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Influence of Eu dopant on optical properties of TiO_2 thin films fabricated by low pressure hot target reactive sputtering

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This work presents the influence of europium dopant on optical properties of $TiO_2:Eu^{3+}$ thin films fabricated by low pressure hot target reactive sputtering. Thin films were deposited from metallic Ti-Eu mosaic target on different substrates (*i.e.*, monocrystalline silicon and SiO_2). Selected samples were additionally annealed for 4 hours in an air ambient at 200 °C after deposition. Thin films were examined by means of scanning electron microscopy with energy disperse spectrometer (SEM-EDS), X-ray diffraction (XRD), optical transmission method and photoluminescence (PL). From SEM-EDS measurements total Eu concentration in fabricated thin films was determined. XRD analysis revealed the existence of crystalline TiO_2 in the form of anatase and rutile in examined samples with smaller and larger amount of Eu dopant, respectively. Optical transmission method showed that doping with selected amount of Eu results in different shift of the fundamental absorption edge for prepared thin films. PL studies showed a red luminescence of $TiO_2:Eu^{3+}$ thin films. The intensity of luminescence increased with the annealing temperature and decreased with larger amount of europium.

Keywords: titanium oxide, europium, thin film, magnetron sputtering, optical properties.

1. Introduction

Lanthanide-doped luminescent materials have recently been intensively studied because of their possible applications in photoelectric devices and optical communication fields (*i.e.*, flat plane displays, solid state laser, high energy radiation detectors, optical data storage, *etc.*) [1–5]. TiO_2 has been used as the favorable host material for rare earth elements, due to its outstanding optical and thermal properties and high stability [2, 5–7]. Due to the intense red emission of Eu^{3+}, insensitive to the variation of temperatures from 12 K to 300 K, TiO_2:Eu thin films are very attractive for many technological applications [1, 6, 8].

For fabrication of lanthanide-doped TiO_2 thin films different techniques have been applied, so far [1, 8]. The magnetron sputtering is one of the most efficient and compatible with the standard silicon and new wide band-gap materials in today's microelectronics technology [9]. Manufacturing of rare earth doped thin films using sputtering methods have been presented only in few reports, but mostly from powder targets [10, 11].

2. Experimental procedure

This work presents the influence of europium on optical properties of $TiO_2:Eu^{3+}$ thin films fabricated by low pressure hot target reactive sputtering (LP HTRS) [9]. Thin films were deposited on different substrates (*i.e.*, monocrystalline silicon and SiO_2) from metallic Ti-Eu mosaic target. Different amount of Eu-dopant in prepared thin films was assured by changing relative Ti:Eu ratio in the starting material being co-sputtered. The process was carried out at low pressure (< 0.1 Pa) of pure oxygen as a working gas and while the metallic target (hot target) was additionally heated. Selected samples were additionally annealed for 4 hours in an air ambient at 200 °C after being deposited.

Elemental analysis was done using SEM-EDS system (OXFORD Link-ISIS). The microstructure was investigated using the X-ray powder diffraction (XRD), performed with the help of DRON-2 powder diffractometer and Fe-filtered Co Kα radiation. Average size of crystallites was calculated from XRD spectra in a conventional way according to the Scherrer formula.

Optical transmission measurements were performed in the spectral range from 200 nm to 1000 nm using Ocean Optics HR4000 spectrometer. Samples were illuminated with white light from a halogen lamp (100 W) at normal incidence. The fundamental absorption edge and the thickness of the thin films were determined from transmission characteristics. For photoluminescence measurements UV argon laser of the 302 nm excitation wavelength has been used. The PL signal has been collected by Ocean Optics HR4000 spectrometer, too.

3. Structural analysis

Eu content in $TiO_2:Eu^{3+}$ thin films was determined by energy disperse spectrometer (EDS) to be around 0.1 at.% and 0.5 at.%, respectively. EDS spectra of Eu doped TiO_2 thin films on silicon substrate have been presented in Fig. 1. Detected Si signal, visible in the spectra, results from the applied substrate.

