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# Cathodoluminescent properties of pulsed-laser-deposited Eu-activated $Y_2O_3$ epitaxial films

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The growth, structural and cathodoluminescent (CL) properties of 4 wt. % europium-doped yttrium oxide ($Eu:Y_2O_3$) thin films are reported. The $Eu:Y_2O_3$ films were grown *in situ* using a pulsed laser deposition technique. Our results show that $Eu:Y_2O_3$ films can grow epitaxially on (100) $LaAlO_3$ substrates under optimized deposition parameters. The epitaxial growth of $Eu:Y_2O_3$ films on $LaAlO_3$, which has a lattice mismatch of ~60%, is explained by matching of the atom positions in the lattices of the film and the substrate after a rotation. CL data from these films are consistent with highly crystalline $Eu:Y_2O_3$ films with an intense CL emission at 611 nm. [S0163-1829(99)10839-7]

Recent studies have shown that thin films of yttrium oxide and yttrium oxysulfide activated optimally with europium are very promising for applications in flat panel field emission displays (FEDs).[1–6] Both of these systems are red phosphors emitting light at 611 and 617 626 nm, respectively. It has been observed that europium-activated yttrium oxysulfide ($Eu:Y_2O_3S$) phosphors exhibit higher photoluminescence (PL) and cathodoluminescence (CL) efficiency than europium activated yttrium oxide phosphor.[7] However, the atmospheric stability as well dynamic current or voltage bias stability of $Eu:Y_2O_3S$ needs to be improved significantly before using it in actual FED devices.[4–6] The $Eu:Y_2O_3$ system, which is relatively less efficient than $Eu:Y_2O_3S$, has shown better stability resulting in wider attention to the $Eu:Y_2O_3$ phosphor system. In addition to improving stability, the brightness also needs to be improved for the successful development of FEDs based on thin film phosphors. The lower brightness and efficiency of phosphor films relative to powders is possibly caused by inferior crystallinity, off-stoichiometry, and multiple internal reflections of the emitted light.[8–10] The objective of this investigation was to grow highly crystalline epitaxial $Eu:Y_2O_3$ films and study their and CL properties. The epitaxial $Eu:Y_2O_3$ films are expected to be better than polycrystalline $Eu:Y_2O_3$ films in terms of brightness and stability. Moreover, due to the difficulty in producing reasonably large and homogeneous single crystal of $Eu:Y_2O_3$ materials, the epitaxial growth of $Eu:Y_2O_3$ films assumes further importance from the point of view of carrying out fundamental studies on phosphor thin films.

4 wt. % Eu-activated $Y_2O_3$ thin films were grown *in situ* using a pulsed laser deposition (PLD) technique which has emerged as one of the most convenient and efficient techniques for the stoichiometric evaporation of multicomponent refractory materials.[11] In the PLD experiments, 4 wt. % Eu-doped $Y_2O_3$ dense target was ablated using a 248-nm KrF pulsed laser. The energy density and repetition rate of the laser beam used were 1.5 $J/cm^2$ and 5 Hz, respectively. Single-crystal (100) oriented lanthanum aluminate ($LaAlO_3$) was used as substrate material. The substrates were $10\times5\times0.5$ mm and attached to the heater face plate placed parallel to the target by silver paste. The substrates were heated at temperatures in the range of 600–750 °C. An oxygen pressure of 200 mTorr was maintained in the growth-chamber during deposition experiments. Assuming a time-dependent linear film-growth, the growth-rate of the film deposited was estimated by dividing the total thickness of the film by the deposition time. The thicknesses of $Eu:Y_2O_3$ films were measured using an EC110 multiwavelength ellipsometer. To check the reproducibility of the results, three samples prepared under identical deposition conditions were used for each measurement.

Shown in Fig. 1(a) is the ($\theta-2\theta$) x-ray diffraction (XRD) scan of a 3.2-$\mu$m thick $Eu:Y_2O_3$ film grown on (100) $LaAlO_3$ substrate at 750 °C. For comparison, we have also shown in this figure a standard XRD pattern of polycrystalline $Y_2O_3$ powder [Fig. 1(b)]. The ($h00$) lines with $h=4$, 6, and 8 are thickened to indicate that only these peaks appear in the XRD pattern of the $Eu:Y_2O_3$ film besides the substrate peaks. This suggests a textured growth of $Eu:Y_2O_3$ film on $LaAlO_3$ substrates. The films grown at lower temperatures ($\leqslant$700 °C) were polycrystalline with wider full width at the half maximum (FWHM) of each peak. Due to the limitation of our heater's capability to obtain higher temperature, we could not perform depositions at temperatures higher than 750 °C. The inset in Fig. 1 shows the rocking

