

Structural and photoluminescent characteristics of yttrium–aluminum oxide films doped with Tb, Eu or Ce

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Abstract

The structural and room temperature luminescent characteristics of rare earth doped yttrium–aluminum oxide films deposited by the spray pyrolysis technique at low temperatures have been studied as a function of the deposition parameters such as substrate temperature and dopant concentration. The spraying solution is prepared by mixing yttrium and aluminum chlorides in water, and the incorporation of the rare earth dopants is achieved by adding chloride salts of these elements to this solution. The photoluminescent emission from Tb- and Eu-doped films have the spectral characteristics typical of radiative transitions among the electronic energy levels associated with the 3+ ionized states of these atoms. The Ce doped films, on the other hand, present a blue emission that is associated with transitions within the energy states of the CeCl₃ molecule used for the doping process of the film. The X-ray diffraction measurements of these films indicated poor crystallinity in general, with small crystalline peaks and a broad amorphous component that tend to be reduced as the deposition temperature is increased. © 1998 Elsevier Science S.A. All rights reserved

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1. Introduction

Rare earth activated luminescent materials have been widely studied in the past mainly in their crystalline and powder form for cathodic ray tube (CRT) phosphors and other related applications such as fluorescent lamps, image intensifiers for X-ray screens among others [1,2]. Recently, the interest in developing reliable luminescent materials for flat panel displays has spurred a renewed research activity on these types of materials in the form of thin films [3]. The approach of using a rare earth ion in a wide band gap material as a luminescent material offers the advantage of light emission with spectral characteristics fairly stable under different operation conditions of the luminescent devices, since they are mainly dependent on the electronic energy levels of the ion and on the host material. On the other hand by changing the rare earth ion it is possible to obtain the

three different colors required for color imaging [4]. Thus terbium, europium, and thulium or cerium have been used for green, red and blue emissions, respectively. With respect to the host material, many inorganic compounds with a wide band gap like ZnS [5,6], ZnO [7], Al₂O₃ [8] and In₂O₃ [9] among others have been studied. Yttrium and yttrium–aluminum oxides have also been used as host materials in the form of thin films for rare earth dopants, however, they require either high deposition temperatures or long annealing postdeposition treatments at relatively high temperatures in order to obtain good luminescent emission from the rare earth dopants [10,11]. The deposition techniques used for these materials range from laser ablation to reactive sputtering and metallorganic chemical vapor deposition (CVD). These techniques require in general expensive vacuum setups and/or complicated systems for handling the source reactants. A less sophisticated technique like spray pyrolysis is certainly more desirable from the point of view of large scale and large area production of these films. In the present work the structural and luminescent characteristics of yttrium–aluminum oxide films deposited by ultrasonic spray pyrolysis at temperatures below 650°C

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are reported. These films have been doped with different concentrations of Tb, Eu and Ce chlorides introduced in the spraying solution in order to obtain luminescent materials in the green, red and blue regions, respectively. X-Ray measurements indicate that these films have poor crystallinity, presenting small peaks associated with different yttrium and yttrium–aluminum oxides including YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$). The photoluminescence emission from these films shows the characteristic spectra associated with inter-level transitions of the electronic energy states that indicate an ionized atomic doping process in the case of Tb- and Eu-doped films, while Ce-doped films present an emission characteristic that seems to be associated with a molecular doping of CeCl_3 in these films. The dependence of the luminescence intensity as a function of substrate temperature during deposition and dopant concentration are reported as well.

2. Experimental details

The ultrasonic spray pyrolysis apparatus has been described in detail previously [12,13]. It consists of an ultrasonic generator used to form a mist from the spraying solution; the mist is carried to a hot substrate placed on a tin bath through a tubing setup using an air flow of 12 l/min. An additional flow of air of 7 l/min is introduced near the sample substrate to provide an additional push to mist towards the substrate surface where the pyrolysis reaction takes place. The whole setup is enclosed in an evacuation chamber to exhaust the resulting vapors from this reaction. The spraying solution used was a 0.03 M solution of Y and Al chlorides in deionized water in a proportion of 3–5 atoms of Y to Al. The dopants were added in the form of chloride salts also to this solution. The deposition temperature was varied in the range from 300 to 650°C in steps of 50°C, the substrates were pieces of Pyrex glass slides of about 1×2 cm, with the exception of the films used to determine the chemical composition; these were deposited on crystalline Si substrates of similar dimensions in order to evaluate the oxygen content in the films. The deposition time was 8 min (5 min for the Ce-doped samples) to an average thickness of 5 μm , measured by a Sloan Dektak IIA profilometer. The films were uniform in thickness throughout the whole sample surface. The photoluminescence spectra were obtained with a commercial spectrofluorometer in the wavelength range of 300 to 800 nm using an excitation light of 250 nm. A Siemens D-5000 X-ray diffractometer with a Cu target was used to obtain the X-ray diffraction patterns of the films. The chemical composition of the films was measured using EDS with a Leica-Cambridge electron microscope Mo. Stereoscan 440 equipped with a Beryllium window X-ray detector. The standard used for the energy dispersion spectroscopy (EDS) measurements was the Multi-element X-ray Reference Standard (Microspec) Serial 0034, part No. 8160-53.

