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STRUCTURAL AND OPTICAL PROPERTIES OF Eu^{3+}:HfO_2 NANOTHICK SOL-GEL WAVEGUIDING FILMS

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Abstract. Eu^{3+} doped HfO_2 films are elaborated using sol-gel process. Crack-free thin films were obtained with excellent waveguiding properties. The nanostructural features of the layers depending on annealing temperature and doping concentration are investigated mainly by waveguide Raman spectroscopy in the very low frequency range and also by transmission electron microscopy. Two different solutions containing europium, with concentrations 0.1 at.% and 10 at.%, are prepared. The high doping content (10 at.%) favours the crystallisation of the metastable tetragonal phase which lies in small nanograin size. This phase coexists with stable monoclinic phase for high doping content. The low doping content (0.1 at.%) crystallises into pure monoclinic phase at 500 °C and the tetragonal phase appears at 750 °C. The size of the nanograin affects the optical properties of the film. The refractive indices are higher for the 10 at.% Eu^{3+} doped samples than for the 0.1 at.% Eu^{3+} doped films.

1. INTRODUCTION

Hafnium dioxide HfO_2 has interesting physical and chemical properties. It is widely used in optical fields because of its high refractive index (≈ 2), low optical loss and scatter in the near UV (below 300 nm) and IR (10 μm) regions. However, HfO_2 presents a high crystalline density (around 10 g/cm^3) which makes it attractive for host lattice activated by rare earths for applications as scintillating materials.

The sol gel technique is proved to be a very suitable method for the development of scintillating films [1]. It arises as an elaboration method of high quality oxide materials, allowing the incorporation of doping agents with an excellent homogeneity on a molecular scale [2], and well adapted to for the preparation of high quality thin films used as planar waveguides [3].

In this work, we have prepared films of Eu^{3+} doped HfO_2 by sol gel process. The characterization of the nanostructural properties of sol gel oxide films is very important to understand their optical properties and to forecast their behaviour when rare earth doped for scintillation applications. The high optical quality of the films allows to use them like waveguides. nanostructural information can be determined by waveguide Raman spectroscopy in the low-wavenumber Raman scattering range (≤ 100 cm^{-1}). The effect of temperature and doping concentration on nanograins size is studied. The Raman analyses are completed by Transmission Electronic Microscopy (TEM) observations. The optogeometric properties (refractive index and thickness) are investigated by m-lines microscopy.

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2. EXPERIMENTAL PROCEDURES

2.1. Chemical process of precursor solution

The HfO_2 doped Eu^{3+} solution is prepared from hafnium tetra-ethoxide ($Hf(OC_2H_5)_4$), 99.9 % (ABCR) and europium (III) nitrate pentahydrate ($Eu(NO_3)_3$, $5H_2O$), 99.9% (Aldrich). Details of the chemical procedure is described in reference [4]. Briefly, hafnium tetra-ethoxide is first dissolved in ethanol before adding a mixture of acetylacetone (acac) and ethanol with a molar ratio $Hf(OC_2H_5)_4$/acac = 1, to chemically stabilized the alcoxide. Europium nitrate is introduced after the hydrolysis of the solution.

2.2. Elaboration of HfO_2 doped Eu^{3+} waveguiding films

The solution is filtered using a 0.2 μm filter and is deposited onto carefully cleaned pure silica (Herasil® from Heraeus) substrates by the dip-coating technique (withdrawal speed of 90 mm/min). After each coating, the films are heat-treated at 400 °C for 15 minutes under oxygen flow to densify the layer and to remove the main part of organic compounds. The films are then heat-treated during 15 minutes at temperatures varying from 500 up to 1000 °C before analyses. Four successive coatings are required in order to get one propagating mode in the film of each polarization (one transverse electric mode: TE_0 and one transverse magnetic mode: TM_0). Twenty stacked layers are necessary to support three TE and three TM modes, i.e. TE_0, TE_1, TE_2, TM_0, TM_1, TM_2 respectively.

