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Preparation and luminescent properties of Eu-doped Ln_2O_3 (Ln = Gd, Lu) thin film by citrate sol–gel process

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Abstract

Ln_2O_3:Eu (Ln = Gd, Lu) luminescent thin films were deposited on sapphire and Si substrates using citrate sol–gel technique. The prepared films in different process conditions were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurement. The influence of viscosity, heating rate and annealing atmosphere on the morphology of Ln_2O_3:Eu films were discussed in detail. It is indicated that crack-free films could be prepared after sintering at temperatures ranging from 500–1100 °C with heating rate of 2.5 °C/min. The photoluminescence properties of the films were highly dependent on the annealing atmosphere, and the highest emission intensity was obtained for the sample by annealing in water vapor/oxygen atmosphere.

Keywords: A. Sol–Gel processes; Thin films; Ln_2O_3

1. Introduction

Europium-doped oxides are some of the most promising phosphors for cathode ray tubes (CRT) and flat panel displays (FPD's) applications [1]. Recently, there has been a growth of interest in using europium-doped sesquioxide Ln_2O_3 (Ln = Gd, Lu) as scintillators for X-ray medical imaging systems owing to its high-effective atomic number. However, the diffusion loss of such bulk scintillators limited the development of high-resolution X-ray detectors. It has been reported that the use of scintillators deposited as thin films would be a suitable solution to reduce the diffusion loss [2,3].

Although thin Ln_2O_3 film has been widely prepared by a variety of deposition techniques, such as electron beam evaporation [4], metallo-organic chemical vapour deposition (MOCVD) [5], ion beam epitaxial technique [6], there were only a few reports on Eu-doped Ln_2O_3 thin film and its luminescence properties, which was prepared by sol–gel method [7,8]. In those cases, the sol–gel precursors used were rare earth isopropoxide, which suffer from high cost, toxicity and difficulty in controlling the experimental processes.

In this paper Ln_2O_3:Eu luminescent thin films were prepared by an alternative citrate sol–gel method, which is based on the chelation of a metallic cation by critic acid, and further polymerization promoted by the addition of ethylene glycol and consequent polyesterification [9–11]. The suitable conditions for producing high-quality Ln_2O_3:Eu thin films and relative luminescent properties were investigated.

2. Experimental

High purity gadolinium/lutetium oxide (Ln_2O_3, Ln = Gd, Lu; 99.99%) and europium oxide (Eu_2O_3; 99.99%) were used as raw materials. After dissolved in concentrated HNO_3 (A.R., analytical reagent), citric acid (CA) was added to the solution in a molar ratio CA/Ln = 4 : 1, then ethylene glycol (EG) was added in a molar ratio CA/EG = 1 : 10. The solution was stirred for 2 h at 80 °C ready for film coating. The viscosity was adjusted by addition of water in the range of 15–40 cP. Silicon and sapphire crystal were cleaned carefully and used as the substrates. The films were deposited by a dip-coating process, with a withdrawal speed of 6 mm/min, and then treated at 110 °C for 60 min to induce the

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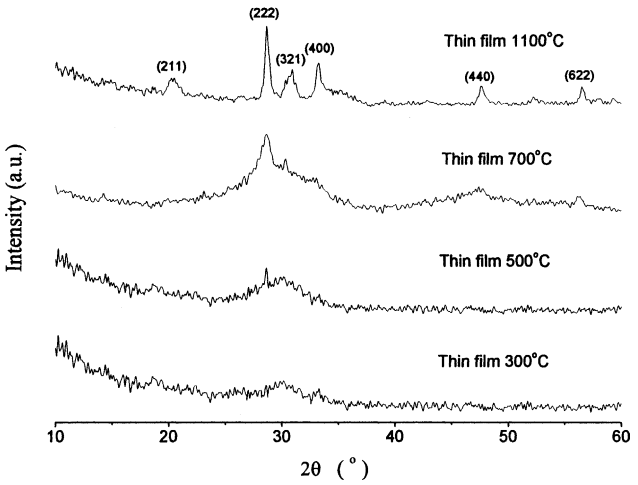

Fig. 1. XRD patterns of Gd_2O_3:Eu thin films with different annealing temperature.

polymerization. After pre-annealing, the films were calcined at 500–1100 °C for 2 h, with the heating rate of 1, 2.5, 5 and 10 °C/min. This deposition procedure was repeated three to five times in order to increase the films thickness.

Phase analysis of the films was performed by X-ray diffraction (XRD) using a Rigaku-Dmax 2550 V diffractometer. Surface morphology of the films was carried out using scanning electron microscopy (SEM). The emission spectra were taken on a Perkin-Elmer LS55 fluorescent spectrometer at room temperature.

