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Luminescent properties of $\text{Al}_2\text{O}_3$:$\text{Tb}$ thin films deposited by spray pyrolysis

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Optical, structural and morphological characteristics of terbium doped aluminum oxide thin films deposited by spray pyrolysis technique have been studied as the function the deposition parameters such as substrate temperature and dopant concentration. The spraying solution is prepared by mixing dimethylformamide with an aluminum acetylacetonate. Tb-doping is achieved by adding to the solution the acetylacetonate in different concentrations. In relation to the optical characteristics (Photoluminescence and Cathodoluminescence) of the films, characteristic emissions associated with radiative transitions between the terbium electronic energy levels, have been observed. The overall spectra observed consist of several peaks associated with such transitions showing a green light emission. X-ray diffraction patterns showed that the films were amorphous and Atomic Force Microscopy measurements have allowed to observe that the surface of the films is flat in general.

Keywords:

1. Introduction

The lanthanide elements, commonly known as the “rare earths” (RE), have been an increasingly important ingredient in a variety of photonic applications [1], ranging from solid-state lasers to color displays to optical fiber telecommunications. RE elements have a partially filled inner ($4f^8$) shell surrounded by completely filled outer ($5s^2$ and $5p^6$) orbitals. This results in optical emission of very sharp lines at wavelengths from the UV to the IR [2,3], which are relatively independent of the host material and are determined by the energy of the transition between $4f$ states of the RE. While the host material has a weak influence on the emission wavelength, it does have a very strong effect on the radiative transition probability. Metallic oxides are attractive host materials for RE dopants to develop advanced phosphors due to their good stability and simple synthetization [4,5,6]. As the deposition technique, spray pyrolysis is a simple technique that allows to obtain good quality films over extended areas at low cost [7].

In this work the optical, morphological and structural characteristics of terbium doped aluminum oxide thin films deposited by spray pyrolysis technique at temperatures below $600^\circ\text{C}$ are reported. The photoluminescence and cathodoluminescence emissions from these films show the characteristic bands associated with interlevel transitions of the Tb electronic energy states that indicates an ionized atomic doping process. The dependence of the luminescence intensity as the function of dopant concentration and substrate temperature during deposition are reported as well.

2. Experimental

Luminescent $\text{Al}_2\text{O}_3$:$\text{Tb}$ thin films were grown by the spray pyrolysis technique\footnote{Luminescent $\text{Al}_2\text{O}_3$:$\text{Tb}$ thin films were grown by the spray pyrolysis technique using a solution of 0.062M with Al and Tb acetylacetonates as precursors diluted in dimethylformamide; the dopant concentrations used were 1, 3, 5, 7 and 10 atom percent (a/o) added also to this solution. The deposition temperature was varied in the range from 400 to 600°C in steps of 50°C. The substrates were silicon and quartz pieces of about 1cm$^2$. The deposition time was 8 min and the thickness of the films was about 1000–1800Å. The photoluminescence spectra were obtained with a commercial spectrophotometer (Perkin-Elmer LS50B) in the wavelength range of 400 to 800nm using an excitation light of 250nm. The spectra were measured with a 430nm filter to block out the excitation signal. The final spectra were the result of an average over 3 scans at 400nm/min. Cathodoluminescence measurements were performed by using a commercial luminoscope ELM2A (source and electron beam controller). The emission is collected by means of an optical fiber connected to a commercial spectrophotometer (Perkin-Elmer LS50B) in its bioluminescence mode. The voltage used was 6kV and the applied current over an area of 3mm diameter approximately, was 0.5mA. Transmission spectra were obtained with a UV-Visible commercial spectrophotometer (UNICAM), in the 200 to 900nm wavelength range using quartz pieces as reference. Surface morphology was analyzed with an atomic force microscope (Park Scientific Instruments Autoprobe CP); the region analyzed was 10µm$^2$ approximately. A SIEMENS D-5000 X-ray} using a solution of 0.062M with Al and Tb acetylacetonates as precursors diluted in dimethylformamide; the dopant concentrations used were 1, 3, 5, 7 and 10 atom percent (a/o) added also to this solution. The deposition temperature was varied in the range from 400 to 600°C in steps of 50°C. The substrates were silicon and quartz pieces of about 1cm$^2$. The deposition time was 8 min and the thickness of the films was about 1000–1800Å.

