

Luminescent materials based on thin metal oxide films doped with rare earth ions

© P. Kanarjov, V. Reedo, I. Oja Acik*, L. Matisen, A. Vorobjov, V. Kiisk, M. Krunks*, I. Sildos

Institute of Physics, University of Tartu,
51014 Tartu, Estonia

* Tallinn University of Technology, Department of Materials Science,
19086 Tallinn, Estonia

Thin luminescent films of $\text{TiO}_2:\text{Sm}$ were prepared by sol-gel-method using spray pyrolysis technique. Various techniques (including IR absorption, Raman, AFM, XPS, photoluminescence) were used to characterize the samples. After a thermal treatment up to 750°C , an intense Sm^{3+} luminescence with a well-resolved fine structure was observed under optical excitation within the fundamental absorption band of the TiO_2 host. After further thermal treatments up to 950°C the luminescence was quenched yet still no anatase-to-rutile phase transformation was observed. The behavior is attributed to nanocrystallinity and segregation of Sm ions onto surface.

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1. Introduction

Rare-earth-doped oxides have been applied in a number of luminescence applications. Although the traditional applications (CRT and lamp phosphors) have matured, new technological challenges like that plane displays, solid state lasers, white light emitting diodes, etc. have raised need for new specialized materials.

We have previously used a couple of techniques to prepare rare-earth-doped TiO_2 films [1,2]. Atomic layer deposition appears to be a promising technique for producing pure crystalline films with precisely controllable thickness. Yet, an intentional incorporation of impurities appears to be complicated. A versatile but expensive doping method is ion implantation. In addition, high concentrations of ion implanted impurities destroy significantly the crystalline structure. In the case of sol-gel-method one can point out excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and low preparation temperature. However, the influence of organic traces on the optical quality of material might be noticeable. Furthermore, traditional sol-gel film-deposition techniques (dip-coating, spin-coating) might not be applicable to complex-shaped surfaces.

The aim of this investigation was to develop a spray pyrolysis technique to obtain rare-earth-activated metal-oxide films as luminescent materials.

2. Experimental

The sol-gel-method using spray pyrolysis technique was used to prepare the samples [3]. The precursor solution contained titanium (IV) isopropoxide (TTIP), acetylacetone (AcAc) and ethanol, with TTIP concentration of 6 vol.% at TTIP:AcAc molar ratio of 1:2. To introduce Sm ions to precursor solution, certain amount of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ was added. The precursor solution was sputtered by a pneumatic

spray system onto high-quality quartz substrate maintained at 320°C . In our deposition system, compressed air served as a carrier gas. Each spray pulse lasted for 60 s, the pulses were separated by a pause of the same duration. Thickness of the films was controlled by the number of spray pulses applied. Whereas the concentration of Sm impurities ranged from 0.5 to 5 at.%, most of the measurements were performed on samples containing 5 at.% Sm.

A number of characterization techniques were used to describe the samples and to optimize the preparation conditions. Transmission spectra revealed thickness and optical properties of the films. IR absorption was used to track the traces of organic precursors. Raman scattering indicates phase content (from amorphous to anatase to rutile during the annealing treatment). X-ray photoelectron spectroscopy (XPS) allowed monitoring thermally activated diffusion of Sm ions into the skin layer of the film. Atomic force microscopy (AFM) was used to monitor growth of crystallites during the annealing treatment.

For measurement of photoluminescence (PL) spectra, a pulsed Nd:YAG laser operating at 355 nm and 10 kHz was used as the excitation source. The laser beam was focused in a backscattering geometry onto about 1 mm^2 spot on the surface of the sample. Spectra were recorded by a spectrograph (Andor SR-303i) equipped with an intensified charge coupled device (Andor DH-501).

The Raman spectra were recorded in a backscattering geometry by using a homemade micro-Raman spectrometer consisting of a confocal microscope with 50x objective, a $\text{Nd}^{3+}:\text{YAG}$ laser operating at 532 nm, a notch filter for removal of the scattered laser light, and Andor SR-303i spectrograph equipped with a EMCCD detector.

3. Results and discussion

IR absorption studies indicate that the films contain initially organic residues as $\text{M}-\text{O}-\text{C}$, CH_2 and CH_3 groups

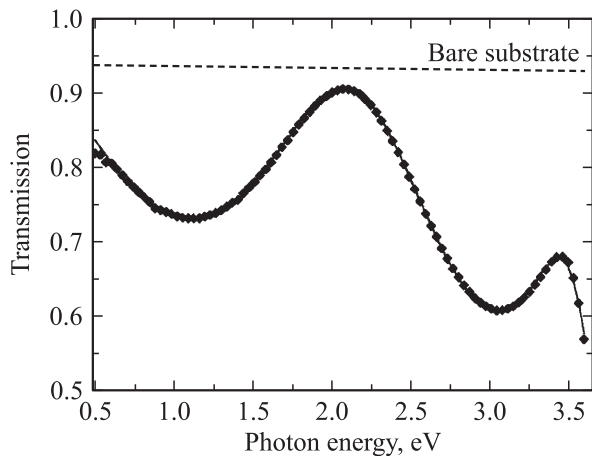


Figure 1. Transmission spectrum of the thickest $\text{TiO}_2:\text{Sm}$ film annealed at 500°C for 2h. Symbols represent experimental data, solid line is a fit to the model.

