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Influence of europium on structure modification of TiO₂ thin films prepared by high energy magnetron sputtering process

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ABSTRACT

In this work modification of TiO₂ thin films structure by doping with europium was described. Nanocrystalline films were prepared by high energy magnetron sputtering process. The influence of europium on the microstructure of TiO₂ was determined based on the results of X-ray diffraction, transmission electron microscopy, Raman spectroscopy and photoluminescence measurements. It was found that undoped film had rutile structure directly after deposition (without additional annealing), while 0.2 at.% and 0.4 at.% of the dopant was sufficient to receive TiO₂ films with anatase form. The type of structure was confirmed with the aid of Raman spectroscopy and by TEM observations. The amount of Eu-dopant had direct impact on PL intensity as well as presence of defect (voids) in the film.

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1. Introduction

Titanium dioxide is a well-known material that has such advantages as high transparency, non-toxicity, high stability (chemical, thermal and mechanical), high photocatalytic activity, etc. [1–5]. TiO₂ occurs in three different crystalline forms – brookite, anatase and rutile, but only last two have practical application [1,2]. Films with the anatase structure are used as active layers in sensor technology [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 TiO₂ can be modified by the change of deposition parameters [10,11], doping [12–15] or post-process treatment (e.g. annealing) [16,17]. Especially, the change of deposition parameters is interesting for industry (no need of special composition of sputtered materials and extra steps of production process). Nowadays, nanocrystalline films are often applied in the industry. Application of so called ‘high energy’ processes results in receiving of well crystalline nanostructure [18–21]. Typically, TiO₂ 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 conventional sputtering results in two-phase system (without extra annealing). Moreover, application of low pressure and increase of

supply power (higher energy of sputtered particles) gives a chance for preparation of coatings with fine nanocrystalline rutile structure (directly after deposition). Such modification increases hardness [20]. As mentioned above, doping is also an important way for modification of TiO₂ properties. According to the literature [22–28] and our previous works [29–35] doping with lanthanides (e.g. Eu, Tb or Nb) has an influence on the microstructure and other properties of TiO₂ films as well as their application area. In this work the effect of Eu-dopant on the structural properties of TiO₂ thin films was described. Europium is 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, respectively [36]. This work contains a relation between ‘high energy’ process, doping with europium and the microstructure of TiO₂ coatings.

2. Experimental part

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 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. The distance between sputtered targets and the substrates (SiO₂, Si) was 160 mm. For the analysis undoped TiO₂ and TiO₂:Eu thin films with 0.2 at.% and

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0.4 at.% of the dopant were used. The thickness of as-deposited coatings was ca. 250 nm.

The surface morphology and elemental composition of TiO_2 and $\text{TiO}_2\text{:Eu}$ 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 by X-Ray Diffraction (XRD). For measurements, Siemens 5005 (Siemens, Germany) powder diffractometer with $\text{Cu K}\alpha$ X-ray and Bragg-Brentano optics was used. The step size was equal to 0.02° in 2θ range, while time-per-step was 5 s. The average crystallites size was calculated using Debye-Scherrer's formula. The crystal structure was also characterized by 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 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.

3. Results and discussion

Influence of europium on the microstructure of titanium dioxide was examined with the aid of SEM (Fig. 1).

As it can be seen (Fig. 1), all prepared coatings were homogenous. For both $\text{TiO}_2\text{:Eu}$ films (at magnification of $\times 200\text{k}$) fine grained

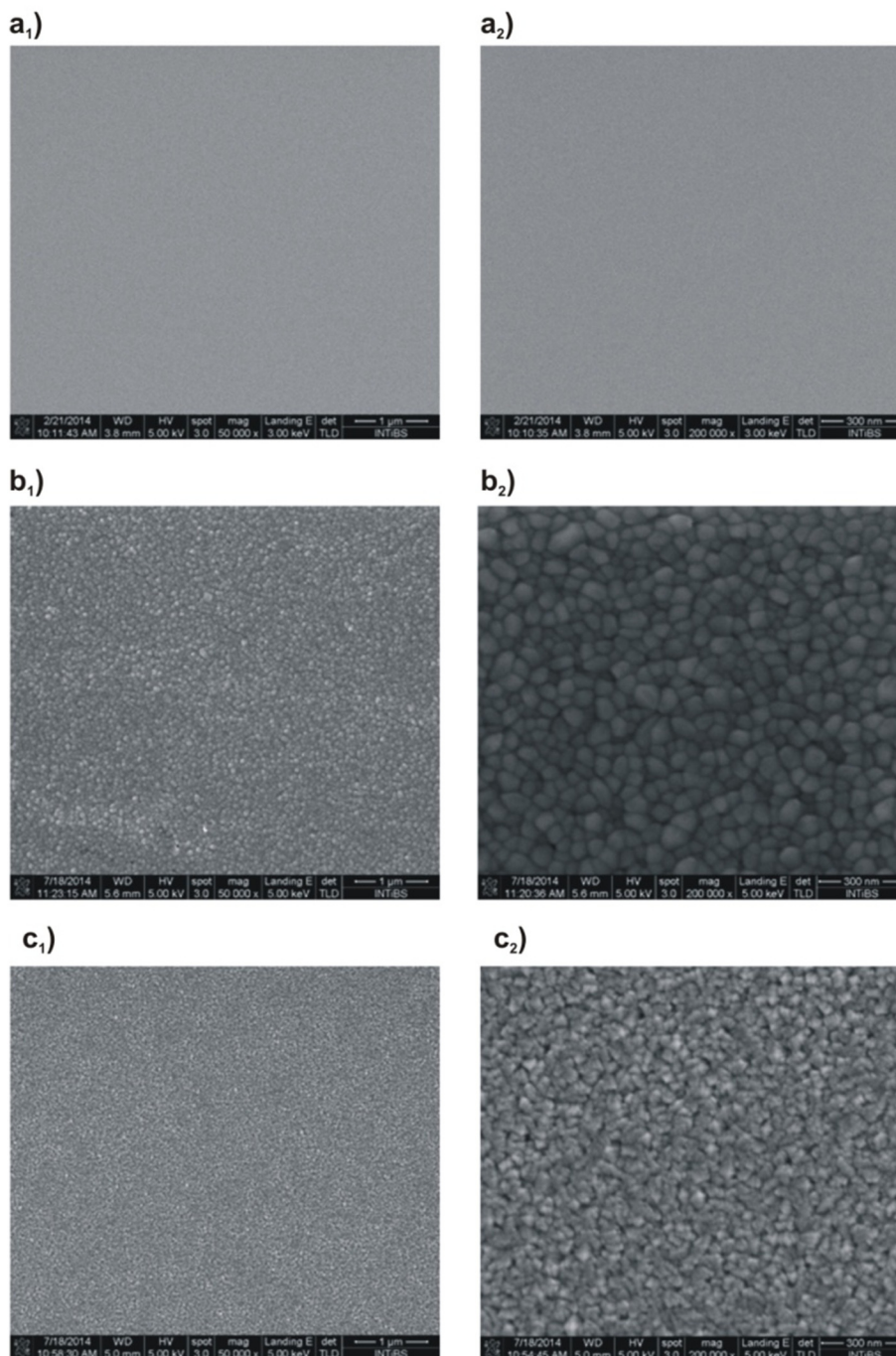


Fig. 1. SEM images of: a) TiO_2 , b) $\text{TiO}_2\text{:}(0.2 \text{ at.\% Eu})$, c) $\text{TiO}_2\text{:}(0.4 \text{ at.\% Eu})$ thin films.

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