3. Results and discussion

3.1. Phase identification by XRD

Fig. 1 shows the XRD patterns of Gd_2O_3:Eu thin films heat treated at 300, 500, 700 and 1100 °C. It can be seen

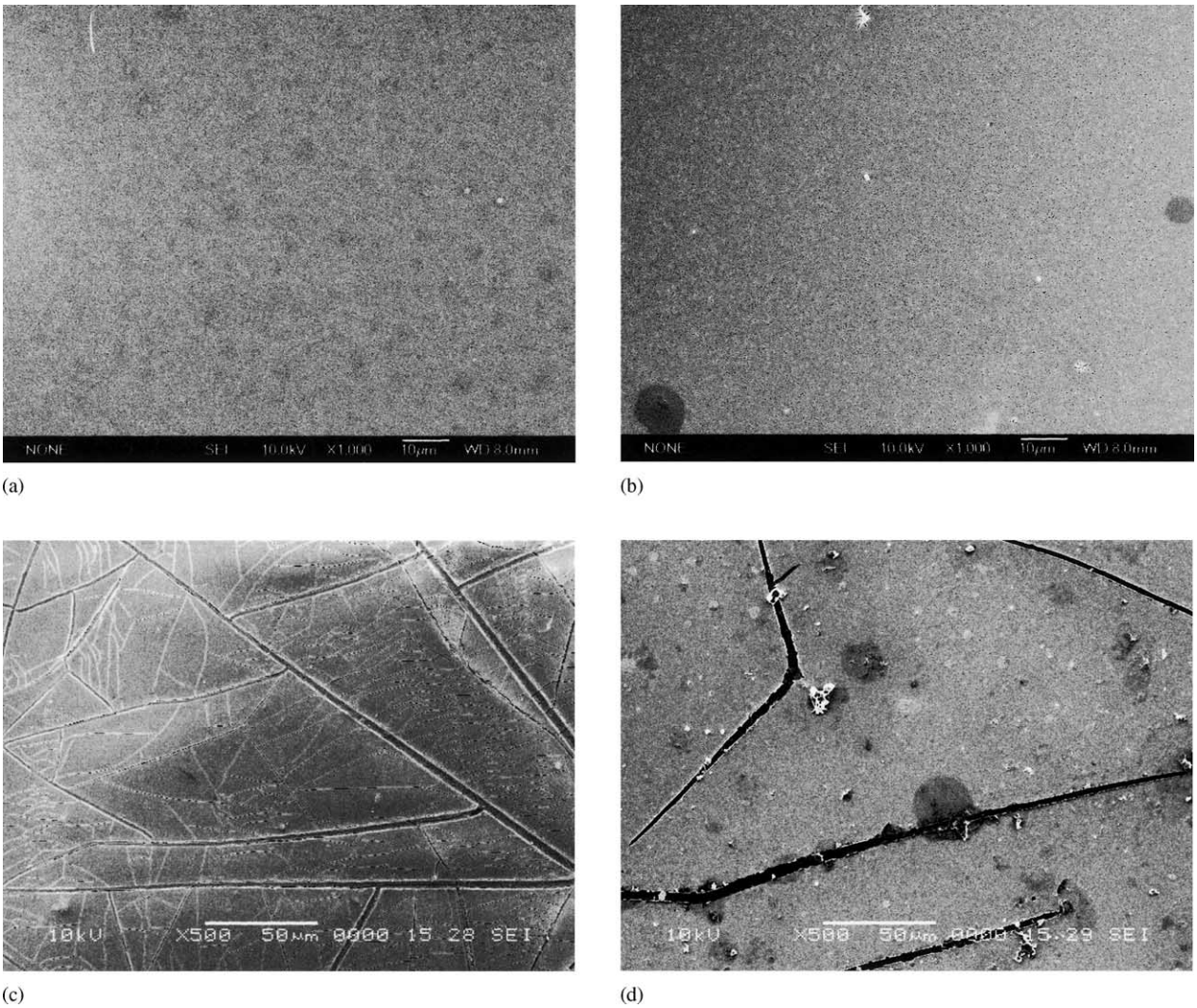

Fig. 2. SEM photographs of thin films prepared in different condition. (a) Single layer, 30 cP and 2.5 °C/min; (b) five layers, 30 cP and 2.5 °C/min; (c) single layer, 40 cP and 2.5 °C/min; (d) single layer, 30 cP and 5 °C/min.

that thin films remain amorphous below 300 °C and begin to crystallize at 500 °C. With the increase of annealing temperature, the crystallinity of the films increases gradually. After annealed at 1100 °C, thin film shows typical diffraction pattern of cubic phase and no second phase is observed.

3.2. Surface morphology

It is well known that the viscosity of the solution and heating rate are the most important parameters for preparation of crack-free films. Fig. 2 shows SEM photographs of thin films prepared at different viscosity and heating rate. It is clear that crack-free films can be obtained at low viscosity than 30 cP with heating rate of 2.5 °C/min (Fig. 2(a)), and no crack appears even when the thickness increased to 920 nm by five repeated coating process (Fig. 2(b)). This result is different with the result of Simoes, which indicated the critical thickness for crack-free films for PLZT films is about 350 nm [10]. However, either higher viscosity or higher heating rate will induce the stress due to volume shrinkage and result in the appearance of crack, as shown in Fig. 2(c) and (d). Obviously heating rate of 2.5 °C/min and viscosity low than 30 cP is the optimal condition for the high-quality film deposition.

