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The study of structural and optical properties of TiO_2:Tb thin films

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This work presents the study of the structural and optical properties of TiO_2:Tb thin films deposited on Si (100) and SiO_2 substrates by magnetron sputtering from metallic Ti-Tb mosaic target. Thin films were studied by means of scanning electron microscopy with energy disperse spectrometer (SEM-EDS), atomic force microscopy (AFM), X-ray diffraction (XRD) and the optical transmission method. From SEM-EDS the total amount of Tb concentration was determined. XRD analysis revealed the existence of crystalline TiO_2 in the form of anatase and rutile, depending on Tb amount in the examined samples. The optical transmission method has shown that Tb doping shifts the fundamental absorption edge of TiO_2 toward the longer wavelength region.

Keywords: terbium, TiO_2, thin films, magnetron sputtering.

1. Introduction

Doping of TiO_2 with selected ions could influence its different properties [1]. Recently, due to its outstanding optical and thermal properties [2], TiO_2 has been investigated as a favorable host material for rare earth (RE) elements [3–5]. For the fabrication of RE-doped TiO_2 thin films different techniques have been applied [4, 5], but manufacturing of RE-doped thin films using sputtering methods has been presented only in few reports so far, and thin films were mostly prepared from powder targets [6, 7].

This paper presents the study of the structural and optical properties of TiO_2:Tb thin films fabricated by the magnetron sputtering method using metallic Ti-Tb target sputtered in reactive oxygen atmosphere.

2. Experimental procedure

In the present paper thin films were deposited from metallic Ti-Tb mosaic target on Si (100) and SiO_2 substrates using the modified magnetron sputtering method as the low pressure hot target reactive sputtering (LP HTRS) [8].

The basic feature of the applied manufacturing process is a possibility of depositing thin films with a densely packed microstructure. The low deposition rate (about 0.1 nm/s) and additional energy from the heated target (hot target) caused that the molecules on the substrate had enough energy to migrate through the surface to the places with a lower potential energy. As a result the layers grew in almost pseudoepitaxial conditions. A next layer was formed when the former had been finished. That caused that the deposited thin films were homogenous with the grain sizes in the range from few to few tens of nanometer.

The additional heating of the target results in its better oxidation, which is a key requirement for manufacturing of thin oxide films from metallic target. Owing to that, the oxide molecules could be formed and sputtered directly from the target.

Such layers have extraordinary physical properties corresponding to the zone T of the Thornton structural zone model [9], extended to the region of low pressure of working gas [10].

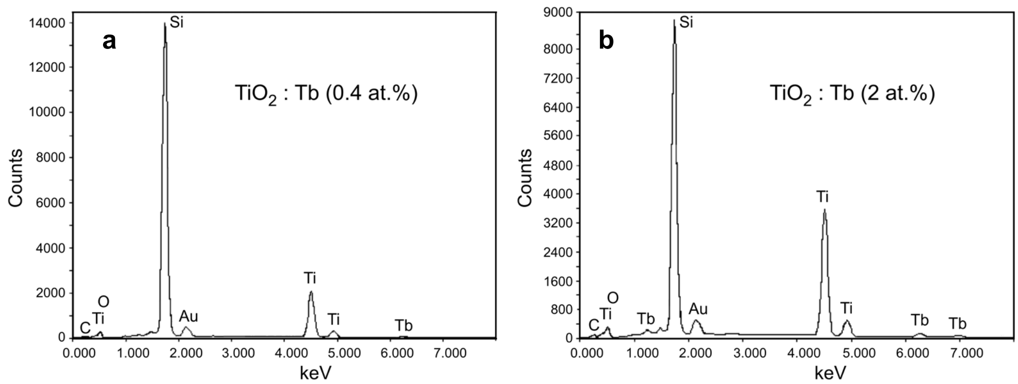

Fig. 1. EDS spectra of as-deposited TiO_2:Tb thin films on silicon: 0.4 at.% Tb (**a**) and 2 at.% Tb (**b**).

