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Photoluminescence properties of Al_2O_3:Eu thin films deposited by spray pyrolysis

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Europuim (Eu) doped aluminum oxide (Al_2O_3) thin films were deposited on silicon and quartz substrates by spray pyrolysis technique, from a solution at 0.062 molar containing aluminum and europuim acetilacetonates. Eu-doping was obtained by adding to the solution the acetilacetonate in different concentrations. Structural, optical and morphological characteristics of the films, as a function of deposition conditions such as variation of the impurity concentration and deposition temperature are presented. In particular in relation to the optical characteristics (photoluminescence) of the films, it has been observed a characteristic emission associated with radiative transitions between the europium electronic energy levels. The overall spectra observed consist on several peaks associated with such transitions showing a red light emission. Structural characterization was performed by measurements of X-Ray diffraction patterns and morphological characterization by atomic force microscopy.

1. Introduction

In the last years most of the work done in the Flat Panel Displays (FPD) area has been focused to the development of luminescent films based oxides of high quality, that can be applied as optically active layers in photoluminescent, cathodoluminescent and electroluminescent devices, for this purpose it is necessary to obtain flat and transparent films in order to obtain a device with a good resolution, contrast and efficiency characteristics.

Metallic oxides are attractive host materials for rare earth dopants to develop advanced phosphors due to their good stability and simple synthetization [1-3]. Trivalent rare-earth doped oxides are some of the most promising phosphors; their $4f^n$ valence clouds are shielded by the $5s^2p^6$ electron cloud and according to this electron configuration, the sharp lines due to the f-f transitions are observed in the optical absorption and emission spectra [4,5]. With respect to the deposition technique, spray pyrolysis is a simple technique that allows to obtain good quality films over extended areas at low cost [6].

In the present work the structural, morphological and optical characteristics of aluminum oxide films deposited by ultrasonic spray pyrolysis at temperatures below 600°C are reported. These films have been doped with different concentrations of Eu acetilacetonates in the spraying solution in order to obtain luminescent materials in the red region. X-Ray measurements indicate that these films are amorphous. The photoluminescence emission from these films shows the characteristic spectra associated with interlevel transitions of the Eu electronic energy states that indicates an ionized atomic doping process. The dependence of the luminescence intensity as a function of substrate temperature during deposition and dopant concentration are reported as well.

2.Experimental

Luminescent Al_2O_3:Eu thin films were grown by the spray pyrolysis technique which has been described in detail previously [7,8]. The spraying solution used was a 0.062 M solution with Al and Eu acetilacetonates as precursors diluted in dimetylformamide; the dopant concentrations used were 5, 10, 15, 20 and 30% added also to this solution. The deposition temperature were 500, 550 and 600°C, the substrates were silicon and quartz pieces of about $1cm^2$. The deposition time was 10 min. and the thickness of the films was about 5000 – 6000 Å.

The photoluminescence spectra were obtained with a commercial spectrofluorometer (Perkin-Elmer LS50B) in the wavelength range of 400 to 800 nm using an excitation ligth of 250 nm, the spectra were measured with a 430 nm filter to block out the excitation signal. The final spectra were a result of an average over 3 scans at 360 nm/min. Transmission spectra was obtained with a UV-Visible commercial spectrophotometer (UNICAM), the wavelength range analyzed was 200 to 900 nm using quartz pieces as reference. Surface morphology was analyzed with an atomic force microscope (Park Scientific Instruments Autoprobe CP), the region analyzed was 10 μm^2 approximately. A SIEMENS D-5000 X-Ray diffractometer with a Cu target (λ = 1.5406 Å) was used to obtain the X-Ray diffraction patterns of the films.

3. Results and Discussion

The photoluminescence emission characteristics for the films are illustrated in Figures 1 and 2, they show the emission behavior of the films as a function of the dopant concentration and as a function of the deposition temperature, respectively. Al_2O_3:Eu films present the characteristic peaks that could be associated with interlevel transitions for the electronic energy levels of Eu^{3+} ions, in particular to those corresponding to transitions from $^5D_0$ to $^7F_0$, $^7F_2$ and $^7F_3$ (590, 619 and 653 nm respectively) [9].

The location of this peaks (594, 616 and 653 nm) are slightly shifted from the expected values, this might be due to the disordered nature of the host material. The luminescent peaks observed are mostly due to luminescent centers originated by the Eu ions in the Al_2O_3 host material. The luminescence emission has an optimum around 600°C and 20% dopant concentration in the spraying solution. Transmission measurements in the UV-Visible range are shown in Figure 3, the transmitance in the visible region is high ~90% for 10 min. deposition time, and decreases as the deposition time increases. deposition temperature range used are shown in Fig. 4.