3.3. Luminescent properties of the films

Emission spectrum of Ln_2O_3:Eu thin films under 254 nm UV excited are shown in Fig. 3. The characteristic transitions $^5D_0$–^7F_J ($J = 1$–4) of Eu^{3+} ion are observed in both doped Lu_2O_3 and Gd_2O_3 cases. The dominate main emission peak correspond to the $^5D_0$–$^7F_2$ transition at 611.0 and 611.6 nm, respectively. These luminescence spectra are in good agreement with previously reported luminescent measurements for polycrystalline powders [1].

Fig. 4 presents the emission spectra of the Ln_2O_3 thin films annealed at various atmospheres at 1000 °C. It is shown that the annealing atmospheres affected the relative intensities strongly. Oxygen atmosphere caused an increase of a factor two relative to air, and the introduction of water vapor could also improve the luminescent intensity. The highest emission intensity was obtained by annealing at water vapor/oxygen atmosphere. The atmosphere might help the decomposition of carbon in the film, which could reduce the luminescent efficiency [12].

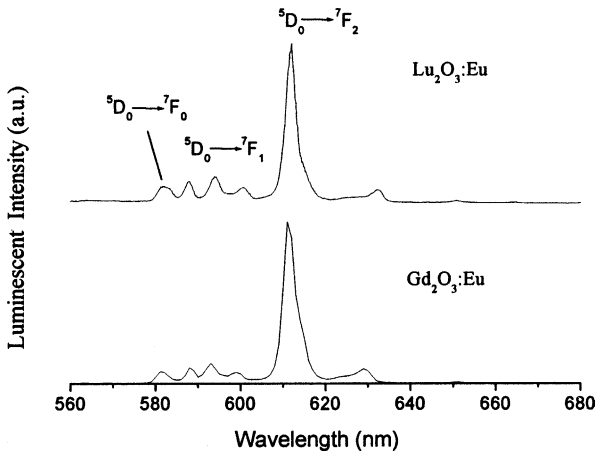

Fig. 3. Emission spectra of Ln_2O_3:Eu thin films under 254 nm UV excited.

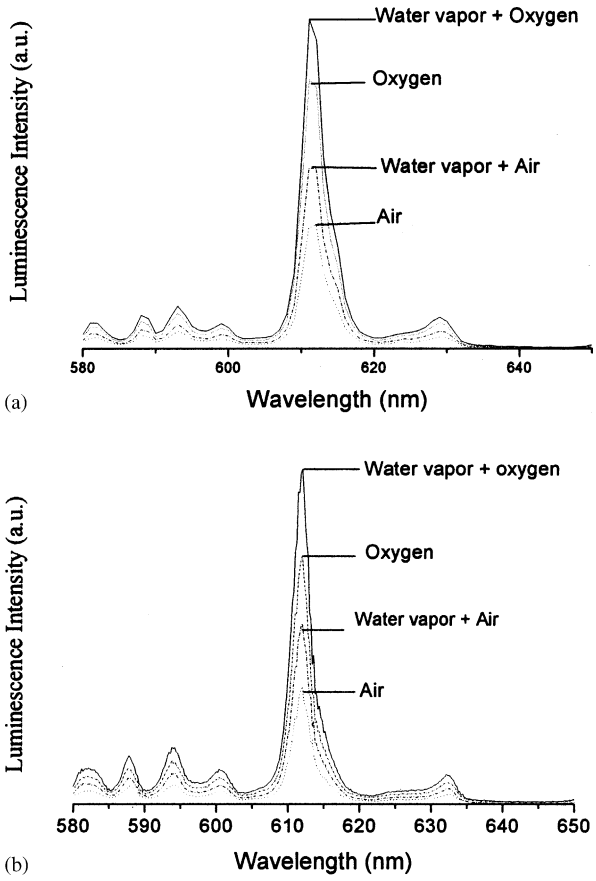

Fig. 4. Luminescent spectra of Ln_2O_3:Eu thin film annealed at various atmosphere. (a) Gd_2O_3; (b) Lu_2O_3.

4. Conclusion

The luminescent Ln_2O_3:Eu thin films were prepared by citrate sol–gel method. Heating rate of 2.5 °C/min and viscosity lower than 30 cP were the optimal condition for the high-quality film deposition. The luminescent intensity increased with the increase of annealing temperature, and the annealing atmospheres affected the relative intensities strongly. The highest emission intensity was obtained for the film by annealing at water vapor/oxygen atmosphere at 1000 °C.

Acknowledgements

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