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Pechini's solution as precursor for Eu(III)-containing ZnO films

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Abstract

The flat-panel-display's (FPD) market and demand for highly efficient and colored luminescent films have been growing quickly. In this work, thin films were obtained from Pechini's solution by dip-coating. The green films were thermally treated at 873 K in order to get ZnO:Eu 1 at% thin film. A Schott® glass plate hydrothermally treated was used as substrate. The films have a mosaic shaped feature that was observed by optical microscopy. That feature is a result of substrate thermal treatment. The film deposition decreases the substrate transmittance in the visible range. When the $^7F_0 \rightarrow {}^5L_6$ (392 nm) Eu^{3+} transition is excited, it is possible to detect emission from $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2, 3 and 4) transitions. The $^5D_0 \rightarrow {}^7F_2$ transition is also observed by using ZnO excitation wavelengths indicating energy transfer from ZnO to Eu^{3+} ion.

1. Introduction

The development of new optical displays for visual communication, especially flat panel displays (FPD), requires highly efficient and colored luminescent films. It is known that our eyes are more sensitive to monochromatic colors than to broadband spectrum colors. Rare-earth (RE) ions are better luminescent centers than transition metal elements because their 4*f* intrashell transitions originate narrow and intense emission lines. The RE luminescent properties depend on the symmetry around them. RE-doped semiconductors have applications in active layers, for instance, thin-film electroluminescent (TFEL) devices [1], optoelectronic or cathodoluminescent devices [2]. RE-doped insulators are used in telecommunications, lasers and amplifiers [3], medical analysis and phosphors [4], etc.

Non-doped and doped zinc oxide (ZnO) films have been extensively studied for academic and practical applications. The latter depend heavily on the preparation method, which determines particle shape, size and crystalline orientation. For instance, photodiodes can be made by orientated ZnO films prepared by RF magnetron sputtering [5], spray pyrolysis allows preparation of oriented transparent and conductor films [6], column-shaped and well oriented (000*l*) films are prepared by pulsed laser deposition, which have bulk acoustic waves (BAW) transducer property [7], highly porous ZnO films with no orientation can be prepared by sol–gel processes and they have high performance on photodegradation of some toxic organic compounds [8], ZnO nanobelts with widths between 50 and 300 nm and even millimeters of lengths are prepared by evaporating the commercial oxide powder at high temperature [9], (000*l*) oriented hexagonal nanowires with room-temperature ultraviolet laser effect is prepared by vapor transport and condensation process [10], laser at short emission wavelengths could be used to read CDs and CD-ROMs packed with much more information than today's versions can hold.

Organic molecules can alter or model inorganic microstructures, offering a very powerful tool for biological, ceramic or semiconductor material designs [11]. Pechini's method [12] takes advantage of this fact and allows the mixture of cations at molecular level and a stoichiometric control by complexing the metal ions in solution by citric acid. Then, a polymeric resin is formed after addition of mono-ethylene glycol. The solution viscosity can be controlled by solvent evaporation, which yields a very good precursor solution to be dipped.

In this work, europium(III)-containing zinc oxide film was prepared from Pechini's solution in order to study its luminescent properties.

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2. Experimental

1 at% europium-zinc Pechini's solution was obtained as described in Ref. [13]. The zinc citrate solution was prepared by addition of citric acid into a zinc acetate solution in molar ratio of 1.2:1. Europium citrate was prepared by direct reaction of europium oxide with citric acid in aqueous media, under heating. After the zinc and europium(III) citrate solutions were mixed, ethylene glycol was added and the mixture was heated at 403 K in order to obtain a polymeric resin.

Hydrothermally treated Schott® glass plate was used as substrate and it was dipped into Pechini's solution with viscosity about $5.0 \times 10^{-2}\,\mathrm{g\,cm\,s^{-1}}$, at 298 K, as determined by a Brookfield LVDVIII rheometer with spindle 18 and a Brookfield TC-500 temperature controller. The emerging rate was $1\,\mathrm{mm\,min^{-1}}$, controlled by a dip-coating apparatus MQBSG 1/302 and microprocessor MQCTL 200-MP. Then, the substrate was thermally treated at 873 K for 1 h. This process was repeated four times to achieve a film with four layers.

The film was characterized by optical microscopy (OM) (DMR coupled to an image analysis and software LeicaQwin), by scanning electron microscopy (SEM) (JEOL JSM T330A) and by transmission microscopy (Phillips CM200). Ultraviolet-visible-near infrared spectroscopy (UV-vis-IR) was carried out with Perkin Elmer Lambda 14P spectrometer. Excitation and emission spectra were carried out by using a Fluorolog SPEX 212L with 450 W xenon continuous lamp. The signal was detected using a water-cooled Hammamatsu R928 photomultiplier.

