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Optical properties of Eu(III) doped nanocrystalline films of TiO_2

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The synthesis of europium (III) doped nanocrystalline TiO_2 films is described. The morphology and structure of the films were determined by transmission electron microscopy (TEM) and the selected area of electron diffraction (SAED) method. The photoluminescence (PL), lifetimes and cathodoluminescence (CL), recorded at room temperature, are reported. It has been found that the cathodoluminescence characteristics are significantly different from the photoluminescence ones. It is concluded that different Eu^{3+} sites contribute to the optical behaviour of Eu^{3+}:TiO_2 films.

1. Introduction

Thin films of luminescent materials have been intensively investigated due to their applications in FED [1, 2], organic and inorganic electroluminescent films [3–6], planar waveguides [7, 8] optical sensors [9] and lasers [10, 11]. These layered materials can be obtained by various methods, depending on the type of materials and future applications. Chemical vapour deposition (CVD) [12], ion and magnetron sputtering [13], and laser ablation [14] are examples of such methods. However, the most often used and relatively cheapest method of obtaining thin films is the sol-gel technique. The sol-gel process involves the formation of sols from precursors and the transformation of these sols first into wet gels and finally (after drying) to xerogels [4]. This technique enables high concentrations of well-dispersed solute molecules (a feature

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typical of solutions) in rigid structures of xerogels to be obtained. Sol-gel films of different thickness are usually produced in two ways: by the dip-coating [5] or spin-coating [6] techniques. The main problems in the preparation of good quality sol-gel films are: the risk of cracking resulting from the shrinkage of gels during drying and the misfit thermal expansion coefficients between the substrate and layer [7]. One of the possible remedies for these problems is to adjust the sol viscosity which affects the layer thickness. It is well known that the risk of cracking during drying is smaller for thinner layers [8].

This work presents a preparation method, and structural and spectroscopic studies of TiO_2 sol-gel films doped with lanthanide ions, used as high-refractivity material for planar waveguide systems. The Eu^{3+} ions were chosen as emitting dopants due to their favourable luminescence properties in the visible region.

2. Experimental

2.1. Apparatus

Photoluminescence (PL) spectra were recorded using a Jobin-Yvon TRW 1000 spectrophotometer and a photomultiplier (Hamamatsu R928). In order to record the PL spectra, the samples were excited with the 532 nm line (2nd harmonic) of a Nd:YAG laser. A Lambda Physics excimer laser was used as the excitation source (λ_{exc} = 308 nm) for lifetime measurements. Emission lifetimes were measured with a Tektronics 1000 TDS 380 oscilloscope. The cathodoluminescence (CL) spectra were recorded with an Ocean Optics Spectrometer SD2000, with a resolution of 0.3 nm. The CL spectra were excited *in vacuo* ($<10^{-6}$ Torr) in the camera of a TESLA electron microscope operating at 60 and 90 kV, with the beam current in the range of 10–120 μA. Morphological and structural studies of thin layers of TiO_2 were performed with a transmission electron microscopy (TEM) Philips CM20 SuperTwin Microscope, operating at 200 kV and providing 0.25 nm resolution. Specimens for the TEM and for electron diffraction (SAED) studies were prepared by dissolving a quartz glass substrate of the obtained samples with HF acid, followed by ultrasonic agitation in methanol. A drop of the suspension was deposited onto a copper microscope grid covered with holey carbon film.

2.2. Preparation

The samples of nanocrystalline TiO_2 doped with europium and silver were prepared by the sol-gel technique. Titanium (IV) butoxide (TBOT, $Ti[O(CH_2)_3CH_3)]_4$) was used as the titanium precursor and acetylacetone (Acac, $CH_3COCH_2COCH_3$) as the chelating and stabilizing sol agent. The films were prepared by a sol-gel process involving four stages: (1) TBOT hydrolysis by stirring the system, TBOT:Acac

:H_2O:C_2H_5OH with molar ratios 1:4:1:27, at 50 °C; (2) addition of europium nitrate ($Eu(NO_3)_3\cdot6H_2O$) to the obtained sol, with the molar ratio Eu/TBOT equal to 0.1; (3) obtaining thin films by deposition and spin-coating (3000 r.p.m) of the sols on silicon and quartz substrates, and (4) gelation of the samples followed immediately by heating at 500 °C for one hour.

