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# Photoluminescence characteristics of Li-doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin-film phosphors on sapphire substrates

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## Abstract

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  luminescent thin films have been grown on sapphire substrates using a pulsed laser deposition technique. The thin-film phosphors were deposited at a substrate temperature of 600 °C under the oxygen pressures of 100, 200, and 300 mTorr. The films grown under different deposition conditions have been characterized using microstructural and luminescence measurements. The crystallinity and photoluminescence (PL) of the films are highly dependent on the oxygen pressure. The PL brightness data obtained from  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films grown under optimized conditions have indicated that sapphire is a promising substrate for the growth of high-quality  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin-film red phosphor. In particular, the incorporation of  $\text{Li}^+$  ions into  $\text{Y}_2\text{O}_3$  lattice could induce a remarkable increase of PL. The highest emission intensity was observed with LiF-doped  $\text{Y}_{1.84}\text{Li}_{0.08}\text{Eu}_{0.08}\text{O}_3$  ( $\text{Y}_2\text{O}_3\text{LiEu}$ ), whose brightness was increased by a factor of 2.7 in comparison with that of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films. This phosphor may hold promise for application in flat-panel displays.

## 1. Introduction

Significant research interest in the growth and characterization of  $\text{Y}_2\text{O}_3$  films has been shown over the last few years because of the promise for applications in metal–insulator–semiconductor (MIS) diodes, transistor gates, metal–oxide–semiconductor (MOS) capacitors, and dynamic random access memory (DRAM) gate dielectrics because of its high band gap

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(5.8 eV) and large dielectric constant (14–18). Because of its high melting point of 2410 °C,  $\text{Y}_2\text{O}_3$  has also been widely used for high-temperature corrosion protection. However, another recent and important application of  $\text{Y}_2\text{O}_3$  has been in electroluminescent displays (ELDs) as a dielectric layer and in fluorescent lamps and cathodoluminescent (CL) displays as the host material for europium used in order to get emission of red light.

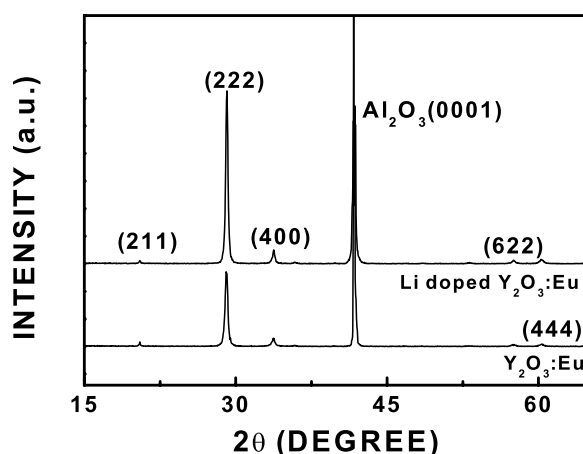
The traditional cathode ray tube (CRT) red phosphor is an Eu-doped oxysulfide ( $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ ) which has an efficiency of 13%, while the reported efficiency value for the oxide is 6.5–8% [1]. The sulfides, however, are known to degrade rapidly under the high current densities needed for field emission display (FED) technology [2, 3]. Therefore, oxide-based phosphors are likely to emerge as the material of choice for the FED red phosphor.  $\text{Y}_2\text{O}_3:\text{Eu}$  is currently one of the most promising oxide-based red phosphor systems. Due to a  $^5\text{D}_0\text{--}^7\text{F}_2$  transition within europium,  $\text{Y}_2\text{O}_3:\text{Eu}$  shows luminescence properties and emits red light with a 612 nm wavelength [4]. Yttrium oxide films have been grown mainly using electron-beam evaporation [5], radio-frequency sputtering [6–8], and sol–gel techniques [9]. The pulsed laser deposition (PLD) technique, which provides a unique process for stoichiometric evaporation of target materials and control of film morphology [10, 11], has been used recently for the growth of yttrium oxide films [12, 13]. It is generally accepted that thin-film phosphors have some advantages over bulk-type powder phosphors such as better thermal stability, reduced outgassing, better adhesion, and improved uniformity over the substrate surface. However, there still remains a fundamental problem in the application of thin-film phosphors which is their low brightness in comparison to that of bulk-type powder phosphors. In thin-film phosphors, brightness may be associated with several factors such as:

- (i) the interaction between film material and substrate,
- (ii) the film processing conditions, and
- (iii) the composition of the film materials.