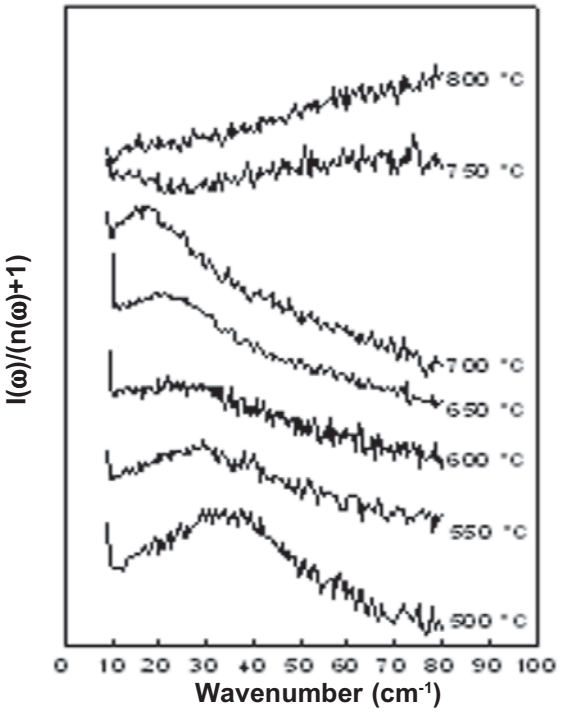

Fig. 1. Room temperature Raman reduced intensity versus frequency for Eu^{3+} (0.1 at.%) doped HfO_2 sol gel films heat-treated at different temperatures and analysed in waveguiding configuration.

2.3. IR analyses of HfO_2 doped Eu^{3+} films

The films dried at 100 °C are sintered at different temperatures from 400 up to 1000 °C before analysing by Fourier Transform Infrared Spectroscopy (FTIR 2000, Perkin-Elmer) carried out between 4000 cm^{-1} and 370 cm^{-1}. FTIR is conducted to determine the thermal decomposition of material and the temperature of crystallisation. The spectra corresponding to the 600 °C and to the 1000 °C heat-treated films indicate that the organic compounds even exist at 600 °C, but are completely eliminated at 700 °C. The crystallization of hafnium oxide begins at 600 °C and is characterized by the bands located above 800 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Nanostructural analyses of HfO_2 doped Eu^{3+} waveguiding films

The experimental set-up, principles and advantages of Waveguide Raman Spectroscopy (WRS) have been described in great details in a previous paper [5]. Raman excitation is carried out at 647.1 nm. The scattered light is analysed using a Jobin Yvon model U-1000 spectrograph and a photon counting system. The structural evolution of the layer depending on the annealing temperature and on Eu^{3+} content has recently been conducted by Villanueva *et al.* [4] at frequencies varying from 4 to 700 cm^{-1}. The authors revealed that films are amorphous below 500 °C. The monoclinic phase appears at low annealing temperatures and is preferentially crystallized for low doping content. The tetragonal phase crystallized at high annealing temperatures and is the predominant phase for high doping content. The size of the nanocrystals constituting the films is determined in this paper using the very low frequency range. To improve the resolution, reduced intensity defined as $I(\omega)/(n(\omega)+1)$, where $(n(\omega)+1)$ is the Bose factor, is plotted versus the Raman shift (cm^{-1}). As an example, these spectra between 4 and 80 cm^{-1} corresponding to the 0.1 at.% Eu^{3+} doped HfO_2 waveguides heat-treated between 500 °C and 800 °C, are reported in Fig. 1. The broad peak arises

Table 1. Nanocrystallites size evolution of HfO_2 doped Eu^{3+} waveguides. ω_0 is determined with an accuracy around ±2 cm^{-1}. (m) means that the film is crystallized into pure monoclinic phase and (t+m) that the film is crystallized in a mixture of tetragonal and monoclinic phases [4]. The both values given into brackets arises from the presence of both phases. The first and second values are determined assuming the film is crystallized into pure tetragonal and monoclinic phase respectively.

Heating temperature (°C)	Mean diameter (nm) of HfO_2 crystallites doped Eu^{3+} 0.1 at.%	Mean diameter (nm) of HfO_2 crystallites doped Eu^{3+} 10 at.%
500	5.2±0.3(m)	[4.2 – 4.8]±0.2(t*+m)
550	6.0±0.4(m)	[4.9 – 5.5]±0.3(t*+m)
600	6.3±0.5(m)	[5.3 – 6.0]±0.4(t*+m)
650	8.5±0.8(m)	[5.5 – 6.1]±0.4(t*+m)
700	10.5±1.1(m)	[6.0 – 6.7]±0.5(t*+m)
750	[9.9 – 11.2]±1.3(t+m*)	[7.5 – 8.4]±0.7 (t*+m)
800	[10.2 – 11.5]±1.4(t+m*)	[15.2 – 17.0]±3.2 (t+m)