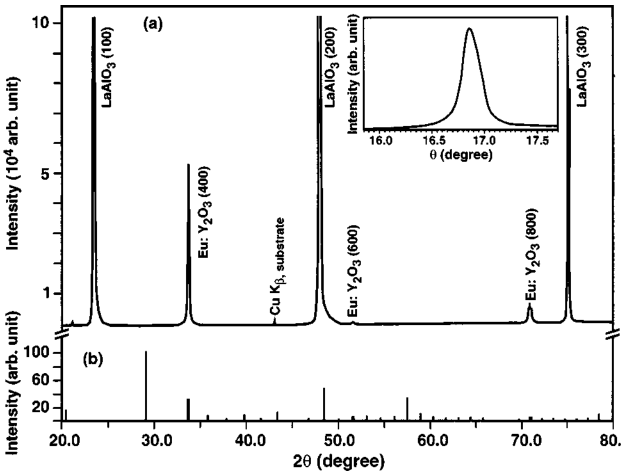

FIG. 1. X-ray diffraction patterns of (a) a 3.2-$\mu$m thick $Eu:Y_2O_3$ film grown on (100) $LaAlO_3$ substrate at 750 °C and (b) $Y_2O_3$ powder. The inset in (a) is the rocking curve of the (400) peak of the same film.

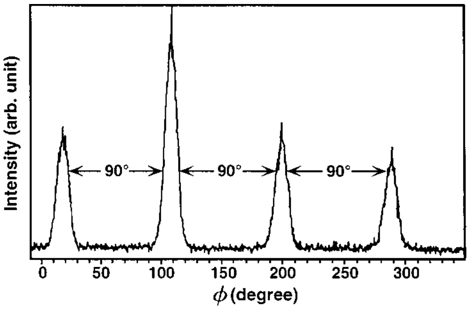

FIG. 2. $\phi$ scan of 3.2-$\mu$m-thick Eu:$Y_2O_3$ (222) family reflections of the film grown at 750 °C on (100) $LaAlO_3$ substrate.

curve ($\omega$ scan) of the (400) peak of this film whose FWHM is only 0.2° confirming that Eu:$Y_2O_3$ films are highly textured.

The degree of in-plane alignment was determined using $\phi$-scan of {222} peaks with $\phi$ rotation axis parallel to the film thickness. The $\phi$-scan result obtained from the same film, whose XRD pattern is shown in Fig. 1(a), is displayed in Fig. 2. Although the FWHM values of the peaks in the $\phi$ scan are wider than those normally reported for epitaxial oxide films,[12] the appearance of only four peaks suggests that Eu:$Y_2O_3$ films grow epitaxial on $LaAlO_3$ substrates if an optimized set of parameters during the deposition is used. Further, the separation of each peak from one another by 90° suggests a cube-on-cube epitaxial relationship between the film and the substrate. The wider FWHM values of peaks in the $\phi$ scan may be due to a possible disorder near the interface. However, this aspect needs to be studied in further detail.

The epitaxial growth of Eu:$Y_2O_3$ films on $LaAlO_3$ substrates is interesting since the lattice mismatch between the film and the substrate is very large. Using the lattice constants of $LaAlO_3$(3.78 Å) and Eu:$Y_2O_3$(10.60 Å), the lattice mismatch between the film and the substrate, given by $(a_s - a_f)/a_s$ (where $a_s$ and $a_f$ are the lattice constants of $LaAlO_3$ substrate and Eu:$Y_2O_3$ film), is found to be ~60%. The realization of epitaxial growth of Eu:$Y_2O_3$ films on such a widely mismatched substrate could be understood by considering the lattice structure and atom positions in each system. Lanthanum aluminate has a perovskitelike crystalline structure at high temperatures. On cooling it transforms at about 500 °C to a rhombohedral phase with the lattice constants $a = 3.79$ Å and $\alpha = 90.5°$.[13] Neglecting the small deviation in angle from 90° in a perfect cubic structure, the structure of $LaAlO_3$ can be considered as pseudocubic, resembling the structure of a standard perovskite. In this structure, the La-O and Al-O layers are sequentially stacked over one other.

