Epitaxial Oxide Thin-Film Phosphors for Low Voltage FED Applications

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ABSTRACT

Epitaxial $ZnGa_2O_4$ and Sr_2CeO_4 thin-film phosphors were successfully grown on (100) MgO, YSZ, and $SrTiO_3$ single crystal substrates using pulsed laser ablation. Cathodoluminescence efficiency was remarkably enhanced by adding lithium in the $ZnGa_2O_4$ and $ZnGa_2O_4$:Mn for both blue and green light emitting thin-film phosphors. The highest efficiencies, in this experiment, were 0.35 and 0.29 lm/W at 1kV for as-deposited blue and green zinc gallate phosphor films, respectively. In case of Sr_2CeO_4 films, the highest luminescence was 0.14 lm/W at 1kV and 0.26 A/m^2 for films annealed at 1000°C in air.

INTRODUCTION

Oxide thin-film phosphors are very attractive for field emission displays (FEDs) which operated with low voltage and high current density. Advantages include high resolution screens, enhanced lifetime at high current density, and excellent thermal and mechanical stabilities. Unfortunately, one of the fundamental problems for oxide thin-film phosphors in applications is inferior luminous efficiency and brightness as compared to powder systems.

Many researchers have studied luminescence for thin-film phosphors in an attempt to improve the properties through increasing light scattering centers using surface modification, reducing defect density by post-annealing at high temperatures, and identifying new phosphor materials.[1-3] Recently, Lee et al.[4] reported that epitaxial phosphor films exhibit superior photoluminescent (PL) intensity as compared to randomly-oriented polycrystalline films on glass substrates. This result indicates enhanced luminescence due to improved intragranular crystallinity via epitaxy. The study of epitaxial phosphor film is useful not only for achieving high luminescence performance, but also in understanding the fundamental properties of the materials. Most known phosphor materials are multi-component materials possessing complex crystallographic structures, making it difficult to find suitable deposition technique and/or substrate materials for epitaxial film growth. We have investigated the growth and luminescence characteristics of several oxide thin-film phosphors including $ZnGa_2O_4$, $Li_xZn_{1-x}Ga_2O_4$, $ZnGa_2O_4$:Mn, $Li_xZn_{1-x}Ga_2O_4$:Mn, and Sr_2CeO_4 for blue and green low voltage cathodoluminscence.

EXPERIMENTAL DETAILS

Blue light emitting $Li_xZn_{1-x}Ga_2O_4$(x=0-0.2), mixtures of $LiGa_5O_8$ and $ZnGa_2O_4$, and Sr_2CeO_4 thin-film phosphors were grown using pulsed-laser ablation. Polycrystalline 1 inch dia. ablation targets were prepared by mixing and pressing Li_2O [Alfa, 99.99%], ZnO [Alfa, 99.999%], Ga_2O_3 [Alfa, 99.9995%] powders, followed by sintering in air at 1250 ^{o}C for 24

hours. To compensate Zn loss in the films, all films were deposited using mosaic targets being composed of phosphor target/ZnO with an area ratio of 50/50.[4] A Sr_2CeO_4 target was prepared using CeO_2[Alfa, 99.994%] and $SrCO_3$[Alfa, 99.99%] powders. Approximately 2μm-thick films were grown using an excimer KrF laser with a wavelength of 248 nm. Detail deposition conditions are summarized in Table 1. Crystal structure was investigated using four-circle x-ray diffraction (XRD) with CuKα radiation (0.15406 nm wavelength). Surface microstructure of the films was observed using atomic force microscope.(AFM) Low voltage cathodoluminescence (CL) was measured with a Plasma Scan PSS-2 spectrometer, and CL intensity measurements were taken with an International Light 1700 photometer equipped with a photopic filter.

Table 1. Summary of film growth conditions.

