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Influence of post annealing on optical and structural properties of Eu and Pd-doped TiO_2 thin films

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This work presents optical and structural characterization of europium and palladium doped titanium dioxide thin films prepared by modified magnetron sputtering. The metallic Eu and Pd dopants have been co-sputtered from a base Ti target (mosaic target) and deposited on SiO_2 substrates. After the deposition samples were additionally annealed in air ambient for 2 hours at the temperatures of 200 °C, 400 °C, 600 °C and 800 °C, respectively. Structural properties of TiO_2:(Eu, Pd) thin films were examined using X-ray diffraction (XRD). XRD patterns recorded after thermal treatment showed the dominating TiO_2-rutile phase, independently of the temperature of annealing. Optical properties were studied as defined by optical transmission. It has been shown, that doping shifts the fundamental absorption edge of TiO_2 toward the longer wavelength range. As the samples were additionally annealed the band gap widening has been observed from 1.7 eV, for as deposited sample up to 2.31 eV for those annealed at 800 °C.

Keywords: transparent oxide semiconductor, thin film, magnetron sputtering, titanium oxide, europium, palladium.

1. Introduction

Titanium oxide is being intensively examined since many years and, at present, its properties are commonly known. The challenge for researches is always answering the question how selected properties would change due to the different hazards, *i.e.*, annealing, temperature, electric or magnetic field, irradiation, stress, *etc.*, or some technological modifications, *i.e.*, intentional doping. For example, connecting transparent oxide semiconductors with relevant modified properties of conventional microelectronics materials allows fabrication of different electronic devices [1]. The magnetron sputtering [2, 3] is one of the most efficient and compatible with the standard silicon and new wide band-gap materials in today's microelectronics technology. Due to the modification of typical magnetron sputtering method and due to the application of relevant dopants (V, Co, Pd) into TiO_2 matrix, nanocrystalline thin films were obtained [4, 5] which are transparent to light in the visible region and with semiconducting properties at room temperature. Pd dopant changes the electrical properties of TiO_2 from dielectric oxide to semiconducting oxide [5, 6]. Magnetron sputtering process could also be applied for fabrication of lanthanide-doped TiO_2 thin films, as well [7, 8]. For example, it has been shown that Eu doping of TiO_2 results in an intense characteristic emission of Eu^{3+} in the red light region, insensitive to the variation of temperatures ranging from 12 K to 300 K [7–9]. That makes it a very attractive material for many technological applications, for example, as photoelectric devices, solid state laser, flat plane displays, optical radiation converters [8, 9].

In this work optical and structural properties of TiO_2 doped with Pd and Eu thin films prepared by modified magnetron sputtering have been investigated. The structure and optical evolution due to the heat treatment at different temperatures have been described.

2. Experimental procedure

Thin films of TiO_2:(Eu, Pd) were prepared by modified magnetron sputtering method on SiO_2 substrates. The metallic Eu and Pd dopants have been co-sputtered from a base Ti target (mosaic target). This sputtering process was carried out in low pressure (< 0.1 Pa) of pure oxygen as a working gas and with additionally heated metallic target [10, 11].

Structural properties were investigated by means of X-ray powder diffraction (XRD), performed with the help of DRON-2 powder diffractometer with Fe-filtered Co$K\alpha$ radiation. Average size of crystallites was calculated from XRD spectra in a conventional way according to the Scherrer formula.

Optical properties of TiO_2:(Eu, Pd) thin films were studied by means of optical transmission method performed within the spectral range from 200 nm to 1000 nm using Ocean Optics HR4000 spectrometer.

The thickness of prepared thin films, determined from transmission spectra was about 1200 nm. The Pd and Eu content, determined by energy disperse spectrometer were 2.8 at.% and 0.3 at.%, respectively.

3. Structural properties

XRD patterns of the as deposited TiO_2:(Eu, Pd) thin films and additionally annealed at different temperatures have been presented in Fig. 1.

XRD patterns recorded after each of thermal treatment (Fig. 1) showed the dominating TiO_2-rutile phase, independently on the temperature of annealing. No separate phase of neither Pd nor Eu have been observed. The annealing process

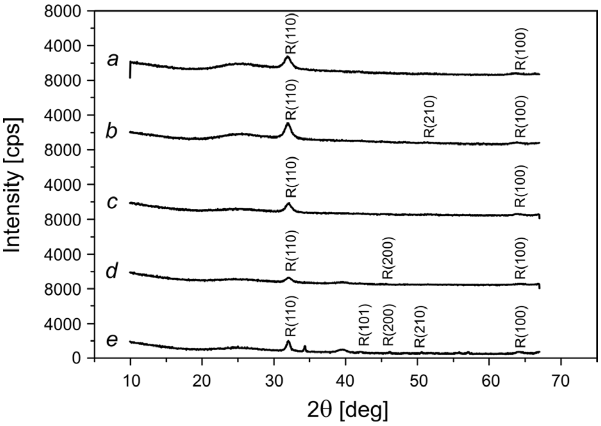

Fig. 1. XRD patterns of TiO_2:(Eu,Pd) thin films, 1200 nm thick, on SiO_2: as deposited (*a*), annealed at 200 °C (*b*), annealed at 400 °C (*c*), annealed at 600 °C (*d*), annealed at 800 °C (*e*).

