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Photoluminescence of Li-doped Y_2O_3:Eu^{3+} thin film phosphors grown by pulsed laser deposition

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Abstract

Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} 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 pressure of 100, 200 and 300 mTorr. The films grown under different deposition conditions have been characterized using microstructural and luminescent measurements. The crystallinity and photoluminescence (PL) of the films are highly dependent on the oxygen pressure. The PL brightness data obtained from Y_2O_3:Eu^{3+} films grown under optimized conditions have indicated that sapphire is one of the most promising substrate for the growth of high quality Y_2O_3:Eu^{3+} thin film red phosphor. In particular, the incorporation of Li^+ ions into Y_2O_3 lattice could induce a remarkable increase of PL. The highest emission intensity was observed with LiF-doped $Y_{1.84}Li_{0.08}Eu_{0.08}O_3$ (Y_2O_3LiEu), whose brightness was increased by a factor of 2.7 in comparison with that of Y_2O_3:Eu^{3+} films. This phosphor may promise for application to the flat panel displays.

1. Introduction

Recently, oxide thin film phosphors have received considerable attention for use in flat-panel displays due to their good luminescent characteristics, stability in high vacuum, and absence of corrosive gas emission under electron bombardment when compared to currently used sulfide-based phosphors. Among those thin film phosphors, significant research interest in the growth and characterization of Y_2O_3 films has been shown over the last few years because of its high luminescence efficiency and low lattice mismatch with silicon (Si) and sapphire substrates. Recent and important application of Y_2O_3 has been in electroluminescent display (ELD) as a dielectric layer and in fluorescent lamps and cathodoluminescent (CL) displays as the host material for europium in order to get emission of red light.

The traditional cathode ray tube (CRT) red phosphor is an Eu-doped oxysulfide (Y_2O_2S:Eu) which has an efficiency of 13 %, while the reported efficiency value for the oxide is 6.5-8 %.[1] The sulfide, 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 potential choice for the FED red phosphor. Y_2O_3:Eu is currently one of the most promising oxide-based red phosphor systems. Due to a $^5D_0$-$^7F_2$ transition within europium, Y_2O_3:Eu shows luminescence properties and emits red light with a 612 nm wavelength.[4] Yttrium oxide films have been

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grown mainly using e-beam evaporation,[5] radio frequency sputtering,[6-8] or 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 in point of better thermal stability, reduced outgassing, better adhesion, and improved uniformity over 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. Pulsed laser deposited Y_2O_3: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 Li^+ co-activators frequently play and important role in the enhancement of the luminescent efficiency of phosphors.[14,15] The addition of Li component positively affects the morphology of particles as well as the luminescent efficiency of phosphors. In this letter, we report our work on pulsed laser deposition, structural characterization, and measurement of luminescence properties of Li-doped Y_2O_3:Eu thin films by changing deposition condition, especially oxygen growth pressure.

2. Experiments

$Y_{2-x}Eu_xO_3$ (x=0.08) and $Y_{2-x-y}Eu_xLi_yO_3$ (x=0.08, y=0.08) powder samples were prepared from stoichiometric amounts of Y_2O_3, Eu_2O_3, and LiF. An excess (~300%) of LiF was added to compensate for the loss of volatile lithium component. For target, powder mixture was palletized into a disk (ϕ = 12 mm, thickness = 2 mm), and sintered at 1350 °C for 20 h. The films were grown by pulsed laser deposition (PLD) method using an ArF excimer laser with a wavelength of 193 nm. The beam of excimer laser was focused on the surface of target with a spot size of 1 mm 2.5 mm. The distance between target and substrate was kept at 35 mm. The laser fluence was approximately 3.5 J/cm^2 and repetition rate was 5 Hz. Y_2O_3:Eu and Li-doped Y_2O_3:Eu thin film phosphors were deposited on Al_2O_3 (0001) substrates at a substrate temperature of 600C under the oxygen pressure of 100, 200 and 300 mTorr. The structural characteristics and the surface morphology of the films were analyzed by using X-ray diffraction (XRD) and atomic force microscope (AFM), respectively. The 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 Discussions

The PL intensity of the Y_2O_3: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 to determine the crystallinity and surface morphology of the films.