(1545 , 1452 and 1415 cm^{-1} , respectively). Both IR and Raman spectra indicate amorphous phase, and no Sm-related luminescence was observed. The basic annealing was performed at 500°C for 2h in air. This treatment results in the development of an anatase structure free of organic residues and appearance of Sm luminescence under the band-to-band excitation of the host as already observed in our previous studies [1,2].

The transmission spectra of thicker films showed quite excellent interference fringes (Fig. 1). The spectra were analyzed assuming a homogeneous uniform layer of film on transparent substrate [4]. The optical constants of the film were modeled by a single Lorentzian oscillator. Curve fitting leads to an excellent agreement between the measured and the modeled spectra as shown in Fig.1.

The evaluated thickness (as well as observed Raman and luminescence signal strength) was closely proportional to the number of spray pulses applied. The thickest film (3 spray pulses, 5 at.% Sm) had a thickness of 137 nm, a refractive index of 2.16 (at 550 nm) and an absorption coefficient of $0.2\mu\text{m}^{-1}$ (at 550 nm). Transmission spectra of thinner films (1 or 2 pulses) did not allow such a reliable interpretation, which might be due to a nonuniform film thickness. There appeared a tendency of increasing thickness with the increased Sm content, which is attributed to differing internal properties of the precursor solution. According to the Bruggeman effective medium theory [5], the observed refractive index still corresponds to a porosity of $\sim 25\%$.

It has been shown previously that quite essential control over the defect structure in anatase single crystals can be achieved by annealing in different atmospheres [6,7]. For example, high-temperature annealing in vacuum or hydrogen ambient leads to the removal of oxygen and defect formation in the bulk, whereas annealing in oxygen ambient ultimately improves the crystal quality. Therefore, we performed an additional annealing at higher temperatures

in air in order to determine the optimum conditions for luminescence. Most intense luminescence was observed after annealing at 750°C (Fig. 2). Annealing at even higher temperatures led to a rapid quenching of the luminescence. At the same time, the Raman signal still indicated an improvement of a good anatase phase, and no anatase-to-rutile transformation could be observed (Fig.3). The fine structure of the PL spectrum also remained unchanged. Therefore the quenching of the luminescence signal cannot be connected to the phase transition.

It is well-known that impurities as well as crystallite size can significantly influence the anatase-to-rutile phase transition temperature [10]. In the case of bulk materials, it has been established that trivalent impurities usually

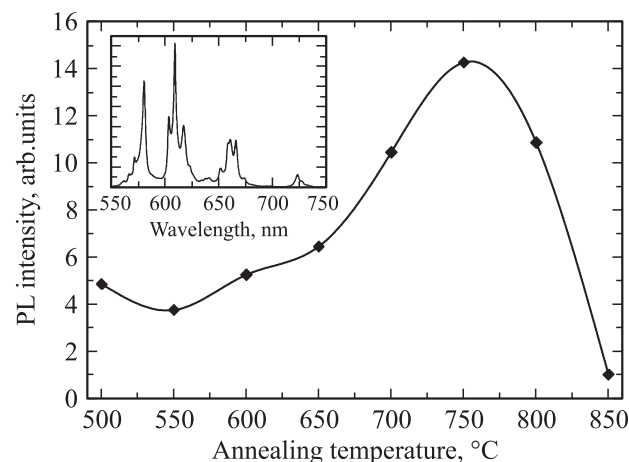


Figure 2. Dependence of the PL intensity of 5 at.% $\text{Sm}^{3+}:\text{TiO}_2$ on the annealing temperature. Each point corresponds to annealing in air for 15 min. Solid line is a guide for eye. The inset displays the Sm^{3+} luminescence spectrum (showing $^4G_{5/2} \rightarrow ^6H_J$ transitions, where $J = 5/2, 7/2, 9/2, 11/2$) corresponding to the annealing at 750°C .

