

# **Study of structural and optical properties of TiO<sub>2</sub>:Tb thin films prepared by high energy reactive magnetron sputtering method**

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This work is focused on structural and optical properties of TiO<sub>2</sub> thin films doped with different amount of terbium. The thin films have been prepared by high energy reactive magnetron sputtering (HE RMS) and by low pressure hot target reactive magnetron sputtering (LP HTRS) processes. Thin films were deposited from mosaic, metallic Ti-Tb target sputtered under oxygen plasma (without argon) at a pressure below 10<sup>-1</sup> Pa. Structural examinations show nanocrystalline nature of prepared thin films with either anatase or rutile phases depending on concentration of Tb 0.4 at.% and 2.6 at.%, respectively. The phase transformation from the anatase to the rutile has not been observed after additional post-deposition annealing even at the temperature up to 1000 K. Based on investigations performed with the help of atomic force microscope high nanocrystalline, close-packed structure has been found. Studies of refraction index revealed higher value for the thin films prepared by the HE RMS than by the LP HTRS methods.

Keywords: TiO<sub>2</sub>, magnetron sputtering, Tb, structural properties, optical properties.

## **1. Introduction**

From a review of the literature published during last decade, a growing pursuit of obtaining dense crystal structure of different coatings with novel properties may be noticed [1, 2]. Especially many papers are addressed to titanium dioxide (TiO<sub>2</sub>) thin film prepared by different deposition methods [3, 4]. Because of industrial usefulness, the most important in this field seem to be vapor physical deposition methods, such as magnetron sputtering [1, 2, 5]. Typically, enhanced energy per molecule which is needed for obtaining a dense structure in sputtering process could be assured by appropriate selection of pressure [6], substrate temperature [7], argon/oxygen ratio [2] and power of plasma discharge [8]. Since depending on application, TiO<sub>2</sub> with different crystal structure, *i.e.* anatase, rutile or mixed anatase-rutile, is required [9], for dense, nanocrystalline structure more energy should be delivered to the thin film

nucleation site. Modification of sputtering process parameters allows to receive desired structural properties of the thin films. That can be realized, for example, by application of additional Ar ions bombardment (ion beam assisted deposition) [10] or by using some of “high energy” processes, like high power impulse magnetron sputtering (HP IMS) [11] or high energy reactive magnetron sputtering (HE RMS) [5].

Besides modification of the preparation process, desirable structure can be obtained by introduction of a specific amount of selected elements during the film growth, *i.e.* by doping. In the present work, structural and optical investigations of the TiO<sub>2</sub> thin films deposited by HE RMS and doped with terbium have been described.

## 2. Experimental

For the purpose of the present work, thin films of TiO<sub>2</sub> and TiO<sub>2</sub> doped with two selected amounts of Tb (TiO<sub>2</sub>:Tb) have been deposited by HE RMS on silica glass (a-SiO<sub>2</sub>) and 100-oriented silicon substrates. Besides using only O<sub>2</sub> as a reactive and working gas at a low pressure, enhanced energy of particles during the film growth was maintained by increasing the target temperature and by using 164 kHz unipolar pulses with the peak amplitude of 1800 V. Details of the preparation method have already been reported elsewhere [5, 12]. The properties of TiO<sub>2</sub>:Tb thin films, prepared by HE RMS process [12], have been compared with the properties of TiO<sub>2</sub> thin films prepared by LP HTRS process [13]. The HE RMS process is a modification of LP HTRS process (increase in supply voltage from 1200 V up to 1800 V) in order to obtain more nanocrystalline and densified structure.

The amount of Tb in analyzed TiO<sub>2</sub>:Tb thin films evaluated with the help of an energy disperse spectrometer (EDS) was 0.4 and 2.6 at.%.

Structural properties of prepared thin films deposited on silica glass substrates were investigated by the X-ray diffraction (XRD) method.

Optical properties were evaluated based on transmission measurements performed with a scientific grade spectrophotometer in a spectral range of 200–1100 nm. The refractive index of manufactured thin films was evaluated based on reverse engineering method using Film Star software from FTG Associates [14].