3. Results and discussion

For the purpose of assessing the quality of the obtained Eu^{3+}:TiO_2 films on Si substrates, morphological studies of the film surfaces were performed. The morphologies were examined with optical and transmission electron (TEM) microscopes. The undoped TiO_2 layers observed under optical magnification (not shown) showed a high homogeneity and a virtual lack of cracks. The TEM picture of nanocrystallites from an undoped film of TiO_2, obtained in a single deposition process, is presented in Fig. 1. Distinct TiO_2 nanocrystals with the sizes of about 15 nm can be seen in the micrographs. The structure of the obtained materials was investigated by the SAED method. All reflexes observed in electronograms (Fig. 2) correspond to the anatase structure of TiO_2 (Table 1).

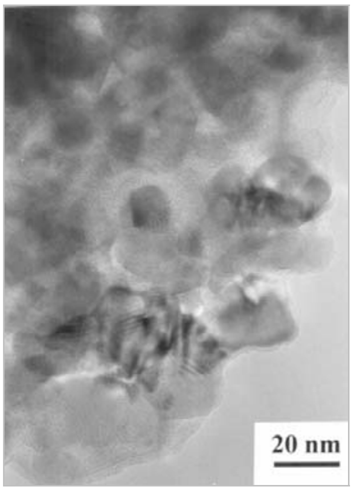

Fig. 1. TEM picture of TiO_2 nanocrystals

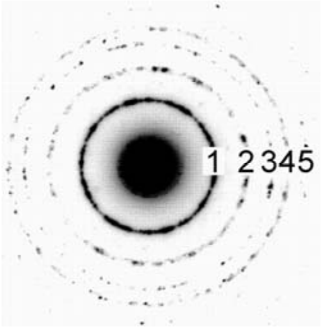

Fig. 2. SAED patterns typical of the anatase phase of TiO_2 samples

In order to determine the thickness of the layers by the optical method, analogous films were synthesized on quartz substrates. In this case, it is possible to estimate the thickness of the ultra-thin films via interference effects [9,10]. For this purpose, optical transmittance measurements of the films produced on quartz substrates were performed (see Fig. 3). The obtained transmittance values were introduced to the equations given by Aktulga et al. [15, 16]:

$$C(\lambda)=\frac{T^{+}(\lambda)-T^{-}(\lambda)}{2T^{+}(\lambda)T^{-}(\lambda)} \tag{1}$$

$$n_s(\lambda)=\frac{1+\sqrt{1+T_0^{2}(\lambda)}}{T_0(\lambda)} \tag{2}$$

$$n(\lambda)=\frac{1}{2}\left(\sqrt{8n_sC+(n_s+1)^2}\;+\;\sqrt{8n_sC+(n_s-1)^2}\right) \tag{3}$$

where λ is the wavelength of the incident light, T_0 is the transmittance of bare substrate, T^{+} and T^{-} are experimentally traced envelope curves of the transmission spectrum and n_s is the refraction index of the substrate.

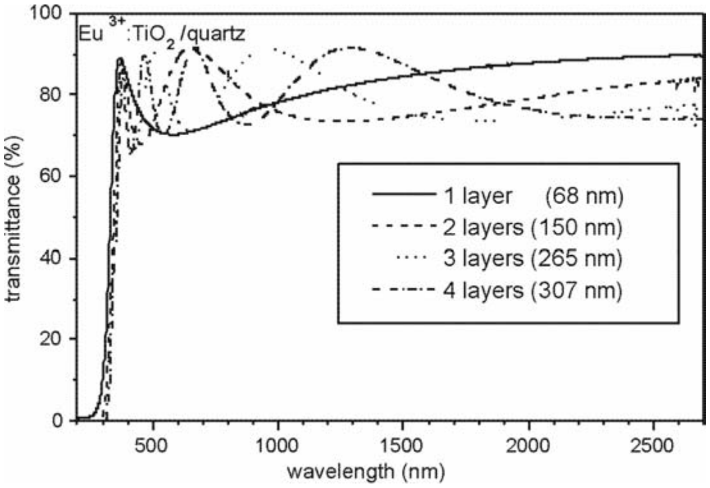

Fig. 3. Transmittance spectra of Eu^{3+}: TiO$_2$ films on quartz substrates

Table 1. Comparison of the interplanar distances obtained for the TiO$_2$ sample with the anatase data

No.	*d* [nm]	Anatase JCPD Nr. 21-1272		
		d (nm)	*I*	*hkl*
1	0.352	0.3520	100	101
2	0.238	0.2431	10	103
		0.2378	20	004
		0.2332	10	112
3	0.189	0.1892	35	200
4	0.169	0.1700	20	105
		0.1666	20	211
5	0.148	0.1493	4	213
		0.1481	14	204

The layer thickness *d* of the obtained samples can be determined from the following equation:

$$d = 4\left(\frac{n(\lambda_i)}{\lambda_i} - \frac{n(\lambda_{i+1})}{\lambda_{i+1}}\right)^{-1} \tag{4}$$

where λ_i and λ_{i+1} are the wavelengths corresponding to two consecutive extrema in the transmittance spectrum.

