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Luminescence of pulsed laser deposited $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors on quartz glass substrates

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Thin film phosphors of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ were deposited on quartz glass plates by pulsed laser deposition and compared with typically used thin film phosphors composed of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ in terms of cathodoluminescence (CL) and photoluminescence (PL). Both the CL and PL of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphor were superior to those of corresponding data on currently widely used $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ red thin film phosphor. In particular, the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphor showed a much better cathodoluminescence at low excitation energy (less than 1 keV) than a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film of the same thickness, indicating that the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphor is a much better candidate for use in field emission displays. © 2002 American Institute of Physics.

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I. INTRODUCTION

Considerable efforts have recently been made to produce thin film phosphors comprised of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ by pulsed laser deposition (PLD) techniques.¹⁻⁷ As a result, significant advancements have been made relative to the luminance and structural stability of thin film phosphors. It should, however, be noted that further enhancement in luminance will be needed to meet the practical requirements for the field emission display applications. There is little doubt that a thin film phosphor is not comparable to the phosphors in a powdered form as far as the luminance is concerned even if the thin film phosphor has advantages over powders in its superior adhesion to the solid substrate surface and reduced outgassing. The lower luminance of thin film phosphors can be attributed to lateral light propagation due to internal reflection, the small interaction volume with the incident beam, and substrate absorption.² It is so difficult to sort out these problems, based on currently available data. An easier way of improving the luminance of thin film phosphors would be to search for thin film phosphors that have an intrinsically high luminous efficiency. In this context, a $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphor represents a good candidate. Very recently $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphor was proposed as a replacement for the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor. Both Seo *et al.*⁸ and Park *et al.*⁹ reported that a $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphor exhibits a much stronger cathodoluminescence (CL) response under low excitation energy (<500 eV) compared with the commercially available $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor, even though their investigation

originally focused on the effect of codopants (Li and Al) on luminance. During those investigations, they also confirmed that even noncodoped $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ exhibited a stronger brightness at low voltage excitation than the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor. Accordingly, the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphor is deserving of consideration in this respect.

II. EXPERIMENT

A $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ target for laser ablation was prepared by means of a conventional ceramic sintering process. 0.12 mol Eu-doped $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ powders were cold pressed without a binder into a pellet and then isostatically cold pressed at 2 ton/cm². The final $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ target of 2.5 cm in diameter was obtained by sintering the pellet at 1300 °C for 24 h in air. $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors were deposited on a quartz glass substrate. It is well known that the quartz glass is superior to the other single crystals or glasses as a substrate owing to its low refractive index and absorption coefficient.⁶ The substrate was maintained at 750 °C using a thermostat. The target was ablated by 248 nm KrF excimer laser with an energy density of 3.23 J/cm² at a 10 Hz repetition rate for 30 min. The target was rotated at a speed of 10 rpm during the laser ablation. The distance between the target and substrate was 3.5 cm. The chamber was initially evacuated to 1.5×10^{-5} Torr, and oxygen gas was then introduced into the chamber to maintain the intended oxygen pressure of 50, 100, and 300 mTorr. For the sake of comparison, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors were also prepared in the same way. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ target was made of a commercially available $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor powder.

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TABLE I. Summary of film characteristics.

Oxygen pressure (mTorr)	Thickness (μm)	rms roughness (\AA)	$I_{C(222)}/I_{M(-402)}^a$	
$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$	0.015	1.47	Complete monoclinic	
	50	1.65	0.3	
	100	1.80	60	
	300	1.09	10	
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	100	1.71	59.7	Complete cubic

^aThe peak area ratios are only for relative comparison of constituent phases between films.

The thickness of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ films was measured using α step and a scanning electron microscopy cross-sectional view image. The crystallinity of thin film phosphors was examined using x-ray diffraction (XRD). **A home-made CL apparatus, consisting of an electron gun (Kimball Physics Inc., model EGPS2X1), vacuum chamber (10^{-6} Torr), and multichannel type charge coupled device area image sensor, was used to measure the CL efficiency in the reflection mode with energies in the range of 400–1000 eV. The photoluminescence (PL) spectra at the UV excitation (254 nm) were monitored using a Perkin Elmer LS50B spectrometer with a xenon flash lamp. The morphology of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film surfaces was analyzed using atomic force microscopy (AFM).**

III. RESULTS AND DISCUSSION

Table I lists the average film thickness, rms roughness, and the major peak area ratio as a function of oxygen pressure. In Fig. 1, AFM images of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film surfaces show rms roughness values. These three parameters play a significant role in determining whether or not the luminescence is active. A simple criterion is that the thicker the film, the rougher the surface and less the monoclinic phase, the higher the luminance. From this criterion one can easily assume that the film deposited at 100 mTorr would exhibit the highest luminance. The conventional oxygen pressure versus thickness (or rms roughness) relation^{1,4} does not hold in our case due to the appearance of a monoclinic phase.