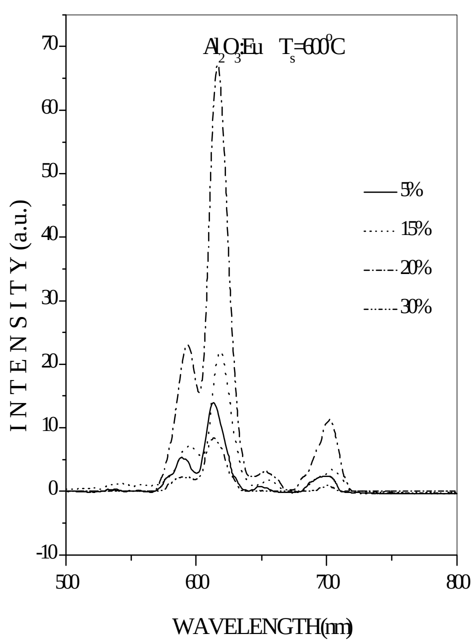

Fig. 1 Photoluminescence spectra for samples deposited at differen dopant concentrations. The emission from these films shows the characteristic peaks associated with radiative transitions between the Eu electron energy levels.

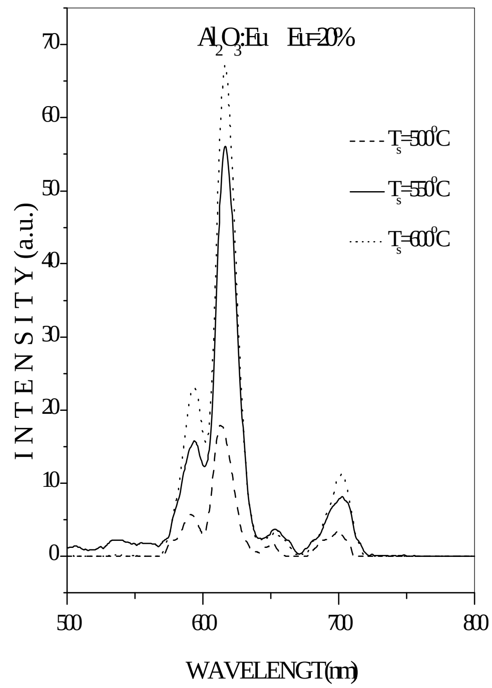

Fig. 2 Room temperature photoluminescence emission from aluminum oxide films doped with Eu deposited at different substrate temperatures. The luminescent peaks are associated with radiative transitions between the Eu electron energy levels.

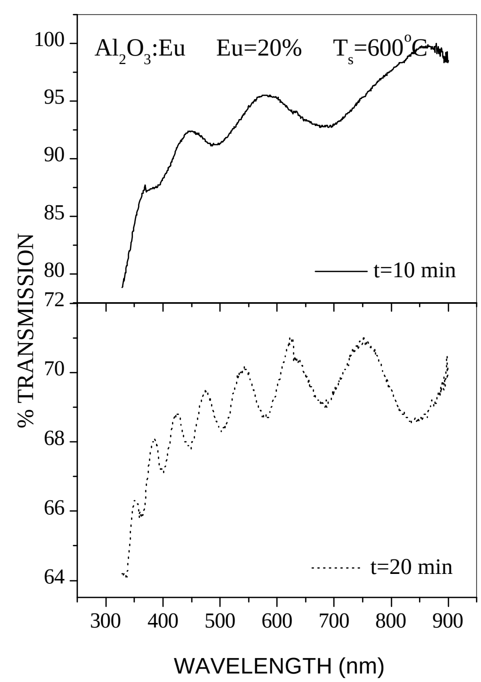

Fig. 3 Transmission spectra for two Al_2O_3:Eu samples deposited at different deposition time. The transmission percentage decreases when the deposition time increases.

Preliminary results show that the surface is flat in general, when the deposition temperature is increased growth differences appear. For the lowest temperature we observe that the surface is very flat, at 550°C the film starts to develop prominent peaks while for the highest deposition temperature (600°C) the film is constituted by wide non-sharp peaks. X-Ray diffraction patterns showed that Al_2O_3:Eu films were amorphous as can be seen in Fig. 5, this is due to the low range of temperature used for the deposition (500°C to 600°C) [10].