In the Table, structural properties of $TiO_2:Eu^{3+}$ thin films have been presented. XRD investigations revealed the TiO_2-anatase phase and TiO_2-rutile phase for examined as-deposited and annealed thin films with 0.1 at.% Eu and 0.5 at.% Eu, respectively. Interplanar distances *d* were similar to the standard ones for both doped thin films [12, 13]. Little smaller *d* after additional annealing at 200 °C suggests additional stress in the structure. The grains size varied in the range of about 6 nm to 18 nm for 0.1 at.% and 0.5 at.% Eu doped TiO_2 thin films, respectively. That indicates high quality nanocrystalline structure of prepared thin films (see the Table).

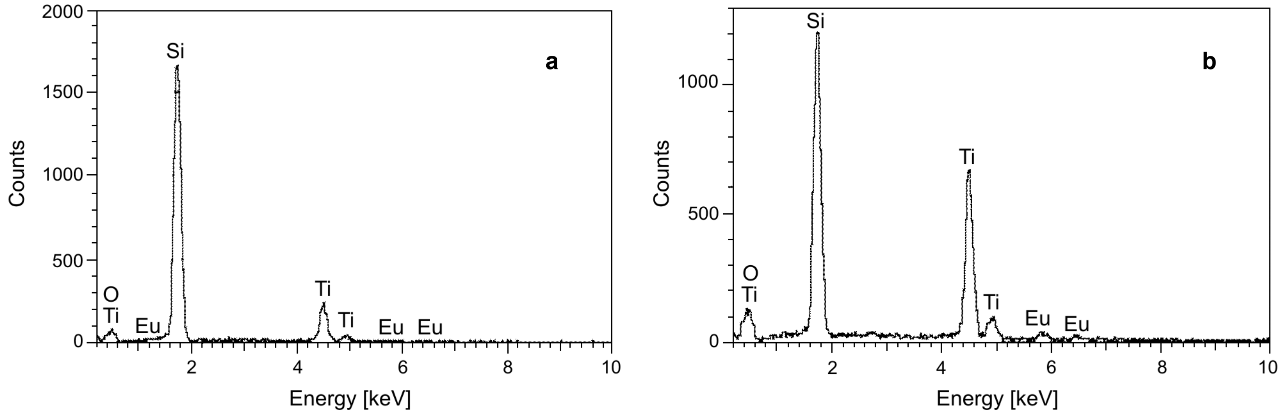

Fig. 1. EDS spectra of as-deposited $TiO_2:Eu^{3+}$ thin films on silicon: 0.1 at.% Eu (**a**) and 0.5 at.% Eu (**b**).

T a b l e. Structural properties of $TiO_2:Eu^{3+}$ thin films. Data have been estimated with respect to the most intense anatase [12] peak (1 0 1) at $2\theta = 29.453$ deg and rutile [13] peak (1 1 0) for 0.1 at.% and 0.5 at.% Eu content, respectively; d – interplanar distance, D – crystallite size.

			Measured pattern			
	Standard pattern		$TiO_2:Eu^{3+}$ thin film (0.1 at.% Eu)		$TiO_2:Eu^{3+}$ thin film (0.5 at.% Eu)	
Parameter	TiO_2-anatase [12]	TiO_2-rutile [13]	As-deposited	Annealed at 200 °C	As-deposited	Annealed at 200 °C
2θ [deg]	29.45	32.00	29.46	29.57	31.93	32.10
d [nm]	0.3521	0.3247	0.3520	0.3507	0.3254	0.3237
D [nm]	—	—	18.2	18.7	6.1	6.0

4. Optical properties

Optical transmission results showed that doping with selected amount of Eu dopant, *i.e.*, 0.1 at.% and 0.5 at.%, results in different position of the fundamental absorption edge which was 330 nm and 350 nm, respectively (Fig. 2). But, such change, in this case, follows rather from structural anatase-rutile transformation in the thin film, manifested by their different optical band gap (3.3 eV for anatase and 3.05 eV for rutile [14]), than the Eu dopant amount itself.

Also, from the transmission spectra, according to the method described by MANIFACIER *et al.* [15], the thickness of prepared thin films was determined, to be about 600 nm and 1300 nm, for 0.1 at.% and 0.5 at.% of Eu, respectively.