Due to the lack of the necessary number of interference peaks in the transmittance spectra of the films obtained in one deposition process, the analyses of the thickness and refractive index were performed only for samples made with a minimum two deposition processes. The *d* values obtained for the investigated films are listed in Table 2. The accuracy of the method used was confirmed by FE-SEM images (Field Emission Scanning Electron Microscope, not shown), which were obtained for samples of the TiO_2 films.

Table 2. Thickness of doped TiO_2 thin films deposited on quartz substrates

Sample	Number of deposition processes	Thickness *d* (nm)	Refractive index *n* (λ = 600 nm)
Eu^{3+}(10 %):TiO_2	2	150	3.22
	3	265	3.24
	4	307	3.23

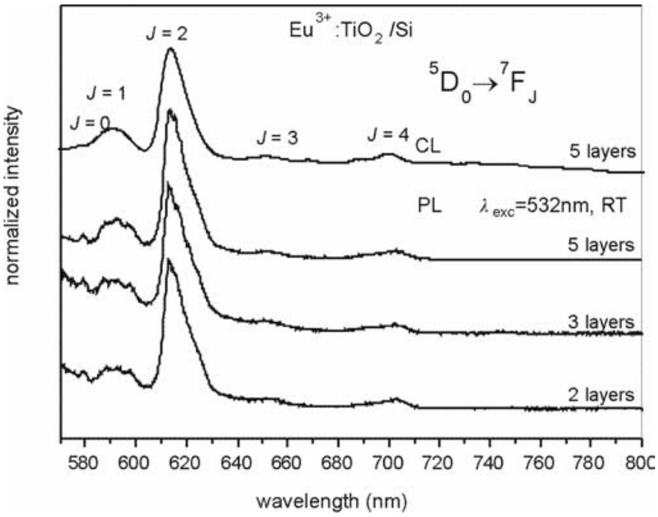

Fig. 4. The PL and CL spectra of samples of 10% Eu^{3+}: TiO_2 on a silicon substrate after various numbers of deposition processes

As can be seen, the thickness of each subsequent layer decreases for successive deposition processes in the case of samples doped with Eu^{3+}. The observed slight increase in the refractive index *n* with the thickness of the films is due to the densification of films deposited earlier during the annealing of successive layers.

The photoluminescence (PL) spectra of TiO_2 films doped with Eu^{3+} ions were recorded at room temperature (Fig. 4). The spectra consist of characteristic of Eu^{3+} emission bands, which were attributed to the $^5D_0 \to {}^7F_{0-4}$ transitions. Assignments of the observed f-f transition are given in Figure 4. The luminescence spectra were characterized by inhomogeneously broadened bands characteristic of the Eu^{3+} multisite systems observed in glasses and solutions.

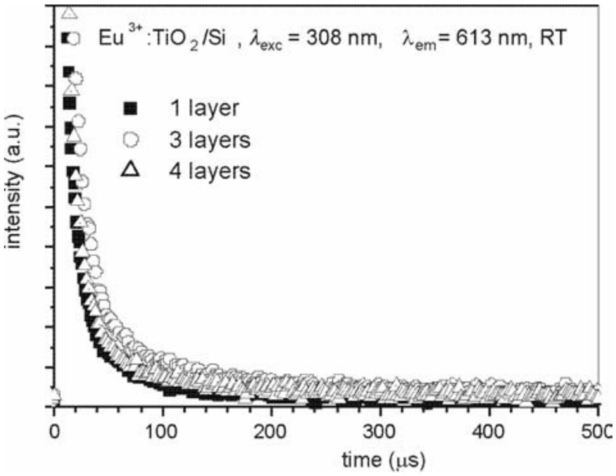

Fig. 5. Decay profiles of Eu^{3+}: TiO_2 samples measured at room temperature

The luminescence decay profiles of Eu^{3+}:TiO_2 thin films are shown in Fig. 5. They are highly nonexponential. This nonexponential decay of Eu^{3+} luminescence is associated with the energy transfer processes between Eu^{3+} ions occupying different sites. Luminescence lifetimes evaluated from the slower components of the decay curves (shown in Fig. 5 for the three selected samples – three layers of TiO_2 doped with Eu^{3+}) are listed in Table 3.