3. Experimental results

The structural characteristics of the yttrium–aluminum oxide films deposited by spray pyrolysis are illustrated in Fig. 1, where X-ray diffraction patterns for Tb-doped films deposited at three different substrate temperatures are shown. These patterns show several small peaks associated with AlYO_3 , Y_2O_3 and YAG crystalline phases on top of a broad peak centered at ~ 32 degrees. The broad peak is indicative of a highly disordered and/or amorphous material. This peak, however, becomes sharper and more intense as the deposition temperature is increased. Table 1 lists the relative chemical content of the rare earth dopant and the chlorine, yttrium, aluminum and oxygen present in the films (as measured by EDS on films deposited on Si substrates) for the different dopant concentration in the spraying solution. The samples doped with Tb and Eu were deposited at 500°C and the films containing Ce were deposited at 350°C. In general, Ce is observed to have the best incorporation efficiency, followed by Eu. Also, the samples doped with Ce present the largest amount of chlorine while the others present about the same amount. The amount of chlorine incorporated in the film seems to be dependent only on the deposition temperature; more chlorine is found in samples deposited at lower temperatures. The photoluminescence emission characteristics for the films with the three different

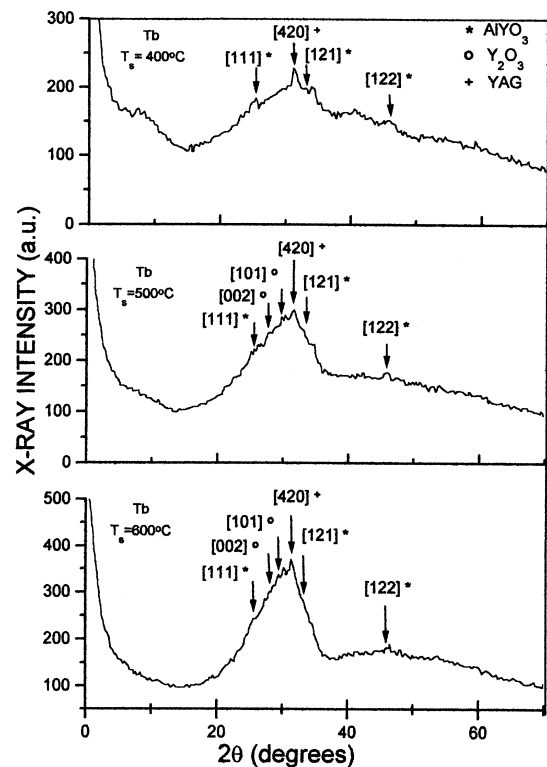


Fig. 1. X-ray diffraction patterns for terbium doped films deposited at three different temperatures, 400, 500, and 600°C. The peaks associated with crystalline forms of AlYO_3 , Y_2O_3 and YAG are indicated in each case. A broad peak centered around the (420) orientation for YAG increases and reduces its width as the deposition temperature is increased.

Table 1

Atomic percent content of the rare earth dopants, chlorine, yttrium, aluminum and oxygen in the films as determined by EDS for different concentrations in the spraying solution