* majority phase

from the surface vibrational modes of the HfO_2 particles. Assuming a spherical shape of the crystallites, the maximum of the size distribution of nanocrystals (i.e. not far from the mean diameter of the nanoparticles) labelled 2*a*, can directly be obtained from the maximum position ω_0 of the band in the low frequency range. 2*a* is deduced using $2a=0.86v/\omega_0 C$ [6], where *C* represents the light velocity in vacuum and v the sound velocity in the bulk HfO_2. This model has been validated many times with TiO_2 [7], ZrO_2 [5] and HfO_2 [8] sol gel waveguides and is well adapted for sol gel films. The longitudinal sound velocities for monoclinic and tetragonal HfO_2 layers are estimated to be 6260 m/s and 5570 m/s respectively. Those values are calculated using the formula detailed in reference [8], the HfO_2 elastic constants measured in reference [9] and a material density of 9.7 g/cc and 10.0 g/cc for the HfO_2 monoclinic and tetragonal phase respectively. The mean diameters obtained for the nanocrystals constituting the films are listed in Table 1. The major phase is determined for each annealing temperature using X rays diffraction and WRS conducted in the low frequency range, i.e. 100 cm^{-1} - 700 cm^{-1}. The very low frequency band associated to the nanoparticle breathing mode, cannot clearly be distinguished for temperatures higher than 800 °C because the film losses its waveguiding properties. As expected, the average grain size increases with annealing temperature. Moreover, the results indicate that low average grain size is favoured by high doping content for temperatures below 750 °C. Liu *et al.* [10] observed the same behaviour by studying ZrO_2 sol gel films doped by different rare earth. The ionic radius of Eu^{3+} (0.108 nm) is larger to that of Hf^{4+} (0.085 nm), which prevents most of Eu^{3+} ions to enter the lattice of HfO_2 to substitute Hf^{4+}. Eu^{3+} ions are probably located on the surface of HfO_2 crystallites, preventing their growth and simultaneously retaining the tetragonal phase at low annealing temperature as suggested by Liu [10]. Gupta [11] explains that the tetragonal structure retention arises from a critical size below which the surface free energy surpasses the volume free energy. Doping acts as an added stabilization energy which is present in nanometric grains. Above 750 °C, the nanocrystal size of the 10 at.% doped layers is higher than those into the 0.1 at.% doped layers. At this temperature, the effect of temperature becomes predominant and the nanocrystal growth is no preferentially governed by doping agent.

Conventional transmission electron microscopy (CTEM) is used to analyse the films heat treated at 1000 °C. The film is peeled off from the substrate and put onto a microscope grid. CTEM studies are performed on a TOPCON EM-002B working at 200 kV. The nanostructure of both films is quite similar after 1000 °C heat-treatment whatever the doping concentration. The bright field observation of the 0.1 at.% Eu^{3+} doped HfO_2 film is presented on Fig. 2a. The film is dense, and fully crystallized into a polycrystalline structure with grain size between 10 and 20 nm. The diffraction patterns (no presented here) indicate the presence of both the tetragonal and the monoclinic phases from 800 °C annealing temperature whatever doping concentration [4]. Dark field