Pulsed laser-deposited  $\text{Y}_2\text{O}_3:\text{Eu}$  thin films have been synthesized by changing substrates (silicon (100), sapphire (0001), and diamond-coated silicon (100)) and by changing processing conditions (substrate temperature, oxygen pressure, and post-annealing). It is well known that even in very small quantities, the  $\text{Li}^+$  co-activators frequently play an important role in the enhancement of the luminescent efficiency of phosphors [14, 15]. Indeed, we have recently investigated the effect of Li substitution on  $\text{SrTiO}_3:\text{Pr}^{3+}$  and  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ . This study showed that the addition of a Li component affects positively the morphology of particles as well as the luminescent efficiency of phosphors. In this paper, we report our work on PLD, structural characterization, and measurement of luminescence properties of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}$  thin films by changing deposition conditions, especially the oxygen pressure.

## 2. Experiments

$\text{Y}_{2-x}\text{Eu}_x\text{O}_3$  ( $x = 0.08$ ) and  $\text{Y}_{2-x-y}\text{Eu}_x\text{Li}_y\text{O}_3$  ( $x = 0.08$ ,  $y = 0.08$ ) powder samples were prepared from stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , and LiF. An excess (~300%) of LiF was added to compensate for the loss of the volatile lithium component. For the target, a powder mixture was pelletized into discs (diameter = 12 mm, thickness = 2 mm), and sintered at 1350 °C for 20 h. The films were grown by the PLD method using an ArF excimer laser with a wavelength of 193 nm. The beam of the excimer laser was focused on the surface of the target with a spot size of 1 mm × 2.5 mm. The distance between the target and substrate was kept at 35 mm. The laser fluence was approximately 3.5 J cm<sup>-2</sup> and the repetition rate was 5 Hz.  $\text{Y}_2\text{O}_3:\text{Eu}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}$  thin-film phosphors were deposited on  $\text{Al}_2\text{O}_3$  (0001) substrates at a substrate temperature of 600 °C under the oxygen pressures of 100, 200, and 300 mTorr.



**Figure 1.** XRD patterns of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate at the substrate temperature  $600^\circ\text{C}$  with oxygen pressures of 200 mTorr.

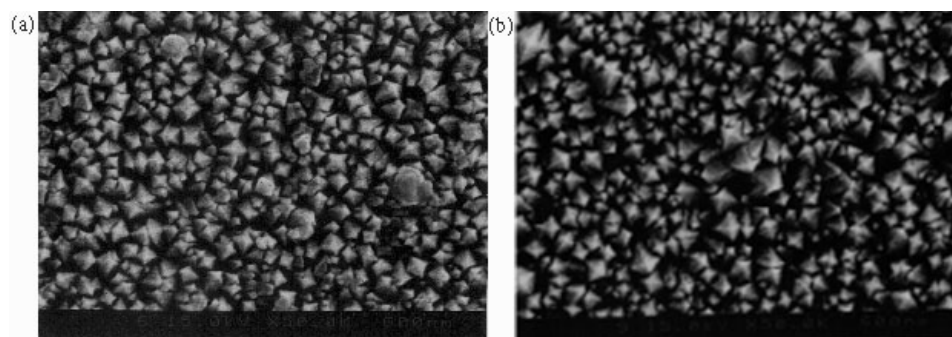
The structural characteristics of the films were analysed by using x-ray diffraction (XRD). The thickness and surface morphology of the films were measured by a scanning electron microscope (SEM) and an atomic force microscope (AFM). The photoluminescence (PL) spectra were measured at room temperature using a luminescence spectrometer broadband incoherent ultraviolet light excitation source with a dominant wavelength of 254 nm.

### 3. Results and discussion

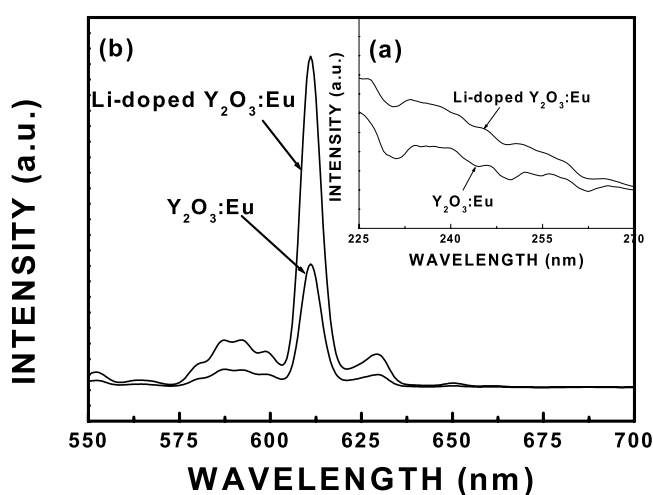
The PL intensities of the  $\text{Y}_2\text{O}_3:\text{Eu}$  films are highly dependent on the crystallinity and surface morphology of the films. The deposition conditions including oxygen pressure and substrate temperature are important factors for determining the crystallinity and surface morphology.