Concentration in solution (a/o)	Concentration measured by EDS (a/o)		
	Tb/Cl (Y, Al, O)	Eu/Cl (Y, Al, O)	Ce/Cl (Y, Al, O)
1	-/4.47 (9.96, 20.81, 64.76)	-/5.22 (12.57, 19.49, 62.71)	0.10/10.94 (8.95, 13.60, 66.41)
5	0.13/4.71 (6.87, 22.31, 65.97)	0.24/3.61 (10.03, 17.48, 68.64)	0.75/11.44 (9.30, 13.31, 65.19)
10	0.34/4.33 (4.57, 25.9, 64.86)	1.42/5.42 (13.13, 23.99, 56.04)	1.46/11.53 (8.14, 11.84, 67.03)
20	0.71/5.38 (3.47, 26.07, 64.37)	1.64/5.30 (5.26, 32.37, 55.44)	2.50/12.90 (5.88, 13.67, 65.04)
30	1.09/5.27 (6.01, 22.10, 65.52)	2.48/7.87 (12.29, 29.57, 47.79)	3.70/14.62 (1.77, 18.55, 61.36)
50	1.65/5.07 (8.5, 19.05, 65.73)	3.87/5.13 (8.29, 21.72, 49.87)	3.77/12.42 (5.64, 10.88, 67.29)

dopants are illustrated in Fig. 2, where the spectra for Tb- and Eu-doped films deposited at 500°C with a 50% concentration of the dopant in the spraying solution and the Ce-doped film deposited at 350°C and 10% dopant in the spraying solution are shown. The Tb- and Eu-doped films present peaks characteristic of transitions within their respective electron energy levels at 490, 548, 590 and 624 nm and 590, 619 and 653 nm, respectively. Besides these peaks, there is a broad emission centered at ~400 nm which seems to be related to the yttrium–aluminum oxide host material and/or the glass substrate. The Ce-doped films present a dominant peak centered at 365 nm. Peak shifts slightly up to 395 nm as the Ce content is increased. The

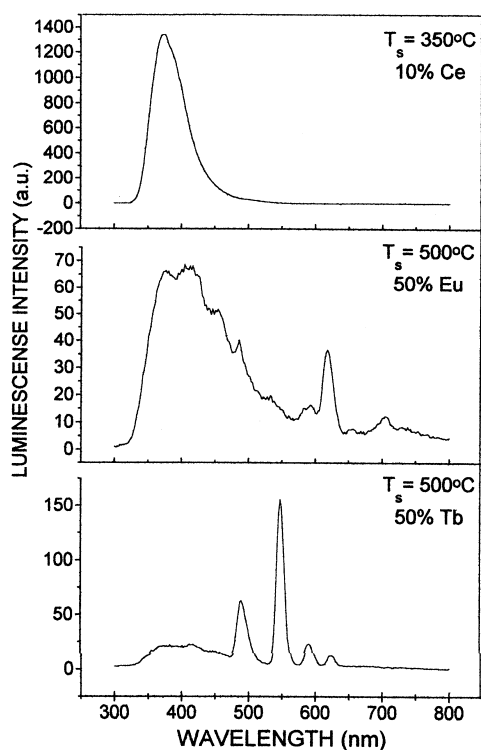


Fig. 2. Room temperature photoluminescence emission from yttrium–aluminum oxide films doped with Ce, Eu and Tb. The light emission from these films shows the characteristic peaks associated with radiative transition between the electron energy levels of the rare earth dopants involved. A broad band centered at about 400 nm originates from the host material and/or the glass substrate.

behavior of the peak intensity to the 548, 619 and 365 nm peaks for Tb-, Eu- and Ce-doped films, respectively, are shown as a function of the deposition temperature in Fig. 3 and as a function dopant concentration as determined by EDS in Fig. 4. The luminescence emission has an optimum around 500°C for Tb- and Eu-doped samples while in the case of Ce-doped samples, it is observed that the light emission decreases drastically for temperatures above 350°C showing a different behavior than the one observed for the samples doped with the other rare earth dopants. These results were performed several times in different areas of a sample and on samples deposited under the same conditions, and in all cases the results were reproducible. The luminescence intensity as a function of the relative doping concentration shows a peak at 2.5 atomic % for Ce-doped films and a quenching for higher concentrations, while the light emission intensities for Eu- and Tb-doped films do not reach saturation nor show quenching behavior for the concentrations achieved in these films.