Target	Substrate Temperature (^oC)	Oxygen Pressure(mTorr)	Laser Fluence (J/cm^2)
$Li_xZn_{1-x}Ga_2O_4$/ZnO	730	100	3.5
Sr_2CeO_4	750	300	4.0

RESULTS AND DISCUSSION

1. $ZnGa_2O_4$ Thin-Film Phosphors

Figure 1 shows x-ray diffraction θ-2θ and ϕ scans for the films using a $Li_{0.25}Zn_{0.75}Ga_{2.25}O$:Mn/ZnO mosaic target. In this study, all films exhibited a $ZnGa_2O_4$ (400) diffraction peak. Some films revealed a Ga_2O_3 peak with very low intensity. In the case of Li_2O added $ZnGa_2O_4$, formation of secondary phase could be expected. No direct evidence for the formation of lithium gallate related secondary phase was found in this experiment. ϕ scans confirm that the films are well aligned in-plane indicating epitaxial films.

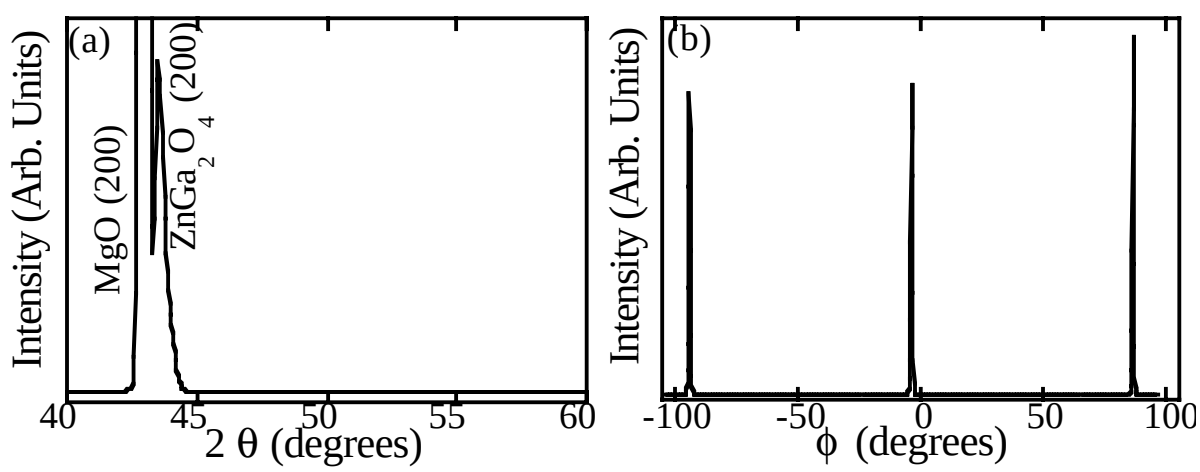

***Figure 1**. X-ray (a) θ-2θ and (b) ϕ scans for the films using $Li_{0.25}Zn_{0.75}Ga_{2.25}O$:Mn/ZnO mosaic target.*

Surface microstructures in the films were observed using AFM as shown in Fig. 2. $ZnGa_2O_4$ films show a smooth surface with root mean square(r.m.s.) roughness of about 2.3 nm while rather irregular-shaped surface features were observed in the lithium added films. The r.m.s. roughness of the $Li_{0.05}Zn_{0.95}Ga_2O_4$ and $Li_{0.25}Zn_{0.75}Ga_{2.25}O_4$ films were approximately 2.9 and 4.9 nm respectively. Mn-doped films show higher values in r.m.s. roughness relatively to the films grown without Mn. The values are 5.6 nm, 3.8 nm, and 8.0 nm for $ZnGa_2O_4$:Mn, $Li_{0.05}Zn_{0.95}Ga_2O_4$:Mn, and $Li_{0.25}Zn_{0.75}Ga_{2.25}O_4$:Mn films, respectively. Consistent relationship between the surface microstructural features and lithium content could not be observed.