## 3. Results and discussion

The XRD results of TiO<sub>2</sub> and TiO<sub>2</sub>:Tb thin films have been collected in Tab. 1. The structure of the TiO<sub>2</sub> thin film prepared by HE RMS has been compared with structural properties previously reported by the authors [6] for the TiO<sub>2</sub> thin films prepared by low pressure hot target reactive magnetron sputtering (LP HTRS). As it could be seen in Tab. 1, the major difference between these two methods is that prepared TiO<sub>2</sub> thin films had either the rutile (HE RMS) or the anatase (LP HTRS) crystal form. Moreover, the rutile crystallites were almost three times smaller than the anatase ones. That indicates the densification of the thin films crystal structure that occurs due to the enhanced energy applied to the nuclei during the thin film growth.

Table 1. XRD results for TiO<sub>2</sub> and TiO<sub>2</sub>:Tb thin films. Designations: *D* – average crystallite size, *d* – interplanar distance,  $\Delta d$  – relative distance between the interplanar distance *d* and standard interplanar distance *d*<sub>PDF</sub>.

Process	Thin film	Phase	<i>D</i> [nm]	<i>d</i> [nm]	$\Delta d$ [%]	Type of stress	Ref.
LP HTRS as-deposited	TiO <sub>2</sub>	anatase	21.3	0.3504	-0.45	compression	[6]
HE RMS as-deposited	TiO <sub>2</sub>	rutile	8.7	0.3250	+0.09	tension	this work
HE RMS as-deposited	TiO <sub>2</sub> :Tb(0.4 at.%)	anatase	11.7	0.3522	+0.06	tension	this work
HE RMS as-deposited	TiO <sub>2</sub> :Tb(2.6 at.%)	rutile	6.6	0.3248	+0.03	tension	this work
PDF no 211272 TiO <sub>2</sub>	–	anatase	–	0.3520	–	–	[16]
PDF no 211276 TiO <sub>2</sub>	–	rutile	–	0.3247	–	–	[17]

From Table 1 one can conclude that TiO<sub>2</sub> thin films doped with Tb had either the anatase or the rutile structure, depending on the amount of Tb dopant. The TiO<sub>2</sub>:(0.4 at.% Tb)-anatase films were composed of crystallites with the average size almost twice smaller as compared to those TiO<sub>2</sub>-anatase films prepared by LP HTRS (11.7 nm and 21.3 nm, respectively). A similar effect was observed in the case of the rutile films. The average grain size of TiO<sub>2</sub>:Tb(2.6 at.%) thin films was 6.6 nm, what is about 30% smaller as compared to undoped TiO<sub>2</sub> (8.7 nm). Therefore it may be concluded that doping the TiO<sub>2</sub> thin films prepared by HE RMS with suitable amount of Tb causes noticeable increase in nanocrystallinity of thin films. Doping with other lanthanides was found to have a similar effect on the TiO<sub>2</sub> structure [15].

Additionally, the type of stress occurring in the investigated films on the basis on the  $\Delta d$  parameter has been determined as:

$$\Delta d = \frac{d - d_{\text{PDF}}}{d_{\text{PDF}}} \cdot 100\%$$

where: *d* – the interplanar distance, *d*<sub>PDF</sub> – the standard interplanar distance from powder diffraction file [16, 17].

The positive sign of  $\Delta d$  testified about tension stresses, while the negative sign of  $\Delta d$  informed about the compressed ones.

AFM images of TiO<sub>2</sub>:Tb thin films with Tb 0.4 at.% (Figs. 1a and 1b) and 2.6 at.% (Figs. 1d and 1e) have been presented. Moreover, the histograms, which display distribution of grains height (Figs. 1b and 1e) and profiles of the surface (Figs. 1c and 1f), have been shown.

The AFM images (Fig. 1) display high nanocrystalline, close-packed structure. The grains of the thin films with anatase structure are considerably bigger (Fig. 1a)





Table 2. Structural parameters of TiO<sub>2</sub>:Tb(0.4 at.%) thin films deposited on a-SiO<sub>2</sub> and Si (100) substrates by HE RMS. Designations:  $D$  – average crystallite size,  $d$  – interplanar distance,  $\Delta d$  – relative distance between the interplanar distance  $d$  and standard interplanar distance  $d_{\text{PDF}}$ .

