Optica Applicata, Vol. XXXIX, No. 4, 2009

Study of structural and optical properties of TiO_2:Tb thin films prepared by high energy reactive magnetron sputtering method

Jaroslaw DOMARADZKI*, Danuta KACZMAREK, Eugeniusz L. PROCIOW, Damian WOJCIESZAK, Karolina SIERADZKA, Michal MAZUR, Marcin LAPINSKI

Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, Janiszewskiego 11/17, 50-372 Wrocław, Poland

*Corresponding author: jaroslaw.domaradzki@pwr.wroc.pl

This work is focused on structural and optical properties of TiO_2 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^{-1} 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_2, 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_2) 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_2 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_2 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_2 and TiO_2 doped with two selected amounts of Tb (TiO_2:Tb) have been deposited by HE RMS on silica glass (a-SiO_2) and 100-oriented silicon substrates. Besides using only O_2 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_2:Tb thin films, prepared by HE RMS process [12], have been compared with the properties of TiO_2 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 densed structure.

The amount of Tb in analyzed TiO_2: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_2 and TiO_2:Tb thin films have been collected in Tab. 1. The structure of the TiO_2 thin film prepared by HE RMS has been compared with structural properties previously reported by the authors [6] for the TiO_2 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_2 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.

T a b l e 1. XRD results for TiO_2 and TiO_2:Tb thin films. Designations: D – average crystallite size, d – interplanar distance, Δd – relative distance between the interplanar distance d and standard interplanar distance d_{PDF}.

Process	Thin film	Phase	D [nm]	d [nm]	Δd [%]	Type of stress	Ref.
LP HTRS as-deposited	TiO_2	anatase	21.3	0.3504	–0.45	compression	[6]
HE RMS as-deposited	TiO_2	rutile	8.7	0.3250	+0.09	tension	this work
HE RMS as-deposited	TiO_2:Tb(0.4 at.%)	anatase	11.7	0.3522	+0.06	tension	this work
HE RMS as-deposited	TiO_2:Tb(2.6 at.%)	rutile	6.6	0.3248	+0.03	tension	this work
PDF no 211272 TiO_2	–	anatase	–	0.3520	–	–	[16]
PDF no 211276 TiO_2	–	rutile	–	0.3247	–	–	[17]

From Table 1 one can conclude that TiO_2 thin films doped with Tb had either the anatase or the rutile structure, depending on the amount of Tb dopant. The TiO_2:(0.4 at.% Tb)-anatase films were composed of crystallites with the average size almost twice smaller as compared to those TiO_2-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_2:Tb(2.6 at.%) thin films was 6.6 nm, what is about 30% smaller as compared to undoped TiO_2 (8.7 nm). Therefore it may be concluded that doping the TiO_2 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_2 structure [15].

Additionally, the type of stress occurring in the investigated films on the basis on the Δd parameter has been determined as:

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

where: d – the interplanar distance, d_{PDF} – the standard interplanar distance from powder diffraction file [16, 17].

The positive sign of Δd testified about tension stresses, while the negative sign of Δd informed about the compressed ones.

AFM images of TiO_2:Tb thin films with Tb 0.4 at.% (Figs. 1**a** and 1**b**) and 2.6 at.% (Figs. 1**d** and 1**e**) have been presented. Moreover, the histograms, which display distribution of grains height (Figs. 1**b** and 1**e**) and profiles of the surface (Figs. 1**c** and 1**f**), 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. 1**a**)