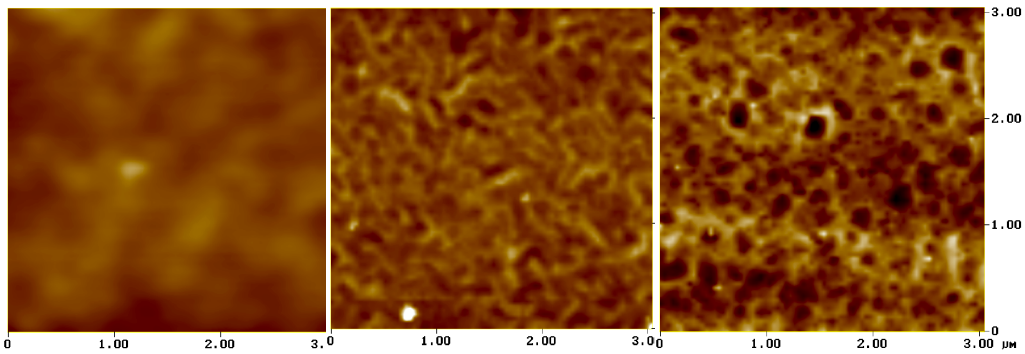

***Figure 2**. Surface morphology of the films deposited using mosaic targets of (a) $ZnGa_2O_4$/ZnO, (b) $Li_{0.05}Zn_{0.95}Ga_2O_4$/ZnO, and (c) $Li_{0.25}Zn_{0.75}Ga_{2.25}O_4$/ZnO. Scan area was 3µmx3µm.*

The peaking wavelengths in CL spectra for blue light emitting lithium-doped $ZnGa_2O_4$ films ranged between 406 and 430 nm. CL emission spectra for green lithium-doped $ZnGa_2O_4$:Mn showed peaking wavelength located from 507 to 509 nm which corresponds to the transition $^4T_1 \rightarrow {}^6A_1$ of the 3d electrons in the Mn^{2+} ion occupying the fourfold coordinated Zn position in the host lattice.[5]

Low voltage CL efficiency for the lithium zinc gallate films with current density at fixed voltage of 1kV are shown in Fig. 3. Without lithium, the film shows efficiencies lower than 0.05 lm/W. The efficiency increased significantly with increasing lithium content. The highest efficiency in this experiment is 0.35 lm/W measured at 1kV and 0.05 A/m^2. Green light emitting phosphor films, $Li_xZn_{1-x}Ga_2O_4$:Mn, exhibit similar behavior as shown in Fig. 4. The CL efficiency increased from 0.03 lm/W to 0.29 lm/W with increasing lithium content in the films. In both cases, the efficiencies are about 5 – 8 times higher as compared to the films without lithium. The results show that an addition of lithium ions in zinc gallate phosphor films remarkably enhances CL characteristics.