4. Discussion and conclusions

The X-ray diffraction patterns obtained for the yttrium–aluminum oxide films indicate the coexistence of crystalline phases of $AlYO_3$, Y_2O_3 and YAG with highly disordered material indicated by the presence of a broad peak located around the peak associated with the (420) crystalline orientation for YAG [11–14]. This peak increases in magnitude and becomes sharper as the deposition temperature is increased. This may indicate some degree of ordering without getting to a total crystallization of the disordered phase. The peaks associated with the crystalline phases are not affected significantly by the deposition temperature, remaining small. This suggests that they are present in the form of small crystalline grains and/or relatively small quantity compared with the disorder material and that up to the highest deposition temperature used, they are not affected in either size or quantity present in the film. The presence of Cl in the films as determined by EDS might indicate that some of this disordered material might be in form of oxychlorides, especially in the case of Ce-doped films in which the amount of Cl is considerably high due

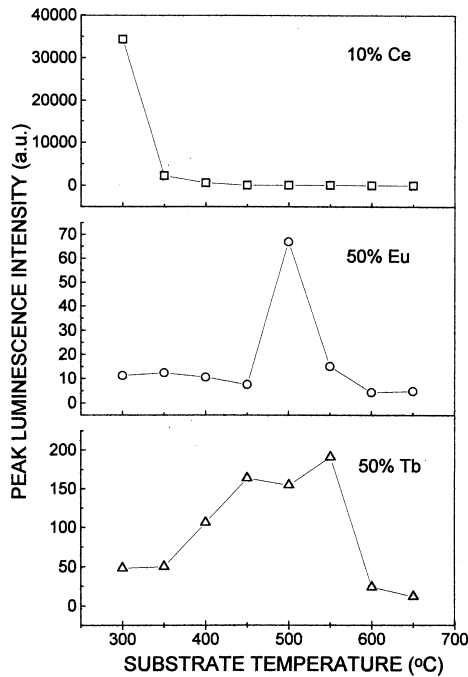


Fig. 3. The light emission intensity for the main peaks, 365, 619 and 548 nm for Ce-, Eu- and Tb-doped films is plotted as a function of the deposition temperature. The luminescence intensity decays drastically for Ce-doped films for temperatures above 350°C while in the other two cases a maximum is observed at 500°C.

to the low deposition temperatures used for this samples. Both Tb- and Eu-doped films were stable under exposure to ambient humidity. This fact reinforces the possibility that oxychlorides are present in the case of Ce-doped films. The luminescence spectra from terbium- and europium-doped films present the characteristic peaks that could be associated with interlevel transitions for the electronic energy levels of Tb^{3+} and Eu^{3+} ions, in particular to those corresponding to transitions from the 5D_4 to 7F_6 , 7F_5 , 7F_4 and 7F_3 of the Tb ion (487, 542, 584 and 619 nm, respectively) and those related with transitions from 5D_0 to 7F_0 , 7F_2 and 7F_3 (587, 611, and 648 nm, respectively) for the Eu ion. The location of these peaks are slightly shifted from the expected values (490, 548, 590, 624 for Tb and 590, 619 and 653 for Eu). These shifts might be due to the disordered nature of the host material. The intensity of the main luminescence emission peaks for these films shows a maximum at $\sim 500^\circ C$. This behavior is probably a result of two competing phenomena: (1) a better incorporation of the rare earth atoms as an atomic impurity into the host material which will result in an increase of the luminescence emission as the deposition temperature is increased, and (2) a softening of the glass substrate at temperatures above 500°C which will favor the diffusion of the dopant into the substrate degrading the luminescence characteristics of the sample. The luminescent characteristics of the films doped with Ce^{3+} show a behavior very similar to that of Al_2O_3 films doped with $CeCl_3$ [15] in which it was found that the light emission observed was related to interlevel transitions of Ce within a

$CeCl_3$ molecular center. As in that case, the luminescence spectrum shows a luminescent peak that seem to be comprised of two overlapping peaks centered at 365 and 395 nm and an apparent shift of the relative intensity from the 365 nm peak to the 395 nm peak with increasing doping density. Also, the decay of the luminescence intensity with increasing deposition temperature is similar to the aluminum oxide case and supports the idea that a similar doping mechanism is occurring in the yttrium–aluminum oxide films. Thus, it is likely that as in the case of aluminum oxide films, the luminescence emission observed in these films is associated with transitions from the 5d to 4f electronic levels of the Ce ion in the $CeCl_3$ molecule embedded into the host material. In general, it is difficult to compare the characteristics of these films with those deposited by other techniques since no quantitative information for the incorporation rate and luminescence of efficiency has been reported for YAG films doped with these rare earths.

In summary, room-temperature luminescent yttrium–aluminum oxide films doped with Tb, Eu and Ce have been deposited by the spray pyrolysis technique at temperatures below 650°C. The luminescent characteristics of these films show that while Tb and Eu incorporate into the host material as an atomic center, Ce is introduced as a molecular center formed by $CeCl_3$. The X-ray diffraction patterns of these films indicate the presence of a small contribution from crystalline phases within a disordered material phase.