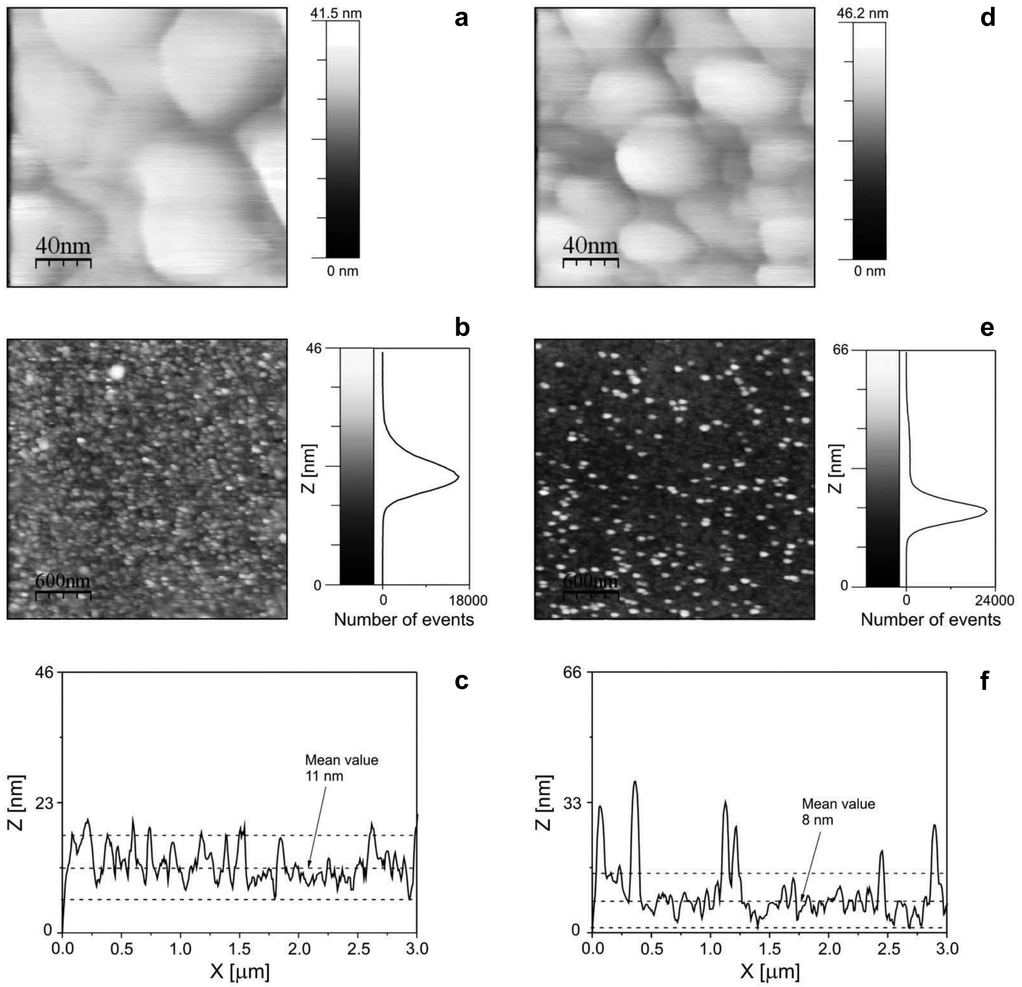

Fig. 1. AFM images of TiO_2:Tb thin films with histograms, which display distribution of grains height: Tb 0.4 at.% (**a**, **b**); Tb 2.6 at.% (**d**, **e**) and profiles of the surface (**c**, **f**). The thin films were deposited on a-SiO_2 substrates by HE RMS method.

than the grains of the rutile one (Fig. 1**d**). From the histograms (Figs. 1**b** and 1**e**) one can conclude that the distribution of grains height on the films surface is almost homogenous. Additionally, surface profiles have been shown in Figs. 1**c** and 1**f**. White spots (Fig. 1**e**) and also high peaks visible in the surface profile (Fig. 1**f**) represent grains of the next formed layer.

The TiO_2:Tb(0.4 at.%) thin films with the anatase phase (Tab. 1) were additionally post deposition annealed in order to observe the anatase to the rutile phase transformation. Usually, the phase transformation from the anatase to the thermodynamically stable rutile proceeds at the temperature not lower than 700 °C [18]. Therefore, for

