



Luminescent and Morphological Characteristics of $\text{Al}_2\text{O}_3:\text{Tb}$ Films Deposited by Spray Pyrolysis Using Acetylacetonates as Precursors

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Terbium-doped aluminum oxide films ($\text{Al}_2\text{O}_3:\text{Tb}$) were deposited by spray pyrolysis technique using aluminum and terbium acetylacetonates as precursors at temperatures up to 600°C. Room temperature cathodoluminescent and photoluminescent characteristics of the films have been studied as a function of the deposition parameters such as doping concentrations and substrate temperature. The observed emission has the spectral characteristics typical of radiative transitions among the electronic energy levels associated with the Tb^{3+} ion. Ultraviolet-visible transmission measurements show that the films are highly transparent in the visible region (a percent transmittance above 88% is observed). Atomic force microscopy measurements indicate that the surface of the films is very flat, showing an average surface roughness of 14 Å or less. The chemical composition of the films as determined by energy dispersive spectroscopy is also reported.

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Trivalent rare-earth (RE) doped oxides phosphors have been used for cathode ray tube (CRT) displays because of their excellent light output and color rendering capabilities.¹ They have also been used successfully in a variety of photonic applications² ranging from solid state lasers, fluorescent lamps, scintillators, X-ray screens to optical fiber telecommunications. RE elements have a partially filled inner ($4f^n$) shell surrounded by completely filled outer ($5s^2$ and $5p^6$) shells, which result in optical emission of very sharp lines at wavelengths from the ultraviolet (UV) to the infrared (IR) when they are excited with an electron beam, UV light or X-rays.³ These sharp lines are relatively independent of the host material and are determined by the energy of the transition between the $4f$ states of the RE. Because of their line rather than broad luminescence characteristics, RE-doped oxide phosphors have emerged as some of the most promising phosphors for applications in display technology. Also, their stability, simple synthesis^{4,5} and environmental safety are characteristics that make them attractive for flat panel display (FPD) applications. Compared to other phosphors such as sulfur-based materials, oxides are fairly stable under the different conditions required for the operation of different types of luminescent devices. For instance, oxides do not contaminate the electron emitters in field emission displays (FEDs) neither tend to degrade rapidly under the high current densities needed for the operation of these types of displays. Also, they are chemically inert under the action of plasmas commonly used in plasma operated FPD.^{6,7}

A large amount of the recent research work related with the development of the FPD has been directed to achieve high quality oxide-based luminescent films, that can be used as active layers in photoluminescent (PL), cathodoluminescent (CL), and electroluminescent (EL) devices. Thin film phosphors have several advantages over powders such as higher lateral resolution (because of the possibility of achieving smaller grains and more compact material), better thermal stability, reduced outgassing (when operation under vacuum is required), improved uniformity over the entire surface, and better adhesion to solid surfaces.⁸ Some of the characteristics required for thin film phosphors to improve luminescent device resolution, contrast, and efficiency are low surface flatness and high transparency in the visible region. Rough films, in general, induce

localized dielectric breakdown because they often create weak spots in multilayered devices, especially when the layers are very thin. Also, film transparency is important because a reduction of absorption and scattering of the emitted light by the luminescent centers results in an improvement of the external efficiency of the luminescent devices.

A variety of oxide-based luminescent films, such as $\text{Lu}_2\text{O}_3:\text{Ce}$,⁹ $\text{Y}_2\text{O}_3:\text{Eu}$,¹⁰ In_2O_3 ,¹¹ $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$,¹² $\text{ZrO}_2:\text{Tb}$,¹³ and $\text{ZnO}:\text{Sm}$ ¹⁴ among others, have been studied for FPD applications. The deposition techniques used to deposit these materials range from laser ablation to reactive sputtering and metallorganic chemical vapor deposition (CVD). Spray pyrolysis is a less sophisticated technique, suitable for large scale and large area production, that has been also used to deposit these type of films. Aluminum oxide films deposited by spray pyrolysis using aluminum chlorides or nitrides as precursors, have been studied as host material for rare-earth activators, such as Eu,¹⁵ Tb,¹⁶ and Ce.⁵ The films obtained with these precursors are rough, thick and opaque, therefore they are inadequate for the applications mentioned above. On the other hand, the deposition of aluminum oxide films by spray pyrolysis, using metallorganic precursors, results in films with excellent flatness, transparency, and density characteristics. In the present work, the morphological and luminescent characteristics of terbium-doped aluminum oxide films deposited by spray pyrolysis using metallorganic precursors, at temperatures up to 600°C, are reported. In particular, the dependence of the CL and the PL intensity from these films as a function of doping concentration and substrate temperature during deposition is analyzed.