XRD measurements have shown that for small Eu-doping levels used here, the structure of Eu-doped $Y_2O_3$ is identical with the structure of pure $Y_2O_3$ with a lattice parameter of 10.604 Å. Thus it is sufficient to consider the atom positions in $Y_2O_3$ compound to study the epitaxial relationship between the Eu:$Y_2O_3$ films and $LaAlO_3$ substrates. The structure of $Y_2O_3$ is closely related to a cubic fluorite structure[14,15] with alternating Y and O layer.[9,10] The atom positions in the Y layer are shown schematically in Fig. 3(a). Shown also in this figure is the atom positions in an La-O layer in $LaAlO_3$ [Fig. 3(b)]. A comparison of atom positions in these layers of film and substrate material suggests that a rotation of the film-plane (Y layer or O layer) by 45° can result into a situation which is very favorable for epitaxial growth of $Y_2O_3$ films on $LaAlO_3$ substrates. Under this arrangement, represented schematically in Fig. 3(c), the lattice mismatch is given by $[\{(2a_s)^2+(2a_s)^2\}^{1/2}-a_f]/[(2a_s)^2+(2a_s)^2]^{1/2}$. In this figure, a Y-terminated layer from a unit cell of $Y_2O_3$ is diagonally superimposed on the 4×4 matrix of $LaAlO_3$ unit cell terminated with a La-O layer. Substituting the values of $a_s$ and $a_f$ in this expression, we find the lattice mismatch between the film and the substrate is only ~1%. This kind of small difference in lattice parameters between the film and substrate can certainly promote epitaxial film growth and explain our results.

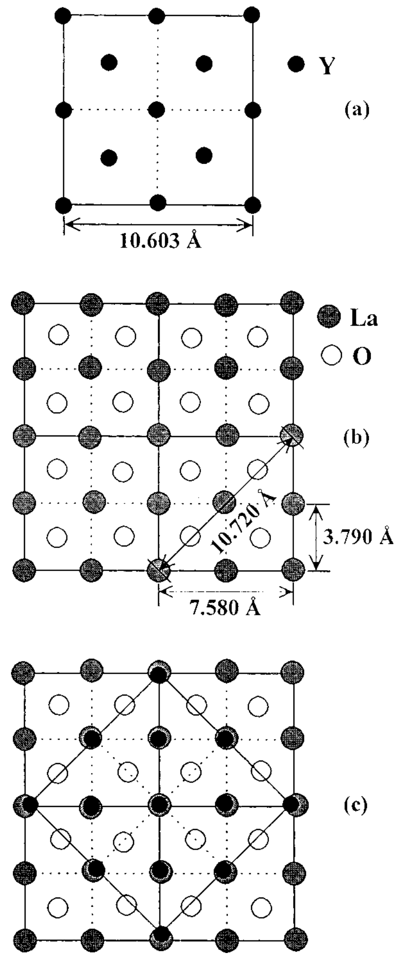

FIG. 3. Schematic representations of atom positions along (a) a Y layer in $Y_2O_3$ lattice, (b) a La-O layer in 4×4 lattices of $LaAlO_3$ compound, and (c) superimposition of Y layer on La-O layer upon 45° rotation.

The cathodoluminescence (CL) brightness of Eu:$Y_2O_3$ films was measured using an Oriel Multispec with a CCD detector. The CL was excited by primary electron beam with different energies (1–5 keV) and current density of 3.2 $\mu$A/cm$^2$. Figure 4 shows a typical CL spectrum recorded at 2 keV and 3.2 $\mu$A/cm$^2$ from a 3.2-$\mu$m-thick Eu:$Y_2O_3$ film on $LaAlO_3$ substrate grown at 750 °C. There are three distinct regimes of transitions marked by I, II, and III respectively. The wavelengths of transmitted light in these regimes are

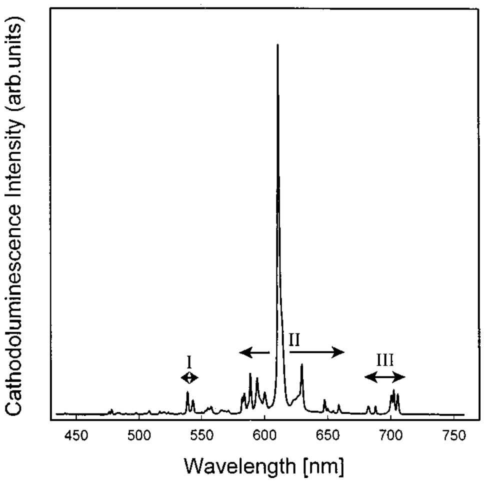

FIG. 4. CL spectrum obtained from a 3.2-$\mu$m-thick Eu:$Y_2O_3$ film.