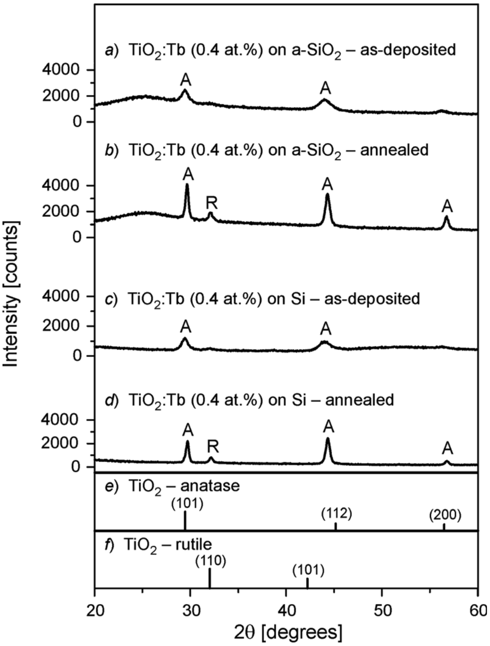

Fig. 2. The XRD patterns of TiO_2:Tb(0.4 at.%) thin films deposited in HE RMS on: a-SiO_2 (*a*, *b*) and Si (100) substrates (*c*, *d*), after deposition (*a*, *c*) and after additional annealing at 800 °C by 2 hours in an ambient air (*b*, *d*). At the bottom of the figure, PDF cards for: the anatase [16] (*e*) and the rutile [17] (*f*) are included.

the purpose of the present study, annealing process of TiO_2:Tb(0.4 at.%) thin films at the temperature of 800 °C for 2 hours in air has been performed.

In Figure 2, the XRD patterns of TiO_2:Tb(0.4 at.%) thin films deposited on a-SiO_2 (curves *a* and *b*) and Si (100) (curves *c* and *d*) substrates have been presented. The results have shown that even at 800 °C there was no complete transformation from the anatase into the rutile structure, but, the two-phase system with a significant majority of the anatase was observed (independently of the kind of substrate). Presented results proved that the Tb dopant at the amount of 0.4 at.%, besides blocking the rutile formation during thin films deposition and increasing the nanocrystallinity of the thin films (Tab. 1), performs one more important function. As it was shown in Fig. 2 and in Tab. 2, Tb stabilizes the anatase structure above the temperature of the anatase transformation into the rutile that is 800 °C.

Because of the significant difference in the ion radius, the replacement of the titanium ions with the terbium ions in TiO_2 lattice is not so probable [19]. However, similar results have previously been reported in the literature [20, 21] concerning stabilization of the anatase structure with europium. Therefore, the stabilization effect of the anatase structure at high temperature by terbium dopant may be explained by analogy to the Eu in the following way. In case of TiO_2 thin films doped

Table 2. Structural parameters of TiO_2:Tb(0.4 at.%) thin films deposited on a-SiO_2 and Si (100) substrates by HE RMS. Designations: D – average crystallite size, d – interplanar distance, Δd – relative distance between the interplanar distance d and standard interplanar distance d_{PDF}.

Substrate type	Thin film	Structure characterization				
		Phase	D [nm]	d [nm]	Δd [%]	Type of stress
a-SiO_2	TiO_2:Tb(0.4 at.%) as-deposited	anatase	11.7	0.3522	+0.06	tension
	TiO_2: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_2:Tb(0.4 at.%) as-deposited	anatase	13.1	0.3519	−0.03	compression
	TiO_2: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_2	rutile	–	0.3247	–	–
PDF [17]	TiO_2	anatase	–	0.3520	–	–

with small amount of terbium (0.4 at.%), the Tb^{3+} ions may form the Tb–O–Ti bindings [22] on the TiO_2 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_2 lattice. This conclusion is confirmed by the fact that the TiO_2: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_2-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_2 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_2, TiO_2:Tb(0.4 at.%) and TiO_2:Tb(2.6 at.%) have been compared. Additionally, for comparison, the n spectrum developed for TiO_2 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_2:Tb(0.4 at.%) with anatase structure, has insignificant lower values than in the case of the thin films with rutile structure: TiO_2 and TiO_2:Tb(2.6 at.%). Considerably smaller n values evaluated for the TiO_2-anatase thin films testify about structure densification that occurs thanks to the Tb-dopant introduction in the thin