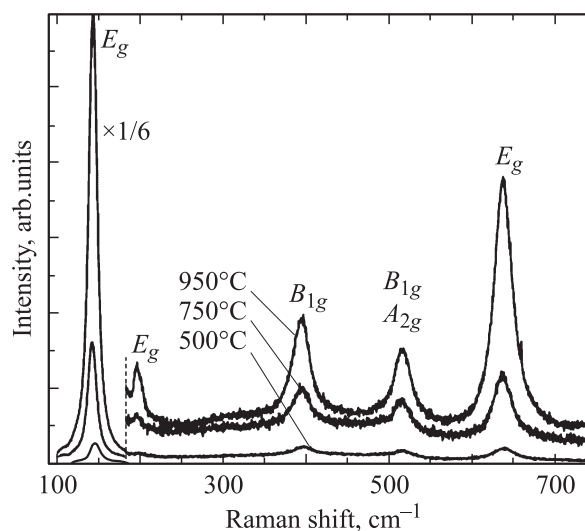


Figure 3. Dependence of the Raman spectrum of 5 at.% $\text{Sm}^{3+}:\text{TiO}_2$ on the annealing temperature. Raman peaks of anatase have been identified according to Refs [8,9].

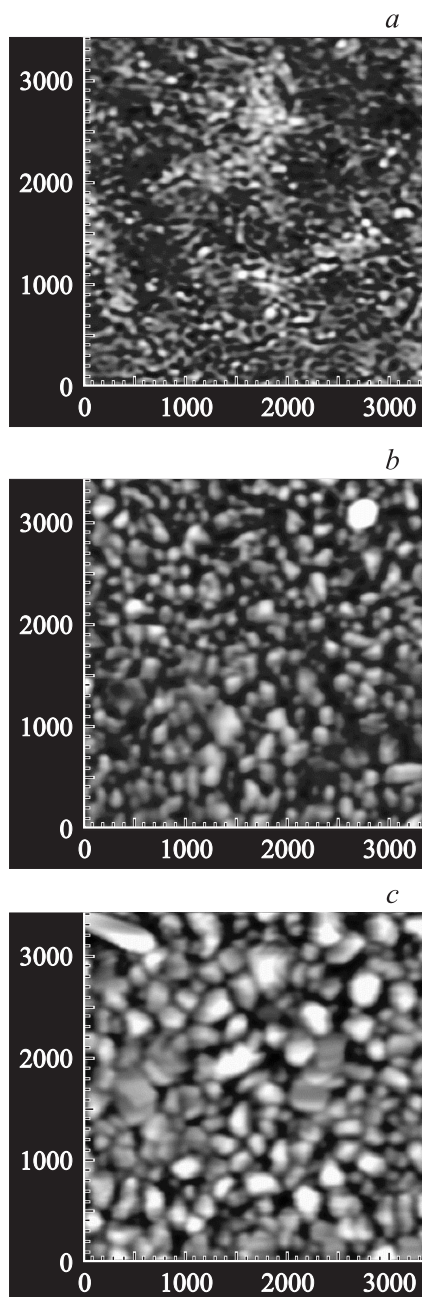


Figure 4. AFM images ($3 \times 3 \mu\text{m}$) of the surface of Sm:TiO₂ film after annealing at 750 (a), 850 (b) and 950° (c). The scale is given in nanometers.

accelerate the transition because they introduce charge compensating oxygen vacancies acting as nucleation centers [11,12]. This scenario does not seem to be applicable in the present case. It has been found, however, that relatively low concentrations of rare-earth impurities can inhibit the growth of nanocrystallites, which, in turn, stabilizes the anatase phase [13].

In order to obtain an insight on the possible reason of PL quenching, AFM and XPS characterization was carried out. AFM images indicate a significant coarsening of

the surface structure during the increase of the annealing temperature from 750 to 950°C (Fig. 4). The average size of the crystallites grows from 50 to 200 nm. The linewidths of Raman peaks also decrease confirming the growth of crystallites. It has been proposed that surface states play an essential role in sensitizing the luminescence of TiO₂ nanoparticles [4]. Therefore, it is possible that the efficiency of luminescence excitation is reduced as the particle size is increased.

XPS spectra indicate a steady improvement of trivalent Sm-related signal (at 1050 eV) during the annealing treatment. It is attributed to the thermally activated segregation of Sm ions onto the surface layer (~ 3 nm) of film. This might eventually lead to a significant reduction of the number of optically active Sm ions in regular lattice sites. Low solubility of rare earth ions in TiO₂ matrix is a natural consequence of the mismatch of both the ionic radii and the valence between host and impurity atoms.

4. Conclusions

We successfully used sol-gel pyrolysis technique to prepare rare-earths activated TiO₂ films with controllable and uniform thickness and quite high refractive index (2.16). An intense Sm³⁺ emission was observed under a photoexcitation of the host matrix. The nanocrystallinity seems to lead to increase of anatase-to-rutile transition temperature. It is probable that the high concentration of rare-earth impurities inhibits the crystallite growth. The quenching of Sm³⁺ luminescence at high annealing treatments is considered as a consequence of either increased crystallite size segregation of Sm ions onto the surface.

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