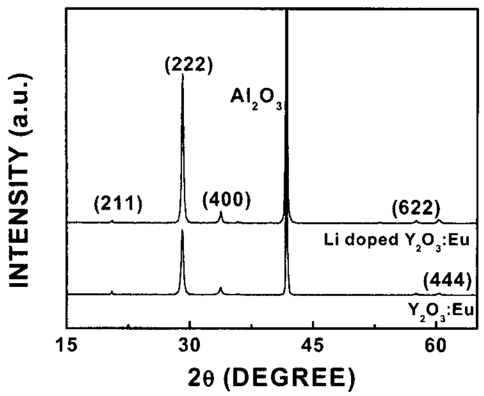

Figure 1. XRD patterns of Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} films deposited on Al_2O_3(0001) substrate at the substrate temperature 600 °C with the oxygen pressures of 200 mTorr.

Figure 1 shows the XRD patterns of the Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} films deposited on Al_2O_3 (0001) substrate at the substrate temperature 600 °C with the oxygen pressure of 200 mTorr. The diffraction data suggest that the (222) surface is preferred orientation for films grown on Al_2O_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 (~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 Y_2O_3 lattice serve as a self- promoter for the better crystallization. In crystallographic aspect, the octahedral grains with (111) planes perpendicular to the Al_2O_3 (0001) planes more loosely pack in comparison with (100) planes, which results in the highly enhanced surface roughness for Li-doped Y_2O_3:Eu^{3+} thin film. Also, it should be pointed out that LiF with low melting temperature (845 °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 Y_2O_3:Eu^{3+} thin film with highly enhanced (222) texture on XRD patterns.

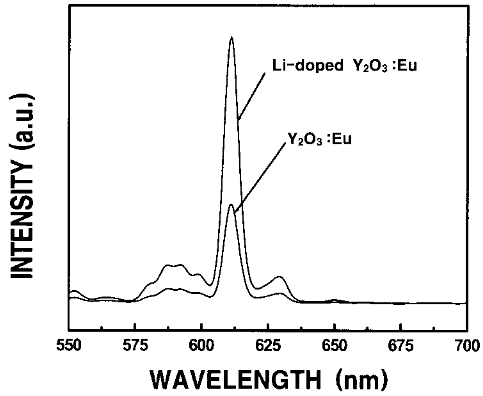

Figure 2. A comparison of the room temperature PL spectra of Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} thin films.

Figure 2 shows the comparison of the room temperature PL spectra of Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} films grown under identical conditions, respectively. The PL spectra were dominated by the red emission peak at 612 nm. Due to the shielding effect of 4*f* electrons by 5*s* and 5*p* electrons in outer shells in the europium ion, narrow emission peaks are expected, consistent with the sharp peak in Fig. 2. The brightness of Li-doped Y_2O_3:Eu^{3+} films was increased by a factor of 2.7 in comparison with that of Y_2O_3:Eu^{3+} films. The improvement in PL performance with the Li-doping may result from improved crystallinity leading to higher oscillating strengths for the optical transitions.[14] For the enhanced PL intensity, it can be suggested that the incorporation of Li^+ ions creates the oxygen vacancies, which might act as a sensitizer for the effective energy transfer due to the strong mixing of charge transfer states. Recently, Yeh et al. reported that the mixing of LiF to Gd_2O_3:Eu can greatly increase its PL intensity.[15] They suggested that LiF simply acts as a lubricant for the complete incorporation of Eu_2O_3 into Gd_2O_3 during the sintering process. The measured CIE chromaticities of both films were same value, x=0.63 and y=0.35 which are in a good agreement with those of commercial Y_2O_3:Eu^{3+} phosphor powder (x=0.64 and y=0.35) obtained from Nichia company in Japan.

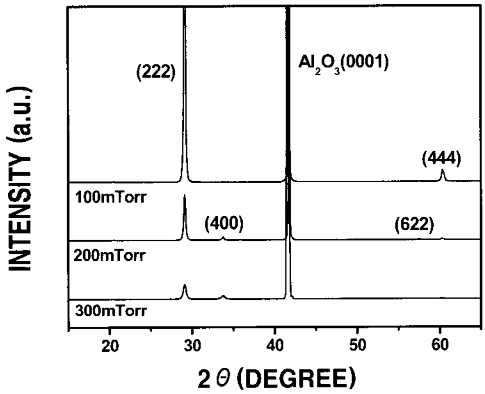

Figure 3. XRD-patterns of the Li-doped Y_2O_3:Eu^{3+} films deposited on Al_2O_3 (0001) substrate at substrate temperature 600 °C with different oxygen pressures of 100, 200 and 300 mTorr.