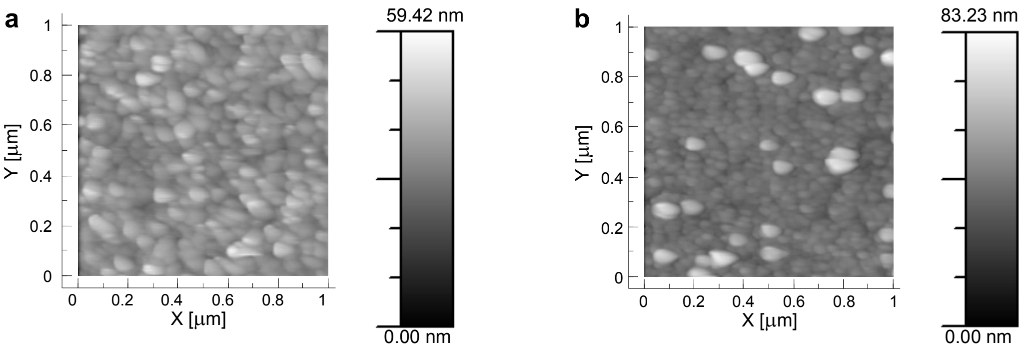

Fig. 2. AFM images of TiO_2:Tb thin films on SiO_2: 0.4 at.% Tb (**a**) and 2 at.% Tb (**b**).

The amount of Tb in TiO_2:Tb thin films was determined by SEM-EDS (Hitachi S-4700N, Noran Vantage).

Topography was studied by the application of AFM (Veeco PicoForce) working in contact mode.

Microstructure was investigated by means of X-ray powder diffraction (XRD) using DRON-2 powder diffractometer with Fe-filtered Co Kα radiation. The average size of crystallites was calculated from XRD spectra in a conventional way according to the Scherrer formula.

Optical transmission measurements were performed in a spectral range from 250 nm to 1100 nm. The fundamental absorption edge and the thickness of the thin films were determined from transmission characteristics.

3. Structural properties

EDS spectra of TiO_2:Tb thin films with Tb content around 0.4 at.% and 2 at.% deposited on a silicon substrate have been presented in Fig. 1. The detected Si signal, visible in the spectra, results from the applied substrate.

The AFM images of TiO_2:Tb thin films with 0.4 at.% and 2 at.% Tb content deposited on SiO_2 substrate have been presented in Fig. 2. As we can see, the thin films consisted of nanocrystallites, in the range of about 40 nm to 70 nm. The dimension and the arrangement of crystallites were almost homogenous on the whole sample surface. Crystallinity of examined thin films rose with an increase in dopant amount (Fig. 2**b**).

The structural properties of TiO_2:Tb thin films have been collected in Tab. 1. XRD investigations revealed the TiO_2-anatase phase and TiO_2-rutile phase for examined thin films with 0.4 at.% Tb and 2 at.% Tb, respectively. The interplanar distance d was similar to the standard one for both doped thin films [9, 10]. Little bigger d for 2 at.% Tb suggests additional stretching in the structure. The grain

T a b l e 1. Structural properties of TiO_2:Tb thin films on SiO_2. Data have been estimated with respect to the most intense anatase [11] peak (101) at 2θ = 29.45 deg and rutile [12] peak (110) at 2θ = 32.00 deg for 0.4 at.% and 2 at.% Tb content, respectively; d – the interplanar distance, D – the crystallite size.

		2θ [deg]	d [nm]	D [nm]
Standard pattern	TiO_2-anatase (21-1272) [11]	29.45	0.3521	—
	TiO_2-rutile (21-1276) [12]	32.00	0.3247	—
Measured pattern	TiO_2:Tb thin film (0.4 at.% Tb)	29.45	0.3521	11.7
	TiO_2:Tb thin film (2 at.% Tb)	31.82	0.3265	6.6

size varied in the range of about 6 nm to 12 nm for 2 at.% and Tb 0.4 at.% doped TiO_2 thin films, respectively. That indicates the high quality nanocrystalline structure of prepared thin films (Tab. 1).