Figure 1 shows the XRD patterns of the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate at the substrate temperature  $600^\circ\text{C}$  with the oxygen pressure of 200 mTorr. The diffraction data suggest that the (222) surface is the preferred orientation for films grown on  $\text{Al}_2\text{O}_3(0001)$ . These diffraction patterns illustrate that the films are uniaxially textured in both cases and the full width at half-maximum (FWHM) of the diffraction peaks is narrower ( $\sim 30\%$ ) for the film grown with Li doping than for the film grown without Li doping. It is evident from these data that the Li contents incorporated into the  $\text{Y}_2\text{O}_3$  lattice serve as a self-promoter for better crystallization.

The surface morphology and roughness of the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films had a strong effect on the PL response of the films. Figure 2 shows the surface morphology of the two thin films. It is clear from SEM images that the grains of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}$  thin film are larger as well as well-defined ones, with octahedral shape, as compared with those of  $\text{Y}_2\text{O}_3:\text{Eu}$  thin film. The measured film thicknesses have the same values:  $\sim 1.3 \mu\text{m}$  on both films. The average grain sizes were 100 and 170 nm for the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films, respectively. The root mean square (rms) roughness of these films, measured by the AFM, was found to increase from 8.5 to 12.8 nm by doping with Li. The increase in rms value with Li doping is attributed to the enhanced grain size. Due to the improved grain size, the density of the grain boundaries in the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films is smaller than that in the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films. Furthermore, since grain boundaries may be sources of dissipation of light generated inside the film, reducing



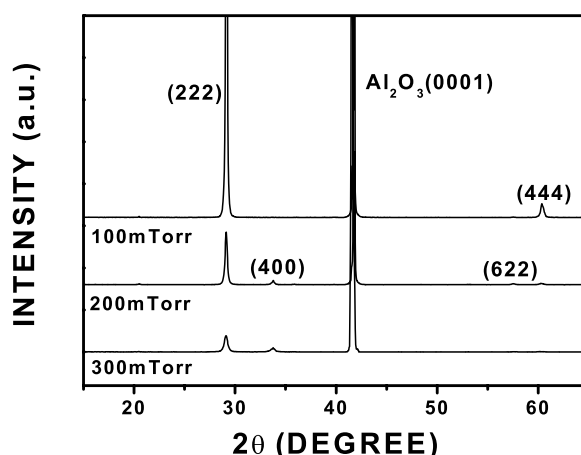
**Figure 2.** Scanning electron micrographs of (a) Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin film and (b)  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin film.



**Figure 3.** A comparison of the room temperature (a) PLE and (b) PL spectra of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin films.

the PL brightness, the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films with fewer grain boundaries exhibit superior PL properties as mentioned below. As regards crystallography, the octahedral grains with (111) planes perpendicular to the  $\text{Al}_2\text{O}_3(0001)$  planes pack more loosely in comparison with (100) planes, which results in the highly enhanced surface roughness for Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin film. Also, it should be pointed out that LiF with low melting temperature ( $845^\circ\text{C}$ ) plays an important role in liquid phase sintering. Thanks to the liquid phase sintering, larger grains are formed, and we obtain the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin film with highly enhanced surface roughness.

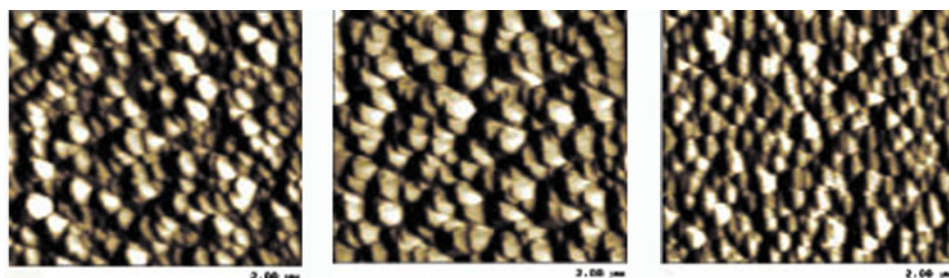
Figures 3(a) and (b) show the comparison of the room temperature photoluminescence excitation (PLE) and PL spectra of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films grown under identical conditions, respectively. The PL spectra were dominated by the red emission peak at 612 nm. Due to the effect of shielding of 4f electrons by 5s and 5p electrons in outer shells in the europium ion, narrow emission peaks are expected, consistent with the sharp peak in figure 3(b). As shown in figure 3(b), the brightness of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films was increased by a factor of 2.7 in comparison with that of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films. The maximum brightness of



**Figure 4.** XRD patterns of the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate at substrate temperature  $600^\circ\text{C}$  with different oxygen pressures of 100, 200, and 300 mTorr.