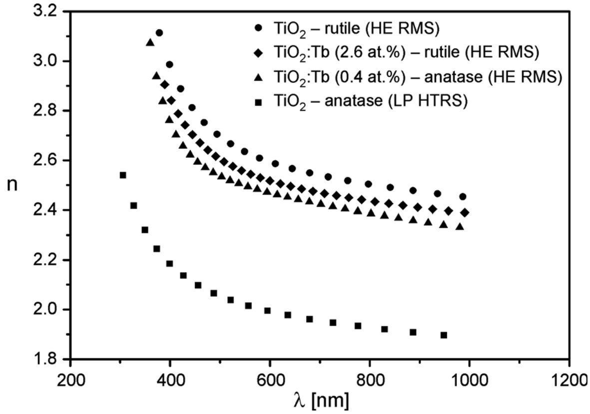

Fig. 3. Characteristics of refraction index n of thin films: TiO_2-rutile, TiO_2:Tb(0.4 at.%)-anatase, TiO_2:Tb(2.6 at.%)-rutile, prepared by HE RMS and TiO_2-anatase prepared by LP HTRS.

T a b l e 3. Optical parameters determined on the basis of optical transmission measurements for the TiO_2 and TiO_2:Tb thin films prepared by LP HTRS and HE RMS.

Deposition process	Thin film	Phase	Thickness [nm]	n (at λ = 600 nm)
HE RMS as-deposited	TiO_2	rutile	252	2.60
HE RMS as-deposited	TiO_2:Tb(0.4 at.%)	anatase	420	2.47
HE RMS as-deposited	TiO_2:Tb(2.6 at.%)	rutile	558	2.52
LP HTRS as-deposited	TiO_2	anatase	522	1.99

films prepared by HE RMS. Therefore, it was possible to receive the thin films with densely packed structure, not only in the rutile form, but also as the dense anatase.

Additionally, in Tab. 3, the optical parameters, determined on the basis of the optical transmission measurements, have been compared. From comparison of the refractive index for prepared thin films one can conclude that densification of the structure, obtained with the aid of the HE RMS, has an effect on an increase (of about 23%) in the refraction index, as compared to the thin film prepared by the LP HTRS. However, the difference between the n values for the thin films prepared by the HE RMS varies from 3% up to 5% only.

4. Conclusions

In this work, the study of structural and optical properties of the TiO_2 and TiO_2:Tb thin films prepared by two types of reactive magnetron sputtering methods has 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_2 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_2-anatase.

Acknowledgements – This work was financed from the sources granted by the NCBiR in the years 2008–2010 as a development research project number N R02 0019 04 and the the statute sources given by Polish Ministry of Science and Education No. 343 646.

References

[1] OKIMURA K., *Low temperature growth of rutile TiO_2 films in modified rf magnetron sputtering*, Surface and Coatings Technology **135**(2–3), 2001, pp. 286–290.
[2] BAOSHUN LIU, XIUJIAN ZHAO, QINGNAN ZHAO, CHUNLING LI, XIN HE, *The effect of O_2 partial pressure on the structure and photocatalytic property of TiO_2 films prepared by sputtering*, Materials Chemistry and Physics **90**(1), 2005, pp. 207–212.
[3] MITU B., VIZIREANU S., BIRJEGA R., DINESCU M., SOMACESCU S., OSICEANU P., PÂRVULESCU V., DINESCU G., *Comparative properties of ternary oxides of ZrO_2–TiO_2–Y_2O_3 obtained by laser ablation, magnetron sputtering and sol–gel techniques*, Thin Solid Films **515**(16), 2007, pp. 6484–6488.
[4] WON D.-J., WANG C.-H., JANG H.-K., CHOI D.-J., *Effects of thermally induced anatase-to-rutile phase transition in MOCVD-grown TiO_2 films on structural and optical properties*, Applied Physics A **73**(5), 2001, pp. 595–600.
[5] KACZMAREK D., PROCIOW E., DOMARADZKI J., BORKOWSKA A., MIELCAREK W., WOJCIESZAK D., *Influence of substrate type and its placement on structural properties of TiO_2 thin films prepared by high energy reactive magnetron sputtering method*, Materials Science-Poland **26**(1), 2008, pp. 113–117.
[6] DOMARADZKI J., KACZMAREK D., PROCIOW E.L., BORKOWSKA A., SCHMEISSER D., BEUCKERT G., *Microstructure and optical properties of TiO_2 thin films prepared by low pressure hot target reactive magnetron sputtering*, Thin Solid Films **513**(1–2), 2006, pp. 269–274.
[7] THORNTON J.A., *Influence of apparatus geometry and deposition conditions on the structure and topography of thick sputtered coatings*, Journal of Vacuum Science and Technology **11**(4), 1974, pp. 666–670.
[8] GUENTHER K.H., *Revisiting structure-zone models for thin-film growth*, Proceedings of SPIE **1324**, 1990, pp. 2–12.
[9] LI G., CHEN L., GRAHAM M.E., GRAY K.A., *A comparison of mixed phase titania photocatalysts prepared by physical and chemical methods: The importance of the solid–solid interface*, Journal of Molecular Catalysis A: Chemical **275**(1–2), 2007, pp. 30–35.
[10] ESINGER W., *On the mechanism of crystal growth orientation of ion beam assisted deposited thin films*, Nuclear Instruments and Methods in Physics Research B **106**(1–4), 1995, pp. 142–146.
[11] MACAK K., KOUZNETSOV V., SCHNEIDER J., HELMERSSON U., PETROV I., *Ionized sputter deposition using an extremely high plasma density pulsed magnetron discharge*, Journal of Vacuum Science and Technology A **18**(4), 2000, pp. 1533–1537.
[12] PROCIÓW E., DOMARADZKI J., KACZMAREK D., BERLICKI T., Polish patent, 2007, No. P382 163.
[13] PROCIÓW E., DOMARADZKI J., KACZMAREK D., BERLICKI T., Polish patent, 2006, No. P 379 365.
[14] Film Star software, FTG Software Associates, Princeton, NJ, 08542 USA.