The photoluminescence spectra were obtained with a commercial spectrophotometer (Perkin-Elmer LS50B) in the wavelength range of 400 to 800nm using an excitation light of 250nm. The spectra were measured with a 430nm filter to block out the excitation signal. The final spectra were the result of an average over 3 scans at 400nm/min. Cathodoluminescence measurements were performed by using a commercial luminoscope ELM2A (source and electron beam controller). The emission is collected by means of an optical fiber connected to a commercial spectrophotometer (Perkin-Elmer LS50B) in its bioluminescence mode. The voltage used was 6kV and the applied current over an area of 3mm diameter approximately, was 0.5mA. Transmission spectra were obtained with a UV-Visible commercial spectrophotometer (UNICAM), in the 200 to 900nm wavelength range using quartz pieces as reference. Surface morphology was analyzed with an atomic force microscope (Park Scientific Instruments Autoprobe CP); the region analyzed was 10µm$^2$ approximately. A SIEMENS D-5000 X-ray...
3. Results and Discussion

The luminescence emission characteristics for the films are illustrated in figures 1 and 2. They show characteristic spectra of photoluminescence and cathodoluminescence respectively. The emission behavior of the films as a function of the dopant concentration and as a function of the deposition temperature are showed in figures 3 and 4 for photoluminescence and cathodoluminescence respectively. From these figures, we can observe that, the main luminescence emission has a maximum at 5 a/o for photoluminescence and cathodoluminescence, with a “quenching” process for higher dopant concentrations. Luminescence intensity behavior as a function of the deposition temperature shows a maximum at 450 °C for photoluminescence, while for cathodoluminescence the maximum occurs at 500 °C.

Figure 1. Room temperature photoluminescence emission from aluminum oxide films doped with Tb. The light emission from these films shows the characteristic peaks associated with radiative transitions between the electron energy levels of Tb.

Figure 2. Cathodoluminescence emission from aluminum oxide films doped with Tb. The light emission from these films shows the characteristic peaks associated with radiative transitions between the electron energy levels of Tb.

Figure 3. The light emission for the main peak (547.5nm) is plotted as a function of a) doping concentration and b) deposition temperature, for photoluminescence measurements. The luminescence intensity decays drastically for concentrations above 5% and for temperatures above 450 °C.

Figure 4. The light emission for the main peak (547.5nm) is plotted as a function of a) doping concentration and b) deposition temperature, for cathodoluminescence measurements. The luminescence intensity decays drastically for concentrations above 5% and for temperatures above 500 °C.
photoluminescence and 500°C for cathodoluminescence. There is a similar behavior for photoluminescence and cathodoluminescence. The maximum luminescence emission is found at the same doping concentration for both the techniques. Nevertheless, the optimum luminescent emission as a function of the deposition temperature is different for photoluminescence and cathodoluminescence. There is not clear explanation for this result, however it should be considered that the phenomena of excitation by photons or by electrons are of very different nature. In cathodoluminescence, besides the direct excitation by the incident electrons, there is an additional effect due to secondary electrons generated inside the phosphor material. This gain is generally accomplished by the impact ionization process which may eventually generates hundreds or thousands of electrons by one energetic electron, whereas only one photon generates one electron-hole pair in photoluminescence case. In addition, other effects associated to quenching of cathodoluminescence are: (a) thermal quenching, due of the local heating, by energetic electrons, (b) Auger effect which produce ejection of electrons leaving the luminescent centers de-excited, etc. The above cited phenomena account for differences of the excitation process by photons or electrons. Therefore, it is possible that the differences on the porosity and/or density of the material as well as the surface roughness resulting from different deposition temperatures could be related to observed behavior of the maximum luminescence. In order to get a better understanding of this behavior, further work in this area is required.

$\text{Al}_2\text{O}_3:\text{Tb}$ films present the characteristic peaks that could be associated with interlevel transitions for the electronic energy levels of Tb$^{3+}$ ions, in particular to those corresponding to transitions from $^5\text{D}_1$ to $^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$ and $^7\text{F}_3$ (490, 548, 590 and 624 nm respectively) for photoluminescence and cathodoluminescence [10,11]. The location of experimentally obtained peaks (492.5, 547.5,
590 and 622.5nm) is slightly shifted from the expected values, which might be due to the disordered nature of the host material. The luminescent peaks observed are mostly due to luminescent centers originated by the Tb ions in the $\text{Al}_2\text{O}_3$ host material.

X-ray Diffraction pattern showed that, the $\text{Al}_2\text{O}_3$:Tb films were amorphous, which might be due to the low range of temperature used for the deposition (400°C to 600°C) [12]. Surfaces morphology of the films for the range of deposition temperature used are shown in figure 5. They show a flat surface in general as well as the differences in growth rate due to the increase of deposition temperature. Transmission measurement in the UV-Visible range is shown in figure 6. We can see that the transmittance in visible region is high ~ 90% for 8 min deposition time.

4. Conclusions

We have obtained aluminum oxide films doped with terbium by the spray pyrolysis technique at temperatures below 600°C, whose luminescent characteristics show that the Tb is incorporated as an atomic center into the host material. The peaks observed in the spectra could be associated with inter-level transitions between electronic energy levels of Tb$^{3+}$ ions. X-ray diffraction patterns indicate that these films are amorphous. UV-Visible transmission measurements show that the films have a high transparency in the visible range of the electromagnetic spectrum and AFM results show that the surface is flat in general appearing growth differences when the deposition temperature is increased.

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