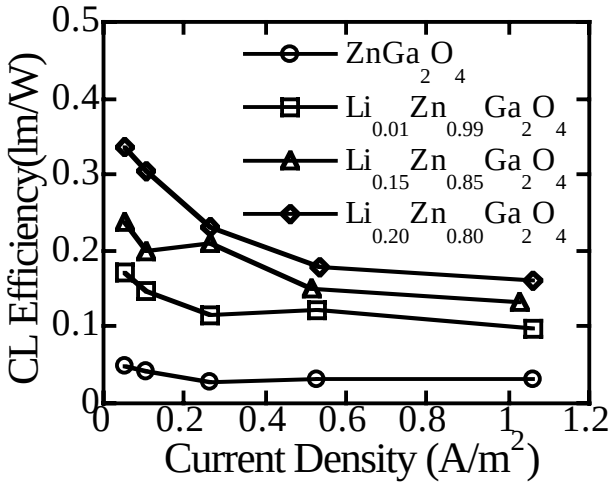

Figure 3. *CL Efficiency forblue films with lithium content measured at 1kV.*

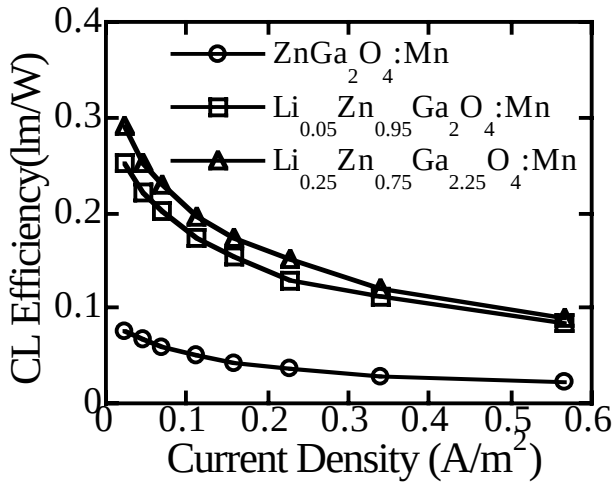

Figure 4. *CL efficiency for green films with lithium content measured at 1kV.*

2. Sr_2CeO_4 Thin-Film Phosphors

X-ray diffraction θ-2θ and ϕ scans of Sr_2CeO_4 films deposited on a (100) YSZ single crystal substrates are shown in Fig. 5. The ϕ scans through the (110) Sr_2CeO_4 confirms in-plane aligned structure for the films. The film on (100) $SrTiO_3$ shows a near singular orientation with a very weak (111) diffraction peak. The films have orthorhombic crystal structure as determined by four-circle x-ray diffraction. High-resolution scans with a Ge analyzer crystal yields lattice parameters of the orthorhombic Sr_2CeO_4 film to be a=0.6115 nm, b=0.1036 nm, c=0.3596 nm on (100) $SrTiO_3$ and a=0.6119 nm, b=0.1035 nm, c=0.360nm on (100) YSZ. These values are in good agreement with the values reported by Danielson.[6] The epitaxial relationships between film and substrate were (100)[010]$_{Sr_2CeO_4}$//(100)[010]$_{SrTiO_3}$ and (100)[010]$_{Sr_2CeO_4}$//(100)[011]$_{YSZ}$.

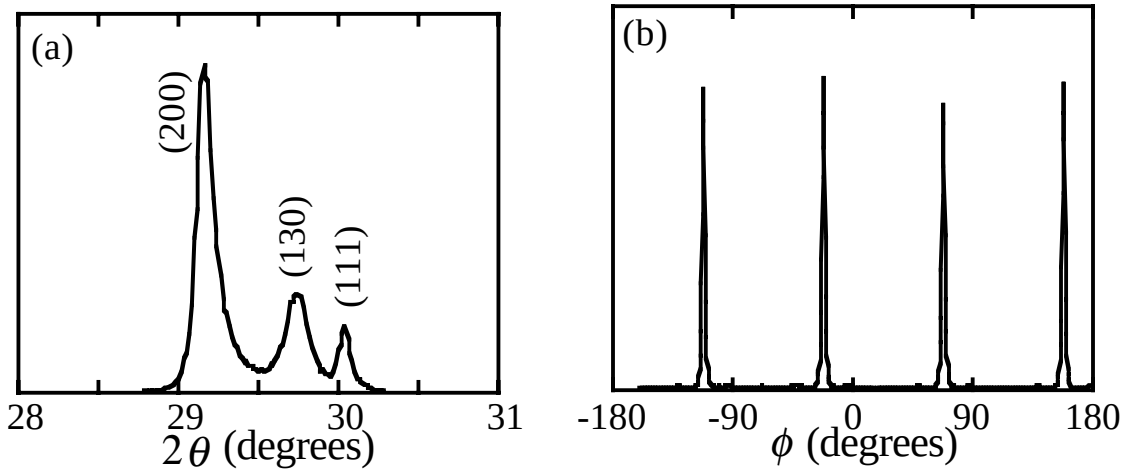

Figure 5. *X-ray (a)θ-2θ and (b) ϕ scans through (110) for Sr_2CeO_4 films deposited on (100) YSZ single crystal substrate.*