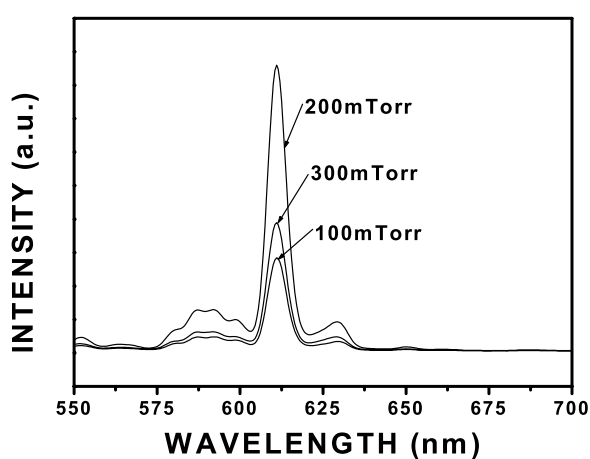
the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films on the  $\text{Al}_2\text{O}_3(0001)$  substrates at the substrate temperature of  $600^\circ\text{C}$  and the oxygen pressure of 200 mTorr was  $\sim 63\%$  of that of the powder materials, as contrasted to  $\sim 23\%$  for the undoped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films grown under identical conditions. The improvement in PL performance with the Li doping may result from not only improved crystallinity leading to higher oscillating strengths for the optical transitions [14], but also reduced internal reflections caused by rougher surfaces. For the enhanced PL intensity, it could be suggested that the incorporation of  $\text{Li}^+$  ions creates oxygen vacancies, which might act as a sensitizer for the effective energy transfer due to the strong mixing of charge transfer states. Occupation of  $\text{Y}^{3+}$  sites by  $\text{Li}^+$  ions would naturally give rise to a substantial number of vacant sites in the oxygen-ion array [15, 16]. Recently, Yeh *et al* [17] reported that the mixing of LiF with  $\text{Gd}_2\text{O}_3:\text{Eu}$  can greatly increase its PL intensity. They suggested that LiF simply acts as a lubricant for the complete incorporation of  $\text{Eu}_2\text{O}_3$  into  $\text{Gd}_2\text{O}_3$  during the sintering process. However, we suggest that the co-doping of  $\text{Li}^+$  ions into the phosphor thin film should be considered in addition to the previous flux effect of LiF on the crystallinity of  $\text{Y}_2\text{O}_3$ . The crystal symmetry of  $\text{Y}_2\text{O}_3$  belongs to the cubic system with space group  $Ia\bar{3}$  whose structure is similar to that of  $\text{Gd}_2\text{O}_3$ . This structure offers two crystallographically different sites to the impurities (i.e.,  $\text{Li}^+$  and  $\text{Eu}^{3+}$  ions), one with  $C_2$  and the other with  $S_6$  symmetry. If we compare the effective ionic radii of constituting ions for Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin film (76.0, 94.7, and 90.0 pm for the  $\text{Li}^+$ ,  $\text{Eu}^{3+}$ , and  $\text{Y}^{3+}$  ions, respectively),  $\text{Li}^+$  and  $\text{Eu}^{3+}$  ions are not assumed to occupy these different sites in a statistical way. It is, instead, expected that the smallest  $\text{Li}^+$  ions will be introduced into  $C_2$ -sites with higher population in the lattice. A more reduced symmetry of these sites would then result in the enhanced luminescent properties. This interpretation is in agreement with the fact that Li co-activator in  $\text{ZnS}:\text{Tm}$  lowers the symmetry around  $\text{Tm}^{3+}$  and alters the energy levels. The measured CIE chromaticities of the two films were same:  $x = 0.63$  and  $y = 0.35$ , which are in good agreement with those of commercial  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor powder ( $x = 0.64$  and  $y = 0.35$ ) obtained from Nichia company in Japan.