Substrate type	Thin film	Structure characterization				
		Phase	$D$ [nm]	$d$ [nm]	$\Delta d$ [%]	Type of stress
a-SiO <sub>2</sub>	TiO <sub>2</sub> :Tb(0.4 at.%) as-deposited	anatase	11.7	0.3522	+0.06	tension
	TiO <sub>2</sub> :Tb(0.4 at.%) annealed at 800 °C	anatase (76%)	28.2	0.3495	-0.71	compression
		rutile (24%)	18.2	0.3239	-0.25	compression
Si (100)	TiO <sub>2</sub> :Tb(0.4 at.%) as-deposited	anatase	13.1	0.3519	-0.03	compression
	TiO <sub>2</sub> :Tb(0.4 at.%) annealed at 800 °C	anatase (88%)	28	0.3494	-0.74	compression
		rutile (12%)	23.4	0.3232	-0.46	compression
PDF [16]	TiO <sub>2</sub>	rutile	–	0.3247	–	–
PDF [17]	TiO <sub>2</sub>	anatase	–	0.3520	–	–

with small amount of terbium (0.4 at.%), the Tb<sup>3+</sup> ions may form the Tb–O–Ti bindings [22] on the TiO<sub>2</sub> crystallites surface, similarly when the Eu at the amount of 0.1 at.% was applied as a dopant [15]. Formation of those bindings is due to strong affinity of the lanthanides to the oxygen and causes that the phase transformation from the anatase into the rutile is blocked up to 800 °C. Such stabilization of the anatase structure is strongly advisable, because of wide application area of the anatase films, like, for example, in photocatalytic thin films [23] and in thin films for transparent electrodes [24].

At the temperature of 800 °C the two-phase system is formed, with considerably major amount of the anatase as compared to the rutile (Tab. 2). Nevertheless, with higher amount of Tb(2.6 at.%), the Tb may form its own oxides, incorporated into the TiO<sub>2</sub> lattice. This conclusion is confirmed by the fact that the TiO<sub>2</sub>:Tb elementary cell sizes, determined on the basis of the XRD measurements ( $a = 459.33$  pm,  $c = 295.92$  pm), are bigger than those for the TiO<sub>2</sub>-matrix standard cell ( $a = 458.4$  pm,  $c = 295.3$  pm) [18, 25]. Therefore, the Tb ions are built in the interstitial positions of the TiO<sub>2</sub> nanocrystallites.

From application point of view, besides structural properties, the optical properties of the thin films are very important. In Figure 3, spectral characteristics of refraction index  $n$  for three, prepared by HE RMS process, thin films, *i.e.*: TiO<sub>2</sub>, TiO<sub>2</sub>:Tb(0.4 at.%) and TiO<sub>2</sub>:Tb(2.6 at.%) have been compared. Additionally, for comparison, the  $n$  spectrum developed for TiO<sub>2</sub> thin film prepared by LP HTRS has been enclosed. It is worth to point out that the refraction index evaluated in the case of TiO<sub>2</sub>:Tb(0.4 at.%) with anatase structure, has insignificant lower values than in the case of the thin films with rutile structure: TiO<sub>2</sub> and TiO<sub>2</sub>:Tb(2.6 at.%). Considerably smaller  $n$  values evaluated for the TiO<sub>2</sub>-anatase thin films testify about structure densification that occurs thanks to the Tb-dopant introduction in the thin



been presented. The results show that by the appropriate selection of the amount of the Tb-dopant and the post-process treatment of the thin films prepared by high energy (HE RMS) process, the TiO<sub>2</sub> thin films with different type of crystal structure, *i.e.* the anatase, the rutile or the two-phase anatase-rutile system, can be obtained. It has been shown that the Tb-dopant inhibits the anatase to the rutile phase transformation at high temperatures. Therefore it stabilizes the TiO<sub>2</sub>-anatase.

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