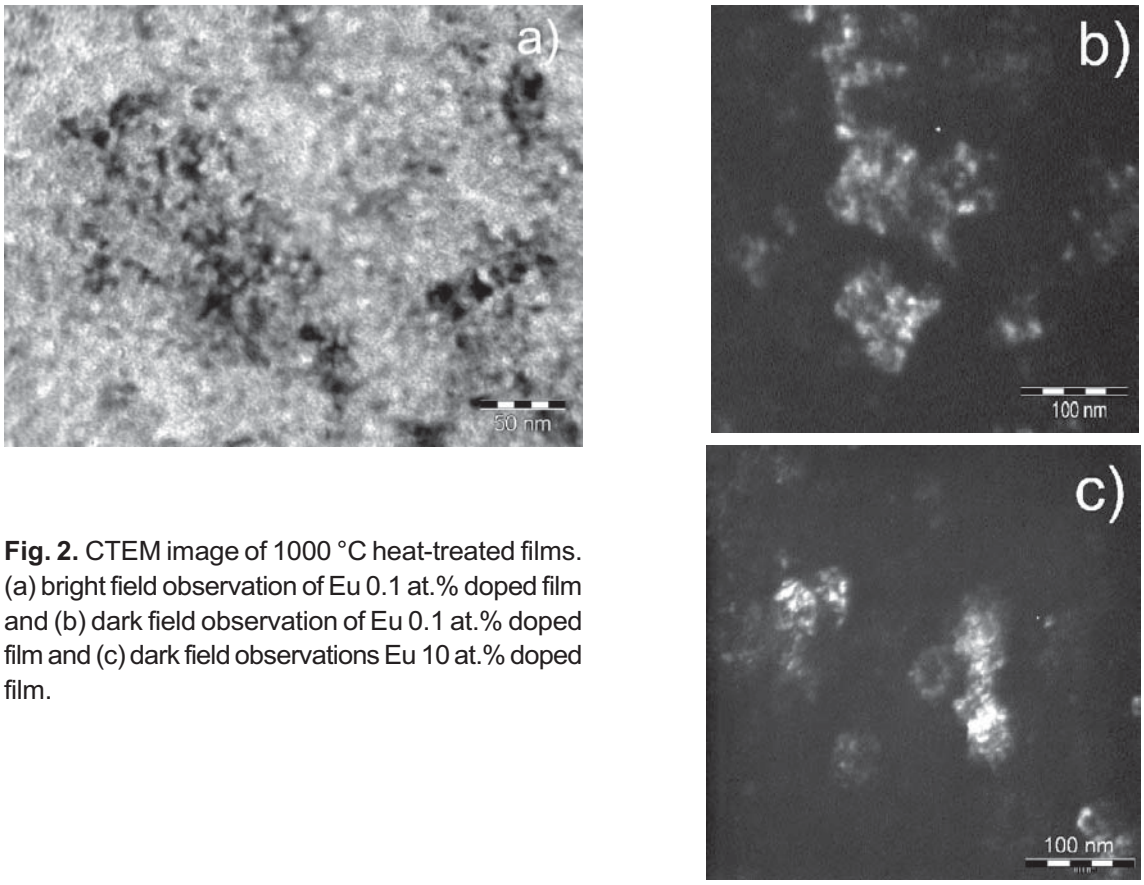

Fig. 2. CTEM image of 1000 °C heat-treated films. (a) bright field observation of Eu 0.1 at.% doped film and (b) dark field observation of Eu 0.1 at.% doped film and (c) dark field observations Eu 10 at.% doped film.

observations reveal no significant apparent distinction between the both phases. Nevertheless dark field analyses of 0.1 at.% Eu^{3+} (Fig. 2b) and 0.1 at.% Eu^{3+} (Fig. 2c) indicate that nanocrystallites agglomerate in a crystallized large envelope which could prevents propagation of light into the films.

3.2. Optical characterizations of HfO_2 doped Eu^{3+} waveguiding films

M-lines spectroscopy [12] is a useful method to determine optogeometric parameters (thickness and refractive index) of waveguiding thin films. The step index profile model is confirmed because the measurements conducted on the same sample at different wavelength provide the same value of thickness. Obviously thickness is not wavelength dependent. Using this model, the evolution of refractive index and thickness versus annealing temperature are conducted on the 0.1 at.% and 10 at.% Eu^{3+} doped HfO_2 films respectively (twenty coated sample). The refractive indices of both samples versus heat treatment are represented in Fig. 3 (λ= 594nm, TE polarization). The refractive indices evolution is similar for both samples. For the 10 at.% doped layers (Fig. 3b), it increases from 1.860±0.001 at 400 °C up to 1.898±0.001 at 600 °C and decreases up to 1.840±0.001 after 1000 °C heat-treatment. A thickness of 733±2nm are measured at 400 °C. It continually decreases up to 663nm±2nm at 700 °C and remains practically constant between 700 and 1000 °C. The increase of refractive index up to 600 °C is ascribed to the crystallization of amorphous HfO_2 and to the simultaneous densification of the films. The maximum of index value appears at 600 °C, probably because organics compounds are not totally removed and fill the pores into the layers. The complete elimination of organic compounds at 700 °C, and the increase of porosity and as a consequence the crystallites growth provides a decrease of refractive indices from 600 °C to 1000 °C. Moreover, the refractive indices are higher for the 10 at.% doped films (Fig. 3b) than for the 0.1 at.% doped films (Fig. 3a). High doping content can help to increase the refractive index of sol-gel HfO_2 layers probably because low crystallites size induces less pinholes and higher density into the films. These finding are similar from those previously published by Liu *et al.* on ZrO_2 doped sol gel film [10]. It is noted that refractive indices measured in both polarisations are similar at 400 °C and 500 °C. Nev-