4. Optical properties

Optical transmission measurements (Fig. 3) showed that an increase in Tb amount shifted the fundamental absorption edge in the longer wavelength region: from ca. 330 nm for pure TiO_2-anatase to ca. 340 nm for TiO_2 (0.4 at.% Tb) (Fig. 3**a**) and from 340 nm for pure TiO_2-rutile to ca. 350 nm for TiO_2 (2 at.% Tb) thin films

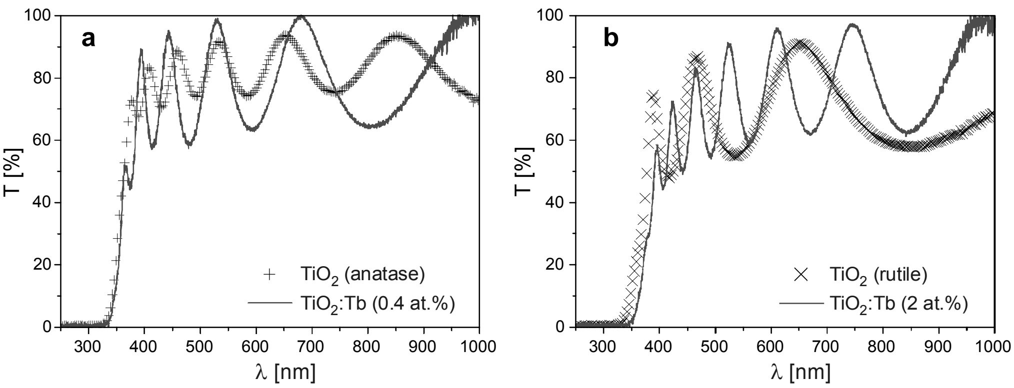

Fig. 3. Transmission spectra of: TiO_2:Tb (0.4 at.% Tb) compared to TiO_2-anatase (**a**) and TiO_2:Tb (2 at.% Tb) compared to TiO_2-rutile thin films on SiO_2 (**b**).

(Fig. 3**b**). The transmission level was about 80%, independently of Tb amount. From the transmission spectra the thickness of prepared thin films was also determined; it amounted to about 800 nm and 1100 nm, for 0.4 at.% and 2 at.% of Tb, respectively. The selected optical parameters are presented in Tab. 2. The optical band gap energy E_g^{opt} for the allowed indirect transitions together with the refraction index n and thickness of examined films have been calculated from the envelope method [13, 14]. The results show small narrowing of the optical band gap with an increase in Tb amount, which origins from different structure types of investigated thin films (Tab. 1).

T a b l e 2. Selected optical parameters of TiO_2:Tb (0.4 at.% Tb) and TiO_2:Tb (2 at.% Tb) thin films on SiO_2.

Thin film	λ_{cutoff} [nm]	Thickness [nm]	n (λ > 500 nm)	E_g^{opt} [eV]
TiO_2:Tb (0.4 at.% Tb)	340	800	1.482	3.26
TiO_2:Tb (2 at.% Tb)	350	1100	1.482	3.02

5. Conclusions

The study of the influence of terbium amount on structural and optical properties of TiO_2:Tb thin films has been presented. Thin films were prepared by magnetron sputtering from metallic Ti-Tb mosaic target. XRD examination and AFM images revealed the high quality nanocrystalline anatase and rutile structures of TiO_2 thin films with 0.4 at.% and 2 at.% of Tb, respectively. Optical investigations have shown that terbium dopant shifts the fundamental absorption edge in the longer wavelength region as compared to pure TiO_2 thin film. The above results give the possibility to obtain nanocrystalline Tb-doped TiO_2 thin films, transparent to light in a visible range with different structural properties.

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