As-deposited films exhibit a broad-band CL emission, peaking at about 465nm as shown in Fig. 6. The small peaking at 505 nm may be due to contamination of Mn from the chamber. Figure 7 shows the CL efficiency versus voltage for as-deposited and subsequently post-annealed Sr_2CeO_4 films on (100) YSZ single crystal substrates. With increasing annealing temperatures up to 1000°C, significant enhancement in the CL efficiency is observed. A 2-μ m thick film annealed at 1000°C in air showed the highest luminous efficiency of about 0.14 lm/W at 1kV and 22μA/cm^2.

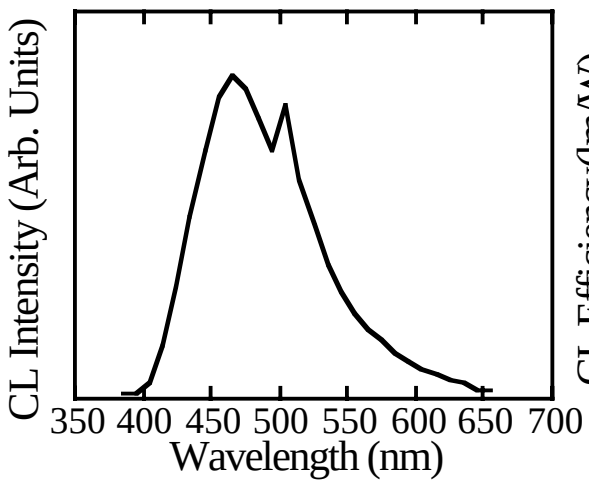

Figure 6. *CL spectra of as-deposited Sr_2CeO_4 Thin-Film Phosphors.*

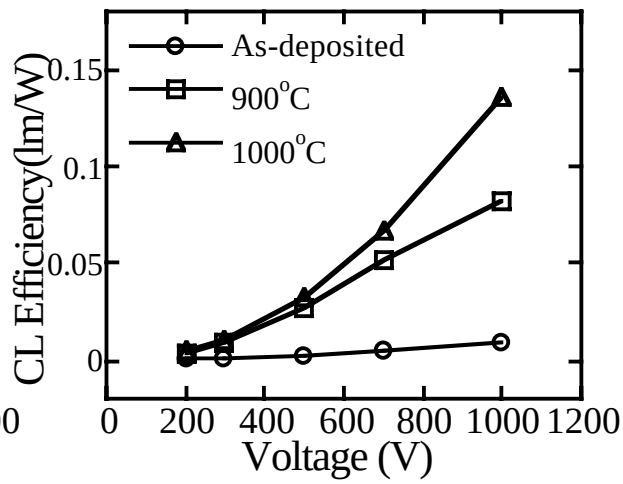

Figure 7. *Variation of CL efficiency for Sr_2CeO_4 films measured at 22μA/cm^2.*

SUMMARY

Blue and green light emitting $Li_xZn_{1-x}Ga_2O_4$ and Sr_2CeO_4 thin-film phosphors were grown on (100) MgO and (100) YSZ substrates using pulsed laser deposition. In $ZnGa_2O_4$, addition of lithium considerably improved low-voltage CL characteristics. The highest efficiencies, in this experiment, were 0.35 and 0.29 lm/W at 1kV for as-deposited blue and green zinc gallate phosphor films, respectively. In the case of Sr_2CeO_4 films, the highest luminescence was 0.14 lm/W at 1kV and 0.26 A/m^2 for films annealed at 1000°C in air. Oxide thin-film phosphors are good candidate for low-voltage FEDs.

ACKNOWLEDGMENTS

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