Experimental

The ultrasonic spray pyrolysis apparatus has been described in detail previously.¹⁷ It consists of an ultrasonic generator used to produce a mist from the spraying solution. The mist is carried to a hot substrate, placed on a tin bath, through a tubing setup using air as a carrier gas (14 L/min). The spraying solution used in this work was a 0.06 M solution of Al-acetylacetonate diluted in *N,N*-dimethylformamide. Five different doping concentrations were obtained by mixing into the spraying solution 1, 3, 5, 7, and 10% of terbium acetylacetonate. The deposition temperature was varied in the range from 400 to 600°C in steps of 50°C. The substrates were either silicon wafers or quartz slides of about 1 cm². The average

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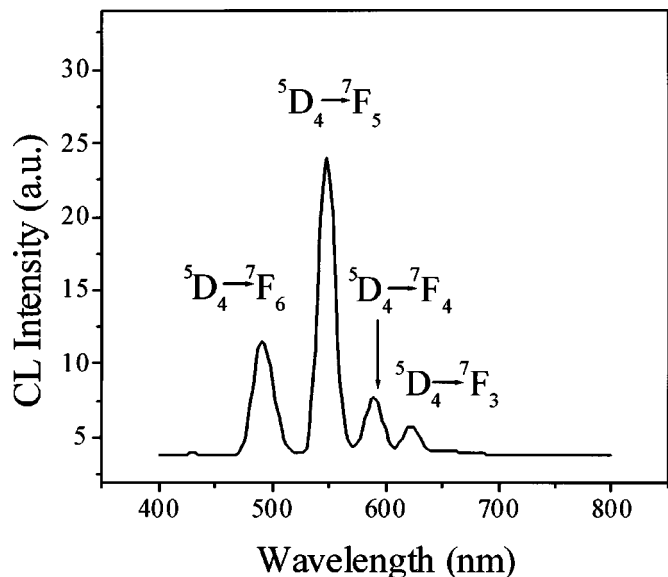


Figure 1. CL emission from aluminum oxide films doped with Tb. The light emission from these films shows the characteristic peaks associated with radiative transitions between the electron energy levels of Tb.

thickness of the films, as measured by ellipsometry, was 1100 Å. The films had a thickness uniformity within a 5%. CL measurements were performed with a commercial luminoscope ELM2A (source and electron beam controller). The light emission was collected with an optical fiber and fed into a commercial spectrofluorometer (Perkin-Elmer LS50B) operated in its bioluminescence mode for its spectral analysis. The accelerating voltage used in the measurements reported was 6 kV and the applied current of the electron beam was 0.5 mA. The spot size of the beam on the sample surface was 3 mm in diameter approximately. The PL spectra were obtained with the spectrofluorometer mentioned above in the wavelength range from 400 to 800 nm. A suitable excitation light wavelength for these PL measurements was found to be 220 nm. The final spectra were a result of an average over three scans at 400 nm/min. The optical transmission spectra were obtained on the samples deposited on quartz substrates with an UV-visible (UV-vis) commercial spectrophotometer (Unicam), in the range from 200 to 900 nm, using blank quartz substrates as a transmission reference. The samples surface morphology was analyzed with a Park Scientific Instruments atomic force microscope (AFM), model Autoprobe CP. The chemical composition of the films was determined from energy dispersive spectroscopy (EDS) measurements performed with a Leica-Cambridge electron microscope model Stereoscan 440 equipped with a beryllium-window X-ray detector.