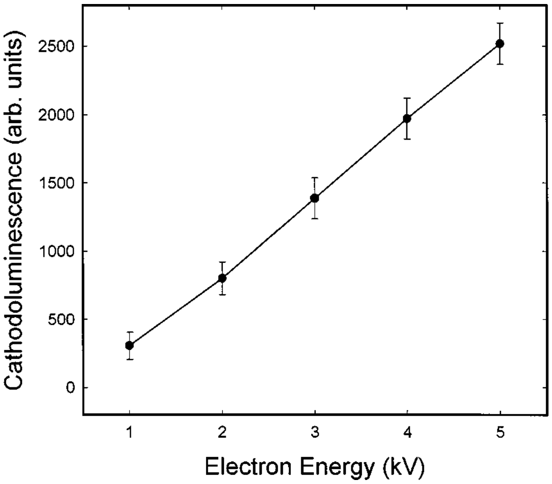

FIG. 5. Variation of CL intensity as a function of electron energy in a 3.2-$\mu$m-thick Eu:$Y_2O_3$ film.

listed in Table I. The origin of these transitions can be understood by considering the energy level diagrams for an $Eu^{3+}$ ion in a $Y_2O_3$ lattice.[16] The origin of transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depend upon the site where $Eu^{3+}$ is located in the $Y_2O_3$ lattice and the type of these transitions is determined by selection rules. An $Eu^{3+}$ ion in $Y_2O_3$ can occupy two types of symmetry sites: a low symmetry site of $C_2$ and a high symmetry site of $S_6$.[17,18] In a unit cell, there are 24 $C_2$ sites and eight $S_6$ sites. All things being equal, it is likely that $Eu^{3+}$ ions will occupy these two types of sites with approximately equal probability.[11] Thus there are about three times as many ions at $C_2$ site than at $S_6$ site.

According to the selection rules, the allowed electric dipole transitions in system with no inversion of symmetry (which is the case with Eu:$Y_2O_3$ system) are those for which $\Delta J \leqslant 6$. The transitions arising from magnetic dipole transitions are those for which $\Delta J = 0, \pm 1$ but the transition $0 \leftrightarrow 0$ is forbidden. Based on these selection rules the nature of transitions taking place in regime I, II, and III are listed in Table I. The splitting pattern depends on the strength of the crystal field and the local symmetry environment. Due to strong shielding of $4f$ electrons of an $Eu^{3+}$ ion from the crystal environment by the $5s$ and $5p$ orbitals, the crystal field splittings can be neglected.[16–18] The local symmetry environment, however, may be different for polycrystalline and epitaxial Eu:$Y_2O_3$ films due to a difference in orientation, defect density and grain boundary density. The change in local environment will result in variation in relative intensities of emission peaks listed in Table I. It is clear from Fig. 4 that there is a only one intense emmision. All other emissions are very small. The most intense emission occurs at 611 nm and is due to $^5D_0 - {}^7F_2$ transition. The occurrence of such an intense emision with respect to other emissions suggests that the coupling of $Eu^{3+}$ ions to the $Y_2O_3$ host lattice is rather weak[19] in Eu:$Y_2O_3$ films. Similar results have been obtained earlier for Eu:$Y_2O_3$ polycrystalline films[16] and Eu:$Y_2O_3$ single crystals[20] which may suggest that polycrystalline and epitaxial or single crystal Eu:$Y_2O_3$ material may qualitatively show similar luminescent properties. But epitaxial Eu:$Y_2O_3$ films will show significant difference in terms of sharpness and relative intensities of emission peaks. An effort to quantify this speculatiuon is underway in our laboratory.

TABLE I.

| Regime | Transition<br>From | <br>To | $\Delta J$ | Nature of Transition |
|---|---|---|---|---|
| I<br>533–545 nm | $^5D_1$ | $^7F_1$ | 0 | Magnetic dipole |
| II<br>579–617 nm | $^5D_0$ | $^7F_0$ | $0 \leftrightarrow 0$ | Electric dipole |
| | | $^7F_1$ | 1 | Magnetic dipole |
| | | $^7F_2$ | 2 | Electric dipole |
| | | $^7F_3$ | 3 | Electric dipole |
| III<br>680–710 nm | $^5D_0$ | $^7F_4$ | 4 | Electric dipole |