Fig. 3 (a)-(c) exhibits the XRD patterns of Li-doped Y_2O_3:Eu^{3+} films grown at substrate temperature 600 °C with different oxygen pressures 100, 200 and 300 mTorr, respectively. All other growth parameters were kept identical during these depositions and the film 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 improved. The FWHM of the (222) peaks are narrower (~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 later.

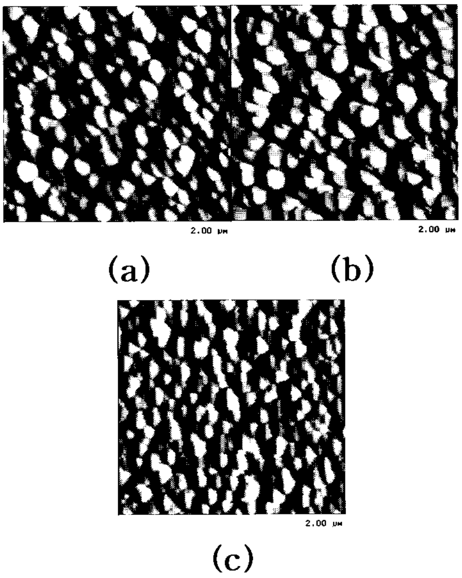

Figure 4. AFM images of Li-doped Y_2O_3:Eu^{3+} films deposited on Al_2O_3 (0001) substrate at the substrate temperature 600 °C with the different oxygen pressures of (a)100, (b)200 and (c)300 mTorr.

Figure 4 (a) to (c) shows the AFM images of the films grown at different oxygen pressures. The grain size, ~170 nm, of the film grown at 200 mTorr is larger than those, ~140 and ~110 nm, of the other films grown at oxygen pressures, 100 and 300 mTorr. The root mean square (rms) roughnesses of the films grown at oxygen pressure 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 value.

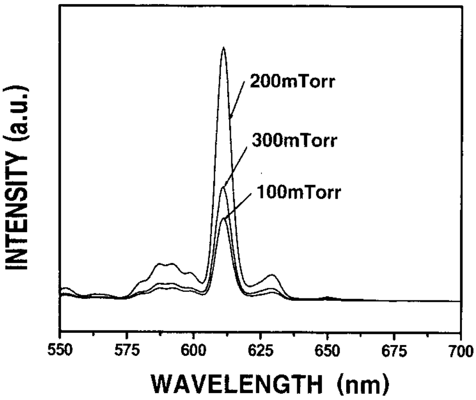

Figure 5. Photoluminescence spectra of Li-doped Y_2O_3:Eu^{3+} films deposited on Al_2O_3 (0001) substrate at the substrate temperature 600 °C with the different oxygen pressures of 100, 200 and 300 mTorr.

Shown in Fig. 5 are the plots of PL spectra of the Li-doped Y_2O_3:Eu^{3+} films with different oxygen pressures. Note that the PL intensity for Li-doped Y_2O_3:Eu^{3+} films has a maximum value at the oxygen pressure of 200 mTorr. According to the results of the Fig. 3 and 5, although the crystallinity of the Li-doped Y_2O_3:Eu^{3+} films has been improved as the oxygen pressure decreases, the PL intensity has been decreased due to the difficency of Li-contents. Under the low oxygen growth pressure, there could be serious loss of volatile Li-contents. Otherwise, according to the results of the Fig. 4 and 5, the PL intensity and rms roughness have similar behavior 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 Y_2O_3:Eu^{3+} and Li-doped Y_2O_3:Eu^{3+} thin film phosphors have been deposited on Al_2O_3 (0001) substrate using a pulsed laser deposition technique. The results presented in this letter suggest that Al_2O_3 (0001) is one of the most promised substrates for the fabrication of high quality Y_2O_3:Eu^{3+} phosphor thin films. The brightness of Li-doped Y_2O_3:Eu^{3+} films was increased by a factor of 2.7 in comparison with that of Y_2O_3: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 Li^+ ions 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 improved. The PL intensity and rms roughness have similar behavior 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 Y_2O_3: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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