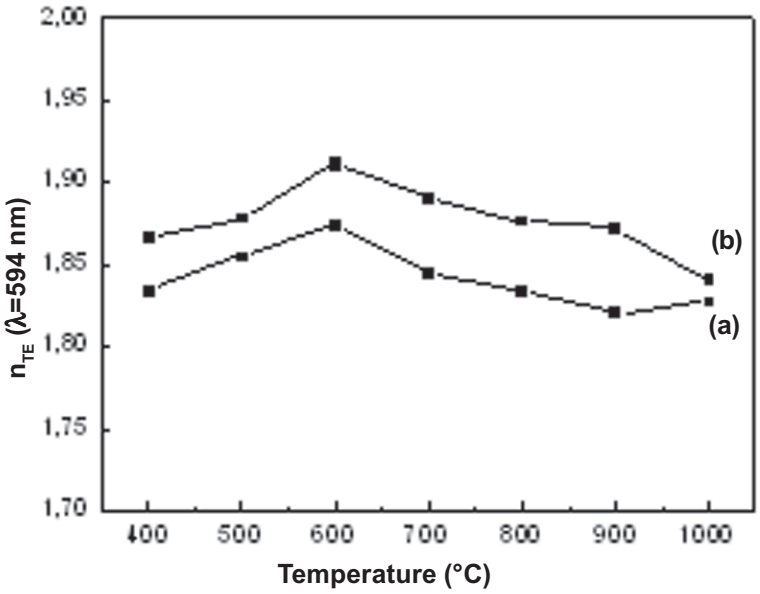

Fig. 3. Refractive indices evolution versus annealing temperature for (a) 0.1 at.% and (b) 10 at.% Eu^{3+} doped HfO_2 films. Measurements are conducted at 594 nm using TE polarization.

ertheless, for temperatures higher than 600 °C, refractive indices measured in TM polarisation are higher than those measured in TE polarisation ($\Delta n = n_{TM} - n_{TE}$ around 0.025) suggesting an anisotropy. The volume expansion of films due to the nanocrystallites growth and the presence of both monoclinic and tetragonal phases (from 700 °C in 0.1 at.% doped films and whatever the temperature for the 10 at.% doped films) are probably the origin of stress-induced phase transformation and compressive stresses in near-surface layers.

Optical losses are measured using a light beam from a 10 mW polarized He-Ne laser (λ=632.8nm) coupled into the waveguide. The scattered guided light is directly analysed by a microcomputer assisted video camera system [13]. The digitalized image is then analysed to determine the propagation losses. Such measurements are conducted on the four coated monomode layers heat-treated at 400 °C and 10 at.% Eu^{3+} doped. The minimum number of deposition operations to produce monomode film reduces the dust contamination risk [3]. The propagation length is larger than 20 mm on the amorphous sample (heat-treated at 400 °C) which confirms the high quality of the coated layer without imperfections (cracks, inhomogeneity…). After 800 °C heat treatment the propagation length decreases to be around 4 mm. The maximum nanocrystal size of around 15 nm deduced from WRS measurement in the very low frequency range confirms that the layers loss their waveguiding properties at annealing temperature higher than 800 °C.

5. CONCLUSION

The nanostructural features of sol gel Eu^{3+}:HfO_2 films are determined for different annealing temperatures and two various doping concentration. A large part of this study is devoted to the determination of the nanometric crystal size of the crystallites constituting the films. WRS conducted in the very low frequency range is a very efficient and well adapted method for nanograins size determination. The mean nanocrystals size determined by WRS can be defined as an 'optical size' which is directly correlated to the propagating properties of the optical planar waveguiding layers.

For temperature lower than 750 °C, the effect of doping concentration is predominant over the temperature. High Eu^{3+} doped films (10 at.%) crystallize into the metastable tetragonal phase which can be correlated to the small crystallite size. High doping concentration restrains the nanocrystallite growth and simultaneously allows to increase the refractive index of the film compared to low Eu^{3+} doped (0.1 at.%) samples. This majority phase is superposed to the monoclinic phase. On the contrary, the metastable tetragonal phase is not present at low temperature in the 0.1 at.% Eu^{3+} doped films. The pure monoclinic phase appears first and the

tetragonal phase crystallized above 750 °C. Further investigations to determine more precisely the proportion of each phase will be conducted in the future using XRD and Raman analysis.

Preliminary luminescent measurements under X-ray excitation are successfully obtained onto Eu^{3+} 10 at.% doped sol gel films but the scintillation yield remains low compared to 10 at.% doped sol gel powders. Spectroscopy measurements under x-ray excitation are in progress and will be presented in a future contribution in order to clarify the lower film efficiency than the powder one.

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