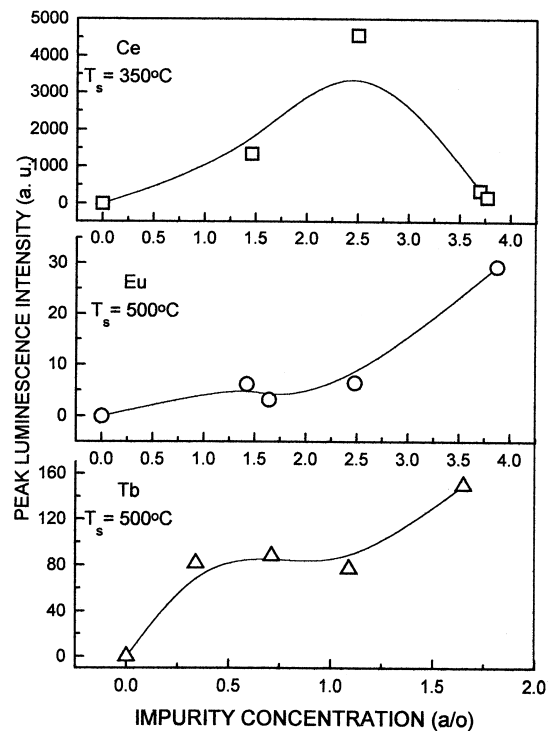


Fig. 4. Luminescence intensity for the main peaks as a function of the impurity concentration as determined by EDS. The Ce-doped films present a maximum at 2.5 a/o and a quenching of the luminescence for higher concentrations, while the Eu- and Tb-doped samples do not reach a saturation effect of the luminescence intensity for the concentrations studied.

AlYO_3 , Y_2O_3 and YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) are among the crystalline phases observed. The disordered material is characterized by a broad peak around the (420) orientation for YAG and is observed to increase in magnitude and become sharper as the deposition temperature is increased.

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References

- [1] J.A. Greer, H.J. Van Hook, M.D. Tabat, H.Q. Nguyen, G. Gammie, P.F. Koufopoulos, MRS Symp. Proc. 345 (1994) 281.
- [2] J.A. Greer, H.J. Van Hook, H.Q. Nguyen, G. Gammie, P.F. Koufopoulos, SID Proc. 35 (1994) 281.
- [3] S.W. Depp, W.E. Howard, Sci. Am. 267 (3) (1993) 90.
- [4] L.E. Tannas Jr., Phys. Today 45 (12) (1992) 52.
- [5] D. Kahng, Appl. Phys. Lett. 13 (1968) 210.
- [6] A. Ortíz, C. Falcony, M. García, A. Sánchez, Semicond. Sci. Technol. 3 (1988) 537.
- [7] C. Falcony, A. Ortíz, M. García, J.S. Helman, J. Appl. Phys. 63 (7) (1988) 2378.
- [8] C. Falcony, A. Ortíz, J.M. Domínguez, M.H. Farías, L. Cota-Araiza, G. Soto, J. Electrochem. Soc. 139 (1) (1992) 267.
- [9] A. Ortíz, C. Falcony, M. García, S. López, Thin Solid Films 165 (1988) 249.
- [10] G.A. Hirata, O.A. López, L.E. Shea, J.Y. Yi, T. Cheeks, J. McKittrick, J. Siqueiros, M. Avalos-Borja, A. Esparza, C. Falcony, J. Vac. Sci. Technol. A 14 (3) (1996) 1.
- [11] N.J. Hess, G.J. Exarhos, J. Non-Cryst. Solids 178 (1994) 91.
- [12] M. Langlet, J.C. Joubert, in C.N.R. Rao (ed.), Chemistry of Advanced Materials, Blackwell, Oxford, 1993, p. 55.
- [13] M. Jergel, A. Conde Gallardo, C. Falcony, S. Strbik, Supercond. Sci. Technol. 9 (1996) 1.
- [14] N.J. Hess, G.D. Maupin, L.A. Chick, D.S. Sunberg, D.E. McCready, T.R. Armstrong, J. Mater. Sci. 29 (1994) 1873.
- [15] C. Falcony, M. García, A. Ortíz, O. Miranda, I. Gradilla, G. Soto, L. Cota-Araiza, M.H. Farías, J.C. Alonso, J. Electrochem. Soc. 141 (1994) 2860.