Results

The characteristic luminescence spectra for the Tb-doped aluminum oxide films are shown in Fig. 1 and 2 for CL and PL, respectively. The spectra shown in these figures correspond to films deposited at 500°C with a 5% doping concentration in the spraying solution. The luminescence spectra peaks observed are associated with interlevel transitions within the electronic energy states of Tb³⁺ ions, and they are located at 490, 547.5, 590, and 622.5 nm. Both type of spectra show similar emission characteristics displaying a dominant peak associated with the transition $^5D_4 \rightarrow ^7F_5$ at 547.5 nm.

The intensity behavior of the dominant peak centered at 547.5 nm for both CL and PL is shown as a function of the doping concentration for samples deposited at 600°C, in Fig. 3a, and as a function of the deposition temperature, in Fig. 3b, for samples with 5% doping concentration in the spraying solution. The lines in these plots have a visual aid purpose only. The luminescence intensity has a maximum at ~5% for both CL and PL. A quenching phenomena

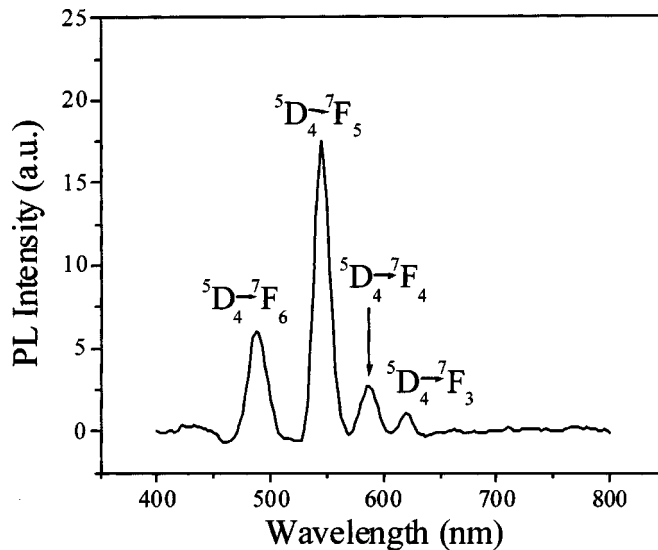


Figure 2. Room temperature PL emission from aluminum oxide films doped with Tb. The luminescent peaks are associated with radiative transitions between the Tb electron energy levels.