Shown in Fig. 5 is the variation in CL intensity as a function of applied electron energy for a 3.2-$\mu$m-thick Eu:$Y_2O_3$ film. The CL data were collected at 10 $\mu A/cm^2$ and voltages from 1 to 5 keV. As can be seen from this figure, the CL intensity of the film increases with the increase in electron energy applied. The increase in CL brightness with an increase in electron energy is attributed to deeper penetration of electron into the film body which is governed by[20] $R_e = 0.0276\,\text{Å}E_b^{1.67}/\rho Z^{0.889}$, where $R_e$ is penetration depth in $\mu$m, $A$,$Z$, and $\rho$ are, respectively, average atomic weight, atomic number, and density of $Y_2O_3$ and $E_b$ is the energy of the electron in keV. The deeper penetration of electrons in Eu:$Y_2O_3$ film body results into an increase in electron-solid interaction volume in which excitation of $Eu^{3+}$ ions, responsible for light emission, takes place. Therefore, an increase in interaction volume (which effectively determines the generation of light inside the film body) with an increase in electron energy brings about an increase in CL brightness of Eu:$Y_2O_3$ film.

In summary, we have synthesized highly crystalline epitaxial Eu:$Y_2O_3$ films on singly crystal (100) $LaAlO_3$ substrates and studied their cathodoluminescent properties. In view of very high mismatch in lattice constants of the film and substrate materials, the epitaxial growth of Eu:$Y_2O_3$

films on $LaAlO_3$ substrates is interesting and is being reported for the first time. The growth of epitaxial $Eu:Y_2O_3$ films is important not only from application point of view but also from basic point of view as growing single crystal of $Eu:Y_2O_3$ material, preferred for fundamental studies, is always more difficult.

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[1] S. J. Duclos, C. D. Greskovich, and C. R. O'Clair, Mater. Res. Soc. Symp. Proc. **348**, 503 (1994).

[2] T. Hase, T. Kano, E. Nakazawa, and H. Yamamoto, in *Advances in Electronics and Electron Physics*, edited by P. W. Hawkes (Academic, New York, 1990), Vol. 79, p. 135.

[3] S. L. Jones, D. Kumar, Rajiv K. Singh, and P. H. Holloway, Appl. Phys. Lett. **71**, 404 (1997).

[4] K. G. Cho, D. Kumar, D. G. Lee, S. L. Jones, P. H. Holloway, and Rajiv K. Singh, Appl. Phys. Lett. **71**, 3335 (1997).

[5] K. G. Cho, D. Kumar, D. G. Lee, S. L. Jones, P. H. Holloway, and Rajiv K. Singh, J. Electrochem. Soc. **145**, 3456 (1998).

[6] K. G. Cho, D. Kumar, P. H. Holloway, and Rajiv K. Singh, Appl. Phys. Lett. **73**, 3058 (1998).

[7] T. A. Trottier, H. C. Swart, S. L. Jones, and P. H. Holloway, J. Soc. Inf. Disp. **4**, 354 (1996).

[8] J. D. Kingsley and G. W. Ludwig, J. Electrochem. Soc. **117**, 353 (1970).

[9] *Flat Panel Display Materials II*, edited by M. K. Hatalis, J. Kanicki, C. J. Summers, and F. Funada, Mater. Res. Soc. Symp. Proc. No. 424 (MRS, Pittsburgh, 1996).

[10] S. L. Jones, Ph.D. Thesis, University of Florida, 1997.

[11] Rajiv K. Singh and D. Kumar, Mater. Sci. Eng. **22**, 113 (1998).

[12] *Epitaxial Oxide Thin Films III* edited by D. G. Schlom, C. B. Eom, M. E. Hawley, C. M. Foster, and J. S. Speck, Mater. Res. Soc. Symp. Proc. No. 474 (MRS, Pittsburgh, 1997).

[13] S. Geller and V. B. Bala, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **9**, 1019 (1956).

[14] F. Jollet, C. Noguera, N. Thromat, M. Gautier, and J. P. Duraud, Phys. Rev. B **42**, 7587 (1990).

[15] K. C. Mishra, J. K. Berkowitz, K. H. Johnson, and P. C. Schmidt, Phys. Rev. B **45**, 10 902 (1992).

[16] G. A. West and K. W. Beeson, J. Mater. Res. **5**, 1573 (1990).

[17] N. C. Chang and J. B. Gruber, J. Chem. Phys. **41**, 3227 (1964).

[18] L. Pauling, Z. Krist. **75**, 128 (1930).

[19] G. Blasse and B. C. Grabmaier, *Luminescence Materials* (Springer, Berlin, 1994).

[20] B. G. Yacobi and D. B. Holt, in *Cathodoluminescence Microscopy of Inorganic Solids* (Plenum, New York, 1990), p. 58.