3. Results and discussion

The hydrothermally treated substrate, observed in Fig. 1(a), has a no rough surface. Fig. 1(b) shows the substrate interface region after it was dipped into Pechini's solution, and at least four different regions can be distinguished: (1) the substrate, (2) a porous interface, (3) a richer porous interface and (4) the film. Fig. 1(c) shows the film after four dip coating (four-layer film) followed by a thermal treatment at 873 K, where a mosaic shaped topography is achieved. The film itself does not present this feature, which is induced by the thermal treatment of the substrate. When the Schott® glass substrate is heated at 873 K, which is close to its glass transition temperature (T_g), the surface cleaves in blocks forming the topography observed in Fig. 1(c). Then, the substrate/film interface region was not observed by optical microscopy after the film was fired.

It is possible to observe that ZnO:Eu particles are approximately spherical with diameter shorter than 300 nm and distributed over the glass blocks, as shown in Fig. 2(a), which also evidences a border between two different blocks. The ZnO:Eu 1 at% particles observed from the film are bigger than the particles observed from the powder in Fig. 2(b). The particles in the powder have a size range between 70 and 90 nm and this suggests that the substrate causes the growing of the particles.

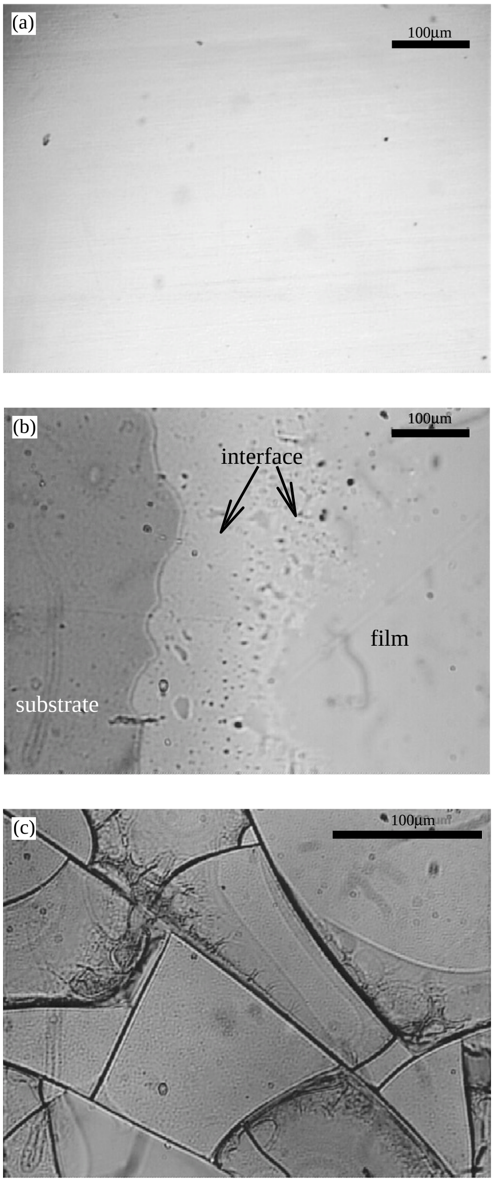

Fig. 1. OM images of (a) substrate, (b) film without thermal treatment and (c) film thermally treated at 873 K, 1 h.

UV-vis-IR spectra of the substrate and of the four-layer film are displayed in Fig. 3. The substrate has high transparency ($T > 70\%$) in the visible and near infrared region but is almost opaque for wavelengths shorter than 300 nm. After the film deposition, the glass substrate becomes less transparent in all measured spectral range with almost no difference in function of the numbers of layers. Two inflexions are detected on the spectrum of the film sample. The first one at ~310 nm is due to a substrate absorption and the