Table 3. Luminescence lifetimes of the $^5D_0 \to {}^7F_2$ transition measured for Eu^{3+}(10 %):TiO_2 samples on silicon substrates (λ_{em} = 613 nm, λ_{exc} = 308 nm, RT)

Number of deposition processes	Lifetime τ (μs)
1	93 ± 3
3	160 ± 4
4	130 ± 7

The estimated lifetimes are relatively short. An increase in the luminescence lifetimes for successive deposition processes was observed. It was probably due to the dehydration process occurring during the annealing. This process is more effective for longer heating times and is also manifested in the decrease of the thickness of each subsequently deposited layer. The influence of OH^- groups on the quenching of the luminescence transitions of Eu^{3+} entrapped in sol-gel derived materials has already been observed for other oxides [17, 18].

The results of CL measurements are also presented in Fig. 5. As can be seen, the CL characteristics differ significantly from the characteristics of the PL spectra. This difference is most probably due to a contribution of different Eu^{3+} sites, excited by the electron beam.

5. Conclusions

The synthesis of Eu^{3+}:TiO_2 films of high optical quality is presented. Their structural and morphological properties have been determined. Photoluminescence spectra at room temperature and luminescence decay curves have been recorded. The luminescence displays inhomogeneously broadened bands characteristic of multisite Eu^{3+} structures. Its decay curves are nonexponential. Average luminescence lifetimes increase with the number of the deposition processes. A detailed analysis of the effect of film thickness on electronic relaxation mechanisms in Eu^{3+}:TiO_2 needs further complementary research. The cathodoluminescence spectra of Eu^{3+}:TiO_2 thin films have been recorded. They display different characteristics as compared to the photoluminescence spectra.

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References

[1] CHO K.-J., RYU J.-T., LEE S.-Y., Solid State Electron., 47 (2003), 633.
[2] FRAN Y.-S., TSENG T.-Y., Mater. Chem. Phys., 61 (1999), 166.
[3] PAIK K.L., BAEK N.S., KIM H.K., LEE J.-H., LEE Y., Opt. Mater., 21 (2003), 135.
[4] WU X., LIU Y., ZHU D., J. Mater. Chem., 11 (2001), 1327.
[5] QIU Y., ZHANG D.Q., QIAO J., SHAO Y., Synthetic Met., 110 (2000), 241.
[6] ATHANASSOV Y., ROTZINGER F., PECHY P., GRAETZEL M., J. Phys. Chem., B 101 (1997), 2558.
[7] ORIGNAC X., BARBIER D., DU X.M., ALMEIDA R.M., MCCARTHY O., YEATMAN E., Opt. Mater., 12 (1999), 1.
[8] NASSAR E.J., GONÇALVES R.R., FERRARI M., MESSADDEQ Y., RIBEIRO S.J.L., J. Alloys Comp., 344 (2002), 221.
[9] ZELLER P.N., VOIRIN G., KUNZ R.E., Biosens. Bioelectron., 15 (2000), 591.

[10] YANAGI H., HISHIKI T., TOBITANI T., OTOMO A., MASHIKO S., Chem. Phys. Lett., 292 (1998), 332.

[11] TURNBULL G.A., ANDREW P., JORY M.J., BARNES W.L., SAMUEL I.D.W., Synthetic Met., 127 (2002), 45.

[12] NISHIDA K., MORISAWA K., HIRAKI A., MURAISHI S., KATODA T., Appl. Surf. Sci., 159–160 (2000), 143.

[13] OKIMURA K., Surf. Coat. Technol., 135 (2001), 286.

[14] EUN D.S., LEE S.Y., Thin Solid Films, 357 (1999), 232.

[15] DEMIRYONT H., SITE J.R., GEIB K.M., Appl. Opt., 24 (1985), 490.

[16] OZER N., DEMIRYONT H., SIMMONS J.H., Appl. Opt., 30 (1991), 3661.

[17] HRENIAK D., JASIORSKI M., MARUSZEWSKI K., KEPINSKI L., KRAJCZYK L., MISIEWICZ J., STREK W., J. Non-Cryst. Solids, 298 (2002), 146.

[18] WRZYSZCZ J., MISTA W., HRENIAK D., STREK W., ZAWADZKI M., GRABOWSKA H., J. Alloys Comp., 341 (2002), 358.

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