Figure 2 shows the PL spectra excited at 254 nm and the

inset in the upper right corner shows the relative luminance as a function of oxygen pressure. The film deposited at 100 mTorr exhibited the highest luminance. This value is slightly higher than that of a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film of similar thickness. The arrow in the inset indicates the relative PL value of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film. The spectral shape as well as changes in luminance with oxygen pressure, i.e., the difference in spectral shape between low oxygen pressure films (1.5×10^{-2} , 50 mTorr) and high oxygen pressure films (100, 300 mTorr), is observed in the $^5D_0 \rightarrow ^7F_2$ transition in the range from 600 to 640 nm. In the case of the high oxygen pressure films, the 611 nm peak is predominant and the other minor peak is located at around 627 nm. On the other hand, in the low oxygen pressure films, the 611 nm peak becomes smaller, and the other peak shifts to 619 nm and also becomes stronger. These two types of spectral shape correspond to different crystalline structures. Gd_2O_3 has the same crystallographic structures as Y_2O_3 , i.e., cubic (1220–1300 °C) and monoclinic (1400 °C) phases. The monoclinic system shows a considerably lower luminance than the cubic system.⁸ The monoclinic Gd_2O_3 provides three different C_s crystallographic sites for the Eu^{3+} ion.⁹ These three sites give rise to a majority of the 5D_0 and 7F_2 Stark levels, which produce numerous peaks in the range between 600 and 640, even though our measurement was not sufficient to resolve them. It is known that the low energy side peaks are stronger than the 611 nm peak in the case of monoclinic $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$,^{9,10} with which our observation is coincident. That is, the low energy side peak (619 nm) is stronger than the 611 nm peak in the low oxygen pressure films. Consequently, we conclude

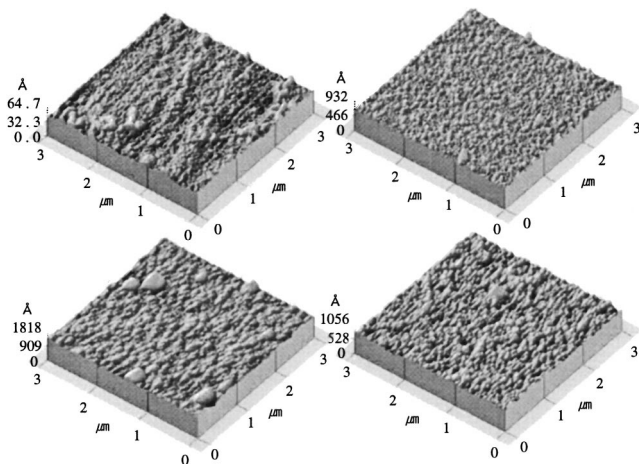


FIG. 1. AFM images of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film surface deposited at (a) 0.015, (b) 50, (c) 100, and (d) 300 mTorr.

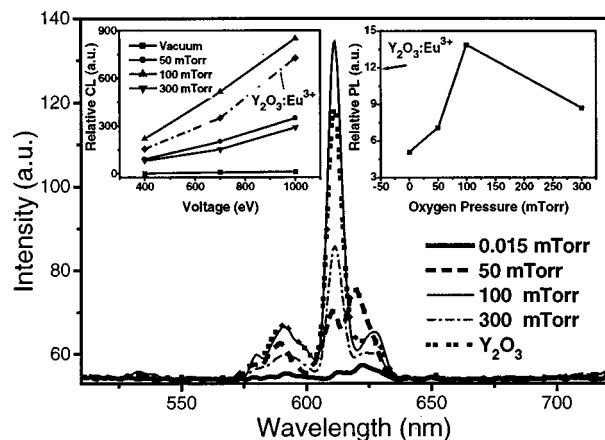


FIG. 2. Emission spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film phosphor deposited at various oxygen pressures. The excitation light wavelength is 254 nm. The insets show relative PL (upper right) and CL (upper left) efficiency.

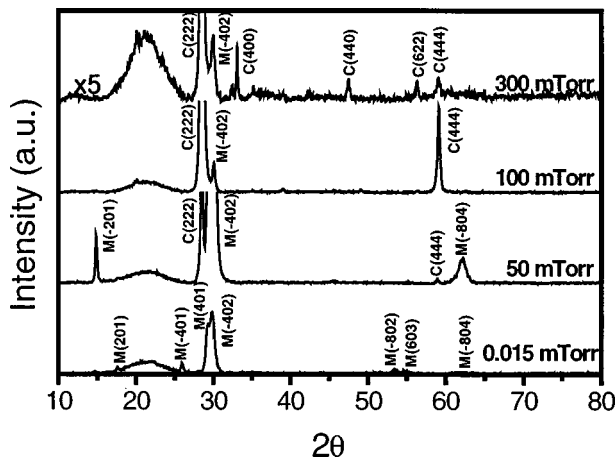


FIG. 3. XRD patterns of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film phosphors deposited at various oxygen pressures.