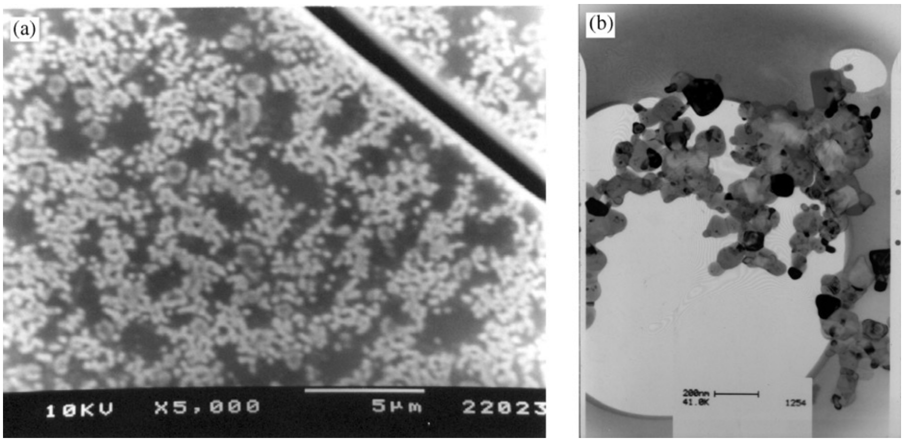

Fig. 2. (a) SEM image of the ZnO:Eu 1 at% film. (b) TEM image of the ZnO:Eu 1 at% powder.

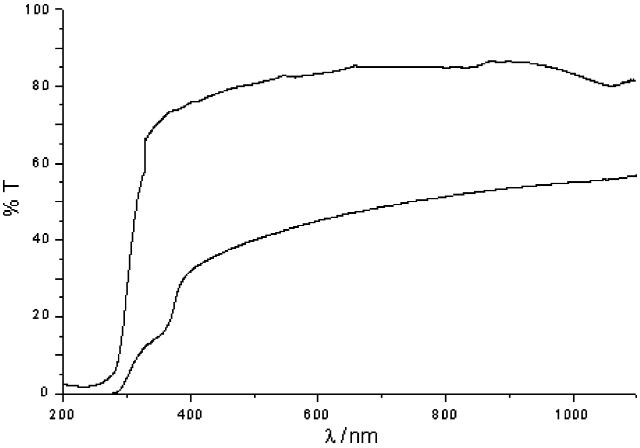

Fig. 3. UV-vis-nIR spectra of substrate and four-layer film sample.

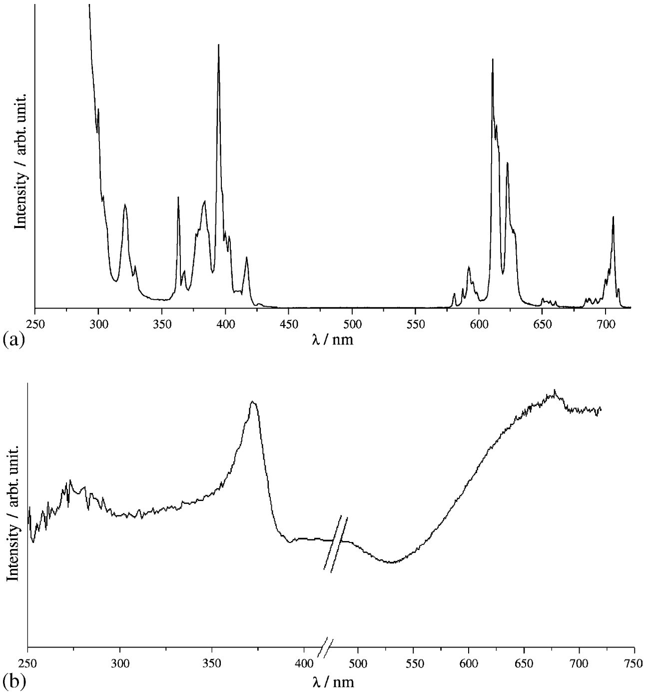

Fig. 4. Luminescence spectra at room temperature. (a) Excitation (monitored at 610 nm) and emission (under 395 nm excitation) spectra of pure Eu_2O_3 with cubic structure. (b) Excitation (monitored at 678 nm) and emission (under 372 nm excitation) spectra of pure ZnO prepared by Pechini's method and fired at 873 K, 1 h.

second one at ~380 nm is attributed to valence band→ conduction band transition of zinc oxide present in the film.

To better compare the emission of the film in different excitations, the excitation and emission spectra of pure europium oxide and pure zinc oxide, are presented in Fig. 4. Fig. 4(a) shows the excitation and the emission spectra of the pure cubic Eu_2O_3. The 340–355 nm and 470–500 nm ranges do not excite the Eu^{3+} ion. Fig. 4(b) shows the excitation and the emission spectra of the ZnO powder prepared by Pechini's method and fired at 873 K. The ZnO treated in those conditions presents a broad emission band covering the entire red visible range, attributed to electronic defects in the prohibited band gap [14]. This emission is specially excited by wavelengths shorter than 380 nm, the valence band→ conduction band transition of zinc oxide. It is important to remark that the ZnO emission is not excited in the range of 385–400 nm.