[15] Domaradzki J., Kaczmarek D., Borkowska A., Schmeisser D., Mueller S., Wasielewski R., Ciszewski A., Wojcieszak D., *Influence of annealing on the structure and stoichiometry of europium doped titanium dioxide thin films*, Vacuum **82**(10), 2008, pp. 1007–1012.

[16] Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Card 21-1272 – PDF.

[17] Powder Diffraction File, Joint Committee on Powder Diffraction Standards, ASTM, Philadelphia, PA, 1967, Card 21-1276 – PDF.

[18] Diebold U., *The surface science of titanium dioxide*, Surface Science Reports **48**(5–8), 2003, pp. 53–229.

[19] Kaczmarek D., Domaradzki J., Wojcieszak D., Wasilewski R., Borkowska A., Prociów E.L, Ciszewski A., *Structural investigations of TiO_2:Tb thin films by X-ray diffraction and atomic force microscopy*, Applied Surface Science **254**(14), 2008, pp. 4303–4307.

[20] Zeng Q.G., Ding Z.J., Zhang Z.M., *Synthesis, structure and optical properties of Eu^{3+}/TiO_2 nanocrystals at room temperature*, Journal of Luminescence **118**(2), 2006, pp. 301–307.

[21] Setiawati E., Kawano K., *Stabilization of anatase phase in the rare earth; Eu and Sm ion doped nanoparticle TiO_2*, Journal of Alloys and Compounds **451**(1–2), 2008, pp. 293–296.

[22] Saif M., Abdel-Mottaleb M.S.A., *Titanium dioxide nanomaterial doped with trivalent lanthanide ions of Tb, Eu and Sm: Preparation, characterization and potential applications*, Inorganica Chimica Acta **360**(9), 2007, pp. 2863–2874.

[23] Mane R.S., Joo O.-S., Min S.-K., Lokhande C.D., Han S.-H., *A simple and low temperature process for super-hydrophilic rutile TiO_2 thin films growth*, Applied Surface Science **253**(2), 2006, pp. 581–585.

[24] Chen T.L., Furubayashi Y., Hirose Y., Hitosugi T., Shimada T., Hasegawa T., *Anatase phase stability and doping concentration dependent refractivity in codoped transparent conducting TiO_2 films*, Journal of Physics D: Applied Physics **40**(19), 2007, pp. 5961–5964.

[25] Jung C.-K., Lee S.B. Boo J.-H., Ku S.-J., Yu K.-S., Lee J.-W., *Characterization of growth behavior and structural properties of TiO_2 thin films grown on Si(1 0 0) and Si(1 1 1) substrates*, Surface and Coatings Technology **174–175**, 2003, pp. 296–302.

Received June 19, 2009
in revised form August 13, 2009