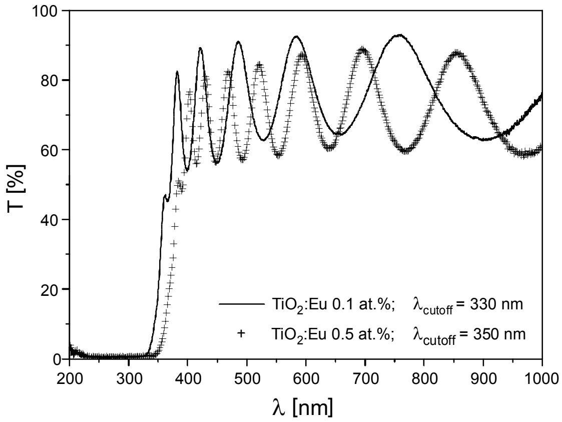

Fig. 2. Transmission spectra of TiO_2:Eu^{3+} – 0.1 at.% Eu (600 nm thick) and TiO_2:Eu^{3+} – 0.5 at.% Eu (1300 nm thick) thin films additionally annealed for 4 hours in the air at 200 °C.

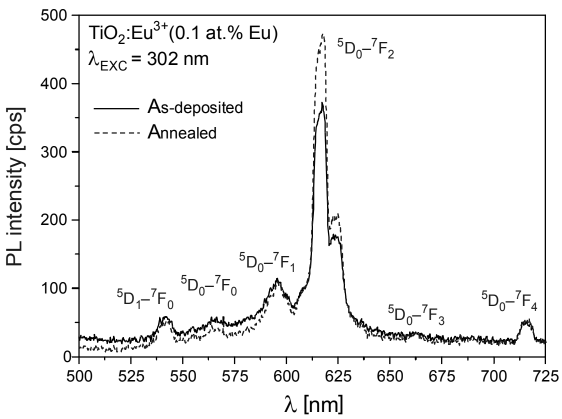

Fig. 3. Photoluminescence spectra of TiO_2:Eu^{3+} – 0.1 at.% Eu (600 nm) thin films on silicon when as-deposited and additionally annealed at 200 °C.

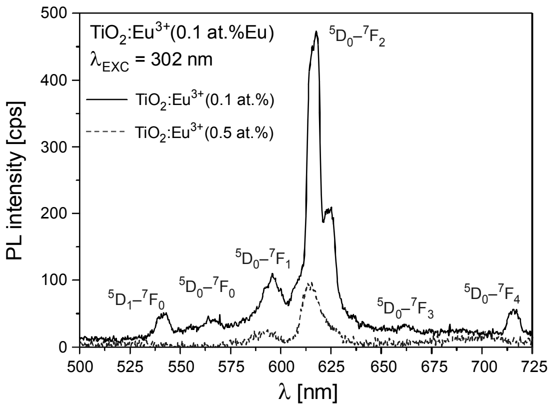

Fig. 4. Photoluminescence spectra of $TiO_2:Eu^{3+}$ – 0.1 at.% and 0.5 at.% Eu (600 nm and 1300 nm, respectively) thin films on silicon additionally annealed for 4 hours in air at 200 °C.

Figure 3 presents photoluminescence (PL) spectra of $TiO_2:Eu^{3+}$ – 0.1 at.% Eu (600 nm thick) thin films on silicon when as-deposited and additionally annealed at 200 °C. Excitating the samples with Ar laser at 302 nm results in strong emission at the wavelength of 615 nm from as-deposited, as well as from the annealed at 200 °C thin films. The annealing process causes some increase of red luminescence intensity for examined thin films.

In Figure 4, the influence of Eu dopant on PL spectra after additional annealing at 200 °C has been presented. It is shown that, an increase of the Eu amount from 0.1 at.% to 0.5 at.% results in decrease of PL intensity. But it has to be remarked, that thin film with 0.5 at.% of Eu had the rutile structure, in which luminescence intensity of europium is worse than that in the anatase structure [1].

5. Conclusions

The influence of europium amount on optical properties of $TiO_2:Eu^{3+}$ thin films have been presented. Thin films were fabricated from metallic Ti-Eu mosaic target by LP HTRS method and additional annealed at 200 °C. Doping of TiO_2 thin films with 0.1 at.% and 0.5 at.% of Eu^{3+} revealed nanocrystalline anatase and rutile structure, respectively. It was shown that the shift of the fundamental absorption edge follows the structural changes in the prepared thin films due to the europium dopant and was comparable to the undoped TiO_2-anatase and TiO_2-rulile thin films. From PL spectra a strong red luminescence that increased after additional annealing was observed for smaller amount of Eu.

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