Excitation and emission spectra of the four-layer film are shown in Figs. 5 and 6. The excitation spectrum acquired by fixing the emission wavelength at 613 nm related to Eu^{3+} ion $^5D_0 \rightarrow {}^7F_2$ transition is shown in Fig. 5(a). The inset reveals two lines, at 392 and 462 nm, assigned, respectively, to the $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions. Beside these two lines, a broad band is detected at higher energy, which is attributed to substrate and/or ZnO absorptions. This spectrum confirms that the Eu^{3+} is not excited in the region of 470–500 nm, neither at 450 nm. The Eu^{3+} ion presence in the supported film is confirmed by the emission spectra shown in Fig. 5(b). Under excitation at 392 nm,

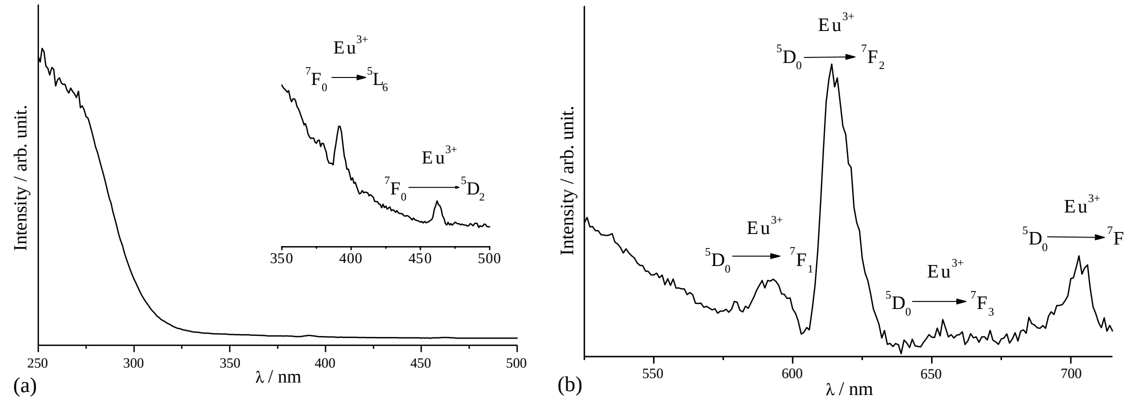

Fig. 5. Luminescence spectra at room temperature. (a) Excitation spectrum of the film monitored at 613 nm, inside a zoom at Eu^{3+} transitions. (b) Emission spectrum of the film under 392 nm excitation.

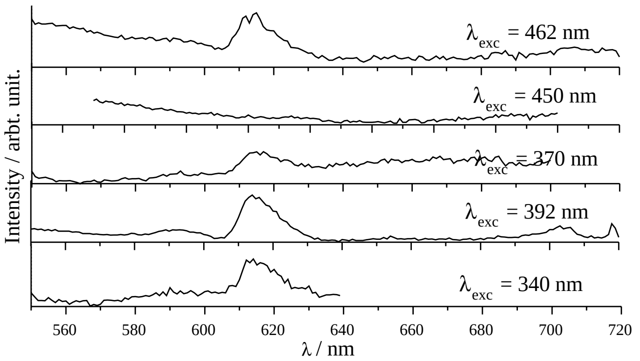

Fig. 6. Room temperature emission spectra of the film under different excitation wavelengths.

lines corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2, 3 and 4) transitions are detected. Since these transitions are broad, it suggests that europium ions are in different sites. Fig. 6 shows the four-layer film emission spectra under different excitation wavelengths. The $^5D_0 \rightarrow {}^7F_2$ transition (613 nm) of Eu^{3+} ions is detected under: Eu^{3+} excitation at 392 and 462 nm, both ZnO and Eu^{3+} excitations at 370 nm, and even only ZnO excitation at 340 nm, excitation of ZnO only; 392 and 462 nm, excitations of Eu^{3+} only; and 370 nm, excitation of ZnO and also of Eu^{3+}. Nevertheless at 450 nm excitation no film emission is observed. Since the film is excited at the wavelengths that excite only the ZnO host, 340 nm for instance, the emission of Eu^{3+} ions observed at 613 nm suggests that there is an energy transfer from the ZnO to Eu^{3+}. At wavelengths shorter than 340 nm, the substrate is excited and its emission covers Eu^{3+} transitions that cannot be detected.

4. Conclusion

Europium(III)-containing zinc oxide films can be obtained from Pechini's solution. All samples thermally treated show a mosaic feature due to substrate surface. The particles are small (~250 nm) with spherical shape. The films are weakly transparent at wavelengths higher than 300 nm and almost opaque at shorter wavelengths. Eu^{3+} ions are detected by luminescence spectroscopy and energy transfer from the host ZnO to europium can be observed.

Acknowledgments

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