Figures 4(a)–(c) show the XRD patterns of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films grown at substrate temperature  $600^\circ\text{C}$  with different oxygen pressures of 100, 200, and 300 mTorr, respectively. All other growth parameters were kept identical during these depositions and the film



**Figure 5.** AFM images of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate at the substrate temperature  $600^\circ\text{C}$  with the different oxygen pressures of (a) 100, (b) 200, and (c) 300 mTorr.

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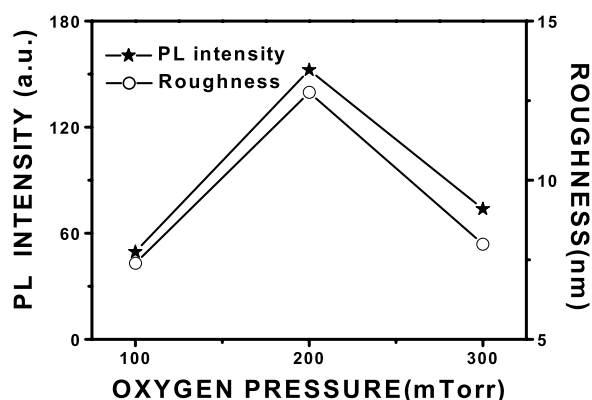


**Figure 6.** PL spectra of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate at the substrate temperature  $600^\circ\text{C}$  with the different oxygen pressures of 100, 200, and 300 mTorr.

orientation was preferentially (111) which changed to a mixture of (111) and (100) orientations as the pressure was increased above 100 mTorr. The change in film orientation is believed to be associated with an increase in the number of density of outgrowths on the film surface with increase in oxygen pressure [10]. As the oxygen pressure decreases, the crystallinity of the films improves. The FWHMs of the (222) peaks are narrower ( $\sim 40\%$ ) for the film grown at 100 mTorr than for the film grown at 300 mTorr, indicating the better crystallinity of the former than of the latter.

Figures 5(a)–(c) show the AFM images of the films grown at different oxygen pressures. The grain size,  $\sim 170$  nm, of the film grown at 200 mTorr is larger than those,  $\sim 140$  and  $\sim 110$  nm, of the other films grown at oxygen pressures of 100 and 300 mTorr. The rms roughnesses of the films grown at oxygen pressures of 100, 200, and 300 mTorr are 7.5, 12.8, and 7.7 nm, respectively. The films grown at 200 mTorr also have maximum rms roughness values.

Shown in figure 6 are the plots of PL spectra of the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films with different oxygen pressures. Note that the PL intensity for Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films has a maximum value at the oxygen pressure of 200 mTorr. According to the results in figures 4 and 5, although



**Figure 7.** PL intensity and rms roughness of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films as a function of oxygen pressure. The substrate temperature was 600 °C for all depositions.

the crystallinity of the Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films has been improved, the PL intensity has been decreased due to the deficiency in Li contents arising as the oxygen pressure decreases. Figure 7 shows the PL intensity of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films as a function of oxygen growth pressure. Shown also in the figure is the corresponding rms roughness of these films. The PL intensity and rms roughness have similar behaviours as a function of oxygen pressure. The increase in oxygen pressure from 100 to 200 mTorr resulted in an increase in surface roughness which in turn increased the PL intensity. The improvement in PL performance is probably brought about by reduced internal reflections caused by rougher surfaces. As the oxygen pressure increases further to 300 mTorr, the rms roughness and PL intensity decrease together.

#### 4. Conclusions

In summary, high-quality  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin-film phosphors have been deposited on  $\text{Al}_2\text{O}_3(0001)$  substrate using a PLD technique. The results presented in this paper suggest that  $\text{Al}_2\text{O}_3(0001)$  is one of the most promising substrates for the fabrication of high-quality  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor thin films. The brightness of Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films was increased by a factor of 2.7 in comparison with that of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films. The improvement in PL performance with the Li doping may result from not only improved crystallinity leading to higher oscillating strengths for the optical transitions, but also reduced internal reflections caused by rougher surfaces. For the enhanced PL intensity, it can be suggested that the incorporation of  $\text{Li}^+$  ions creates oxygen vacancies, which might act as a sensitizer for the effective energy transfer due to the strong mixing of charge transfer states. As the oxygen pressure decreases, the crystallinity of the films improves. The PL intensity and rms roughness have similar behaviours as a function of oxygen pressure. The increase in oxygen pressure from 100 to 200 mTorr resulted in an increase in surface roughness which in turn increased the PL intensity. Growth of as-deposited Li-doped  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  thin films with such a high brightness is very encouraging for the application of thin-film phosphors in display technologies.

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