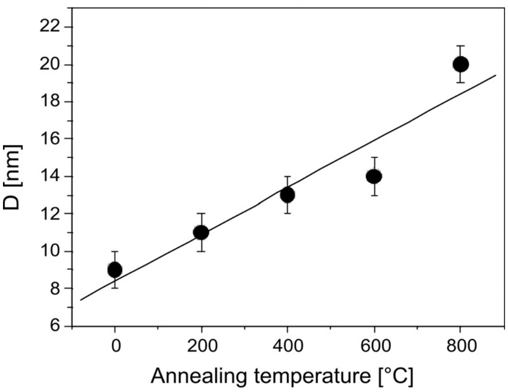

Fig. 2. The dependence of crystallite size *D* on temperature of additional heat treatment of the TiO_2:(Eu, Pd) thin films for 2 hours in air ambient.

enhances the crystallinity of the thin films, which makes the increase in the crystallite size from ca. 10 nm, for the as deposited thin film, up to 20 nm for the annealed at 800 °C. The evolution in size of crystallites *D*, determined for the most intense (110) rutile peak for each particular annealing temperature has been presented in Fig. 2 and collected in the Table. It is clearly seen that the growth in grain size is almost linear in the investigated temperature range.

4. Optical properties

Transmission characteristic (*T*) of TiO_2:(Eu, Pd) thin films have been presented in Fig. 3. Incorporation of Pd and Eu dopants into TiO_2, shifts the position of its fundamental absorption edge (*i.e.*, ca. 320 nm [12]) toward the longer wavelength

T a b l e. The crystallite size D, optical band gap E_g^{opt}, Urbach energy E_u and the refraction index n for the as deposited and annealed TiO_2:(Eu, Pd) thin films.

Sample	D [nm]	E_g^{opt} [eV]	E_u [eV]	n at 900 nm
As deposited	9.8	1.70	0.38	1.458
Annealed 200 °C	11	1.78	0.28	1.470
Annealed 400 °C	13	1.86	0.27	1.475
Annealed 600 °C	14	2.03	0.18	1.474
Annealed 800 °C	19	2.31	0.06	1.483

region (Fig. 3). The optical band gap energy E_g^{opt} for the allowed indirect transition together with the Urbach energy E_u and refraction index n have been calculated from the envelope method [13, 14]. The selected optical parameters are summarized in the Table.

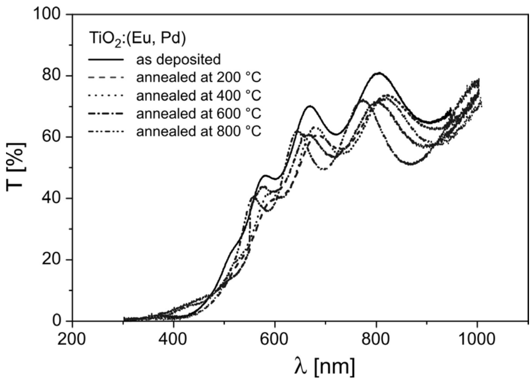

Fig. 3. Optical transmission spectra for the TiO_2:(Eu, Pd) thin films, 1200 nm thick, as deposited and annealed at: 200 °C, 400 °C, 600 °C and 800 °C, respectively.

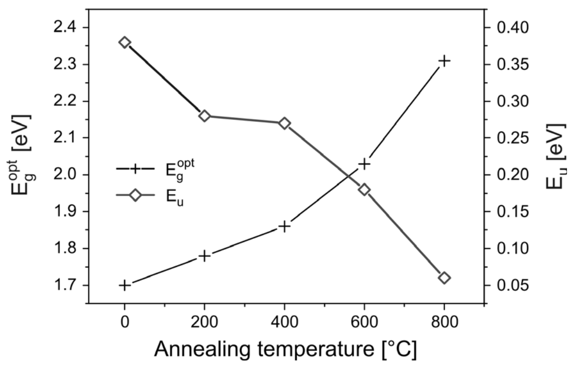

Fig. 4. The dependence of optical band gap E_g^{opt} together with the Urbach energy E_u on annealing temperature.

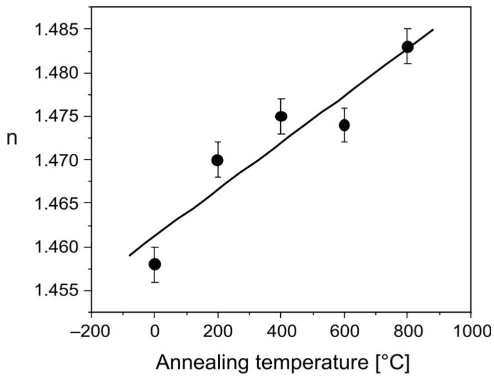

Fig. 5. The dependence of refraction index *n*, determined for 900 nm, on annealing temperature.

Figure 4 presents the dependence of optical band gap on annealing temperature together with the Urbach energy. The effect of the band gap widening is clearly visible. As the temperature of additional annealing increases, the optical band gap increases, too. It is also worth to point out, that this dependence is accompanied by the decrease in the width of absorption tail, *i.e.*, the Eu.

Figure 5 presents the dependence of refraction index *n* on the annealing temperature. Similar to the Fig. 2, almost linear dependence of *n* on annealing temperature was observed.

The above results (Figs. 4 and 5) are consistent with XRD data and suggest that major contribution in the evolution of optical properties is due to the crystallization of prepared thin films upon addition heat treatment.

5. Conclusions

The evolution of structural and optical properties of TiO_2:(Eu, Pd) thin films annealed at different temperatures were described. It was shown that the fundamental absorption edge of TiO_2 was shifted through the longer wavelength range due to the Pd and Eu doping. The optical band gap of fabricated thin films has changed from ca. 1.7 eV up to 2.31 eV after additional annealing.

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