that the low oxygen pressure films contain a considerable amount of monoclinic phase. On the contrary, the high oxygen pressure films (100, 300 mTorr) consist largely of cubic phase. The cubic structure provides two different crystalline sites, i.e., S_6 and C_2 site.^{11,12} In fact, the electric dipole transition of Eu^{3+} ion at S_6 site scarcely arises on account of the strict inversion symmetry. Therefore, the ${}^5D_0 \rightarrow {}^7F_2$ transition originates mostly from the C_2 site, which shows a relatively poor inversion symmetry. The high oxygen pressure $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ films and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film show the typical shape of the emission spectrum of the ${}^5D_0 \rightarrow {}^7F_2$ transition at the C_2 site in the cubic structure. The crystallographic structure identification by the PL spectra is confirmed by XRD data which are given in Fig. 3. The inset in the upper left corner in Fig. 2 shows the relative luminance obtained from the CL spectra as a function of excitation energy in terms of voltage. The CL luminance trend with respect to oxygen pressure is similar to the PL data. Unlike the case of PL where only a slight improvement was obtained in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film over the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film, however, the CL efficiency of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film is greatly enhanced compared with a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film of similar thickness.

Figure 3 shows the XRD patterns of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ films as a function of oxygen pressure. The crystallographic structure of the films varies with the oxygen pressure. We found that the film deposited in vacuum (1.5×10^{-2} mTorr) exhibited a complete monoclinic structure even if the overall crystallinity is not very good. No trace of cubic structure was detectable in this film. The mixed structure of cubic and monoclinic phases is detected in the film deposited at an oxygen pressure of 50 mTorr. The cubic phase exhibits a preferred (111) orientation in this case. The predominant growth in the $\langle 111 \rangle$ direction has been also observed in the case of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors.^{1-6,13-15} A possible explanation for the predominant growth in the $\langle 111 \rangle$ direction is that Gd_2O_3 (or Y_2O_3) has a bixbyte-type structure with ordered oxygen vacancies in which the (111) orientation has the lowest surface energy, leading to a preferred growth in the $\langle 111 \rangle$ direction.¹⁴ As the oxygen pressure reaches 100 mTorr, the cubic structure becomes dominant and a very small portion of monoclinic phase remains. Thus, the pre-

ferred growth orientation becomes more prominent in this film. The film deposited at 300 mTorr shows thoroughly different features. The crystalline structure of the film deposited at 300 mTorr consists of a considerable amount of cubic phase and a relatively small portion of monoclinic phase, and the crystallinity becomes worse compared to the 100 mTorr film, as evidenced by the fact that the full width at half maximum of the (222) peak increases from 0.022° (at 100 mTorr) to 0.06° (at 300 mTorr). According to Zhang *et al.*,¹⁴ the poor crystallinity at high oxygen pressure may be due to the reduced mobility of the Gd_2O_3 species caused by more frequent collisions with gas particles. Another conspicuous point in the 300 mTorr film is that representative peaks corresponding to powder form appear while the cubic phase still maintains the weak preferred $\{111\}$ orientation.

We found that the crystallographic structure and preferred growth orientation were highly dependent on the oxygen pressure. The oxygen pressure dependence on crystallographic structure, observed in our high oxygen pressure films (100, 300 mTorr), is in agreement with literature dealing with Y_2O_3 films of cubic structure. Zhang *et al.*¹⁴ and Jones *et al.*¹ showed independently that the preferred (111) orientation disappears as oxygen pressure increases in a cubic Y_2O_3 film. Zhang *et al.*¹⁴ proposed that the oxygen vacancy might change with oxygen pressure, and such a change would be beneficial to growth in the other directions. On the other hand, Jones *et al.*¹ concluded that the change in film orientation is associated with an increased number of outgrowths which act as nucleation centers for grains of other orientations. It should be, however, noted that our low oxygen pressure films (0, 50 mTorr) consisted mostly of monoclinic phase, which has never been observed in the case of Y_2O_3 films. Considering the fact that monoclinic Gd_2O_3 is obtained in a strong reducing atmosphere,¹⁶ the low oxygen pressure could be favorable for monoclinic Gd_2O_3 film formation. A more detailed investigation is now underway using synchrotron radiation with various processing variables, such as substrate, temperature, laser power, distance, and etc.

IV. CONCLUSION

In conclusion, we obtained a higher PL and CL efficiency in a $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film than in a $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ film of similar thickness and roughness. The findings herein also show that film characteristics and luminescent properties can be altered significantly by the PLD processing conditions. The typical oxygen pressure dependence of thickness, roughness, and, in turn, luminance, which has been widely accepted in explaining $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ films, is no longer applicable to the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ film deposited under our processing conditions due to the appearance of a monoclinic phase. The existence of a monoclinic phase could be a key factor in the deterioration of luminance of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ films, so that the monoclinic phase should be reduced to enhance PL and CL efficiency. For further improvements, we are now attempting to introduce codopants (Al, Mg, Ca) into the film phosphors. Such materials have already proven to be useful in enhancing luminance in investigations of powder phosphors.

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