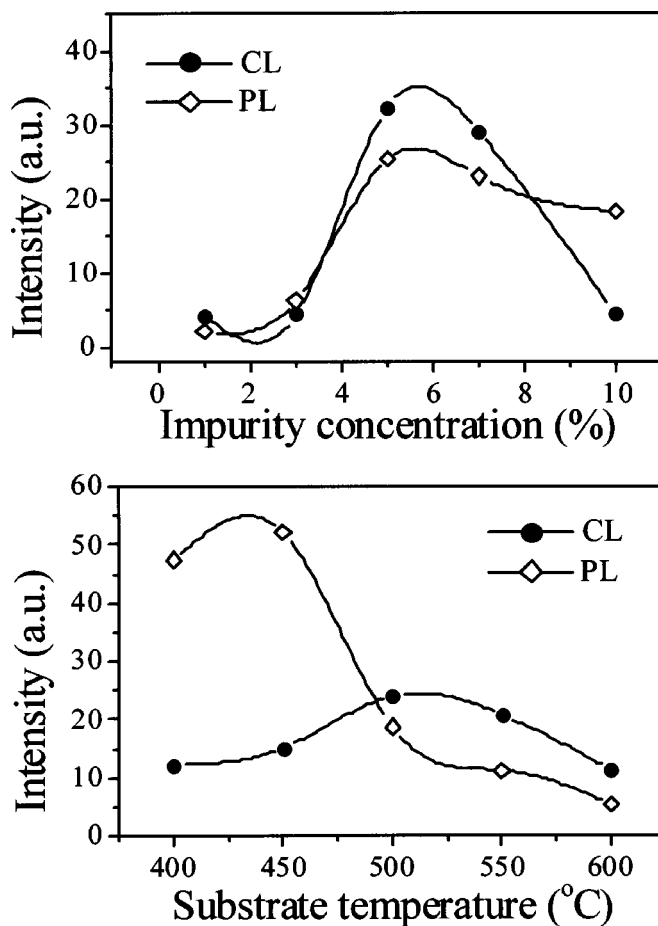


Figure 3. CL and PL emission intensities for the main peak (547.5 nm) are plotted as a function of (a) impurity concentration for samples deposited at 600°C and (b) deposition temperature for samples with 5% doping concentration in the spraying solution. Both CL and PL intensities decays drastically for impurity concentrations above 5%. The maximum luminescence emission intensity for CL occurs at 500°C and at 450°C for PL.

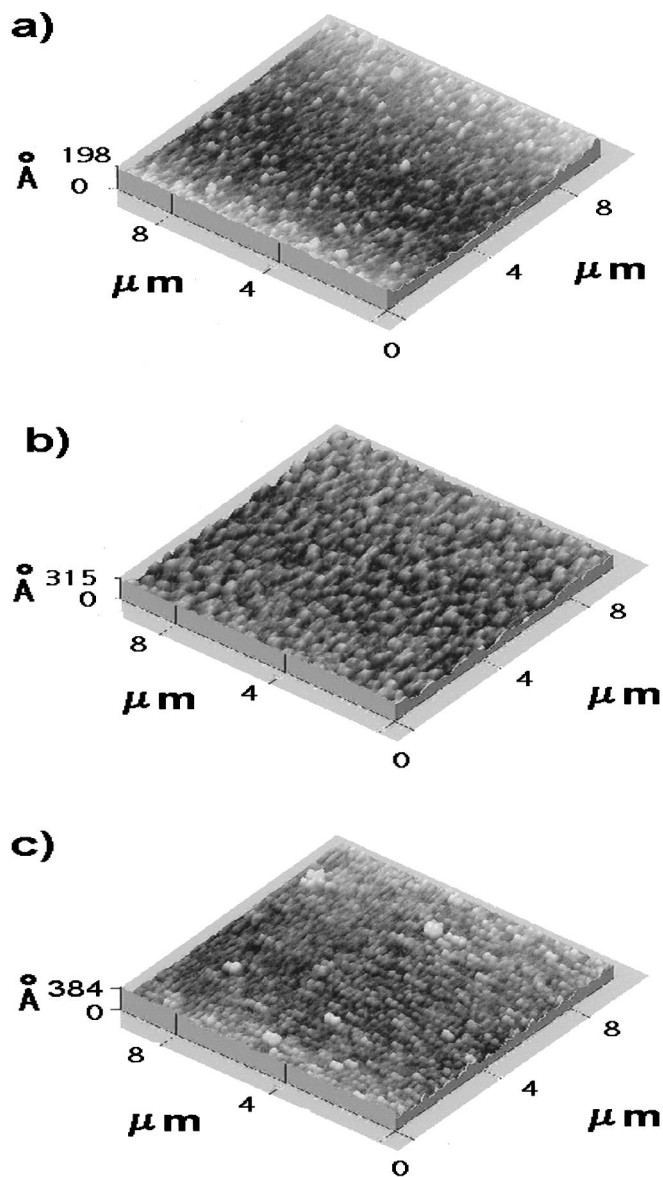


Figure 4. Atomic force microscopy (AFM) images of $\text{Al}_2\text{O}_3:\text{Tb}$ films deposited on silicon substrates at different deposition temperatures, (a) $T_s = 400^\circ\text{C}$, (b) $T_s = 500^\circ\text{C}$, and (c) $T_s = 600^\circ\text{C}$.

is observed at high doping concentrations in both cases. On the other hand, the luminescence intensity curve as a function of deposition temperature presents a maximum at $\sim 450^\circ\text{C}$ for PL and at $\sim 500^\circ\text{C}$ for CL.

