address: amor@zut.edu.pl