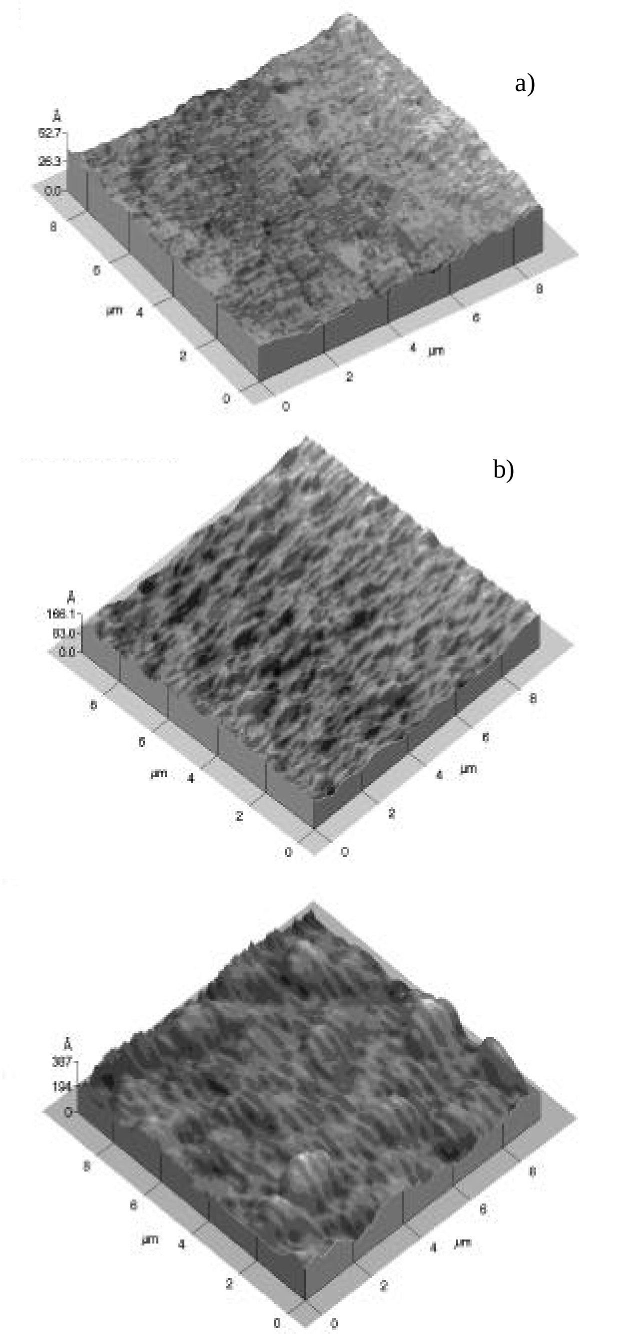

Fig. 4 Atomic Force Microscopy images of Al_2O_3:Eu films deposited on silicon substrates at different deposition temperature. a)T_s= 500°C, b) T_s= 550°C and c) T_s= 600°C.

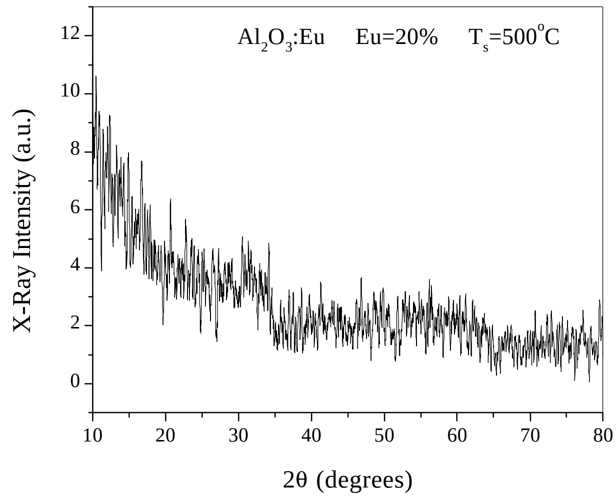

Fig. 5 X-Ray diffraction pattern from aluminum oxide film doped with europium grown by spray pyrolysis on silicon substrate.

4. Conclusions

Room temperature luminescence aluminum oxide films doped with Eu have been deposited by the spray pyrolysis technique at temperatures below 600°C. The luminescence characteristics of these films show that Eu incorporate into the host material as an atomic center. X-Ray diffraction patterns indicate that these films are amorphous. UV-Visible transmission measurements show that the films have high transparency in the visible region of the electromagnetic spectra (~90%). Preliminary AFM results show that the surface is flat in general appearing growth differences when the deposition temperature is increased.

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