The surface morphology for samples deposited at 400, 500, and 600°C is illustrated in Fig. 4, where atomic force micrographs for these samples are shown with vertical scales from 0 to 198 Å, 0 to 315 Å, and 0 to 384 Å, respectively. Similar morphology is observed in all cases, although, the average roughness of the films changes with deposition temperature as illustrated in Fig. 5. A maximum average roughness value of 14 Å is observed at 450°C .

Table I lists the relative atomic percent (atom %) content of terbium, aluminum, and oxygen present in the films, as measured by EDS, for the different doping concentration in the spraying solution and substrate temperatures during deposition studied. The incorporation of the Tb activator in the films is observed to be more efficient for deposition temperatures up to 500°C . Above this temperature, the incorporated amount of Tb in the film decreases for the same doping concentration in the spraying solution. The presence of car-

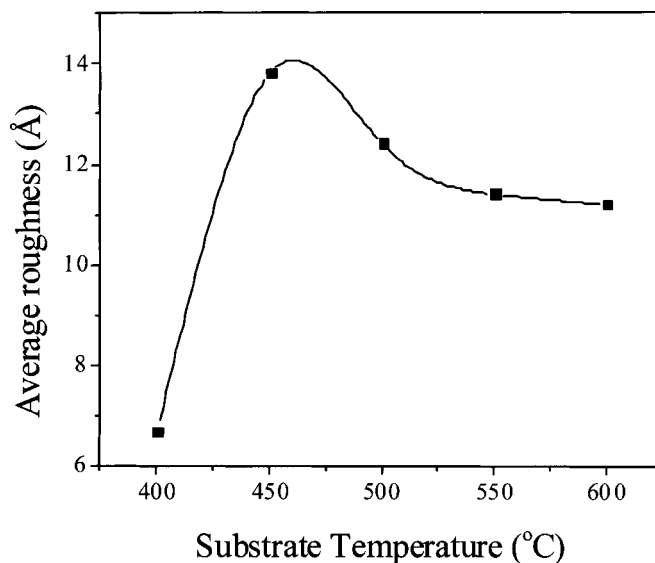


Figure 5. Average roughness as measured by AFM technique for $\text{Al}_2\text{O}_3:\text{Tb}$ films deposited at different substrate temperatures.

bon in these films was not quantified because it was detected to be present in low amounts (always below 3 atom %) and no specific influence on the films luminescence was observed. Also, the oxygen to aluminum atomic ratio was larger than the 3 to 2 expected ratio for stoichiometric Al_2O_3 , for most of the samples.

Figure 6 shows a typical percent transmission curve for these films in the UV-vis region. In this case the curve corresponds to a 1100 Å thick sample deposited on a quartz substrate at 600°C (8 min deposition time). X-ray diffraction (XRD) patterns, not shown in this paper, indicate that all films studied were mostly amorphous within the resolution of our equipment.

Discussion

The luminescence spectra from terbium-doped films present the characteristic peaks that are associated with interlevel transitions for the electronic energy states of Tb^{3+} ions. In particular, those corresponding to transitions from the $^5\text{D}_4$ level to the $^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$, and $^7\text{F}_3$, levels, giving peak emissions centered at 490, 547.5, 590, and 622.5 nm, respectively,¹⁸ are present. Most of the emitted light corresponds to the 547.5 nm peak, showing a dominant green luminescence emission. The luminescence behavior with doping concentration is similar for both CL and PL emissions. At low temperatures, the luminescence intensity increases as the deposition temperature increases. This behavior is most likely associated with the increasing incorporation of the terbium atoms as an atomic impurity into the

Table I. Atomic percent of terbium, aluminum, and oxygen in the films as determined by EDS for different concentrations in the spraying solution and deposition temperatures used.

Concentration in solution (atom %)	Deposition temperature ($^\circ\text{C}$)	Concentration measured by EDS (atom %)		
		Terbium	Aluminum	Oxygen
1	600	0	24.8	75.2
3	600	0	34.7	65.3
5	600	0.1	37.1	62.8
7	600	0.2	34.2	65.6
10	600	0.3	48.7	51
5	400	1.0	38.8	60.1
5	450	1.3	22.7	76.0
5	500	1.1	21.7	77.2
5	550	0.4	47.3	52.3

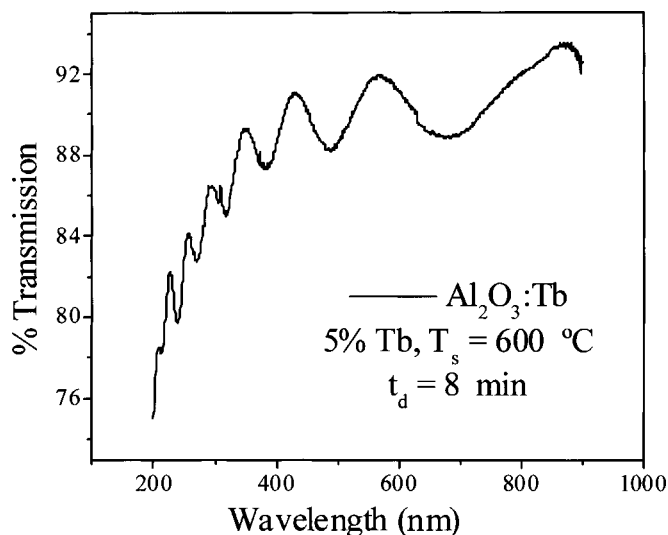


Figure 6. Typical transmission spectrum for a $\text{Al}_2\text{O}_3:\text{Tb}$ sample deposited at 600°C .

host material. After reaching a maximum at a doping concentration of 5% in the spraying solution, a quenching phenomena for higher concentrations is observed. This quenching effect has been reported for other materials^{4,15,19} and it has been associated with reaching an ion density that favors interaction among Tb ions at the nearest neighbor sites.

The luminescence emission as a function of the deposition temperature has a maximum at 500°C for CL and 450°C for PL. The difference in the maximum location for both types of emissions could be associated with the different nature of the excitation phenomena in each case and with the role that surface roughness plays in it. It has been reported²⁰ that increasing surface roughness and/or thickness of a phosphor film results in an enhancement of the PL emission, while CL emission is less affected by these parameters. As shown in Fig. 5, there is an overall increase of the film roughness as the deposition temperature is increased, presenting a maximum at 450°C . On the other hand, Table I information indicates that the terbium incorporation in the film is less efficient as the temperature is increased above 500°C . It is therefore proposed that the observed luminescence behavior with temperature is the result of a competing effect between the increase of the film roughness and the reduction of terbium ions incorporated in the film. Since the CL is less affected by the roughness of the film the net result is that its intensity variation with temperature is softer and a shift in the maximum location would be expected in comparison with PL, as it is observed in Fig. 3. The chemical composition obtained from EDS for the oxygen to aluminum ratio is in the range of 1 to 3.5 (Table I). This variation could indicate that differences on the porosity and/or density of the material arise with different deposition conditions. The terbium-doped aluminum oxide films deposited by spray pyrolysis exhibited a high percent of transmittance in the visible region. Values higher than 88% were obtained by optical transmission measurements in the UV-vis region. It is believed that the degree of surface flatness obtained on these films helped a great deal in achieving these characteristics.

Conclusions

We have obtained aluminum oxide films doped with terbium by the spray pyrolysis technique at temperatures below 600°C . The luminescent characteristics show that Tb is incorporated as an atomic center into the host material. The peaks observed in CL and PL spectra are associated with interlevel transitions between electronic energy states of Tb^{3+} ions, showing a dominant green light emission. It was found that the behavior of the luminescent emission with the deposition temperature was largely determined by a competing effect between the increasing film roughness and a reduction of terbium incorporation as the deposition temperature increased. It is proposed that this effect and the difference in the response, in particular for the film roughness, between PL and CL explain the different behavior observed for these emissions as a function of deposition temperature. AFM results showed that the surface of the films is very flat in general (the highest surface roughness value was 14 \AA). UV-vis transmission measurements show that the films have a high transparency in the visible ($>88\%$ transmission). XRD measurements indicate that the films are mostly amorphous for the range of deposition temperatures studied.

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