Photo- and cathodoluminescence characteristics of blue-light-emitting epitaxial Sr_2CeO_4 thin-film phosphors

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Orthorhombic epitaxial Sr_2CeO_4 thin-film phosphors were grown on (100) $SrTiO_3$ and yttria-stabilized-zirconia (YSZ) single crystal substrates with epitaxial relationships of (100) $[010]_{Sr_2CeO_4}//(100)[010]_{SrTiO_3}$ and $(100)[010]_{Sr_2CeO_4}//(100)[011]_{YSZ}$, respectively. As-deposited films exhibit a broadband photoluminescence (PL) emission, peaking at about 477–481 nm with a maximum cathodoluminescence (CL) intensity at about 465 nm. Enhanced PL intensity was observed for the films deposited on (100) YSZ and $SrTiO_3$ substrates as compared to deposits on c-plane sapphire substrates, correlating with improved intragranular crystallinity and reducing defects via epitaxy. Postannealing in air significantly enhanced both of the PL and CL intensities. Luminous efficiency of 0.14 lm/W at 1 kV and 22 μA/cm^2 was observed for a 2-μm-thick film annealed at 1000 °C in air. © *2000 American Institute of Physics.* [S0003-6951(00)02427-X]

Oxide thin-film phosphors are highly desirable for field emission display and electroluminescent device applications. Unfortunately, one of the fundamental problems for oxide thin-film phosphors in applications is inferior luminous efficiency and brightness as compared to powder systems. It has been proposed that the inferior luminescent properties are caused by internal reflection from planar interfaces and inferior crystallinity.[1–3] Many researchers have tried to understand the luminescence mechanism for thin-film phosphors and improve the properties through surface modification, postannealing at high temperatures, and identifying superior phosphor compounds. Recently, Lee *et al.*[4] reported that epitaxial phosphor films can exhibit superior photoluminescent (PL) intensity as compared to randomly oriented polycrystalline films on glass substrates. This result indicates that enhanced luminescence due to improved intragranular crystallinity is possible via epitaxy. The study of epitaxial phosphor films is useful not only for achieving high luminescence performance, but also in understanding the fundamental properties of the materials. Unfortunately, many known phosphor materials are multicomponent materials possessing complex crystallographic structures, making it difficult to find suitable deposition techniques and/or substrate materials for epitaxial film growth.

Recently, a Sr_2CeO_4 compound, possessing one-dimensional chains of edge-sharing CeO_6 octahedra, was identified by Danielson *et al.* as a promising blue luminescence material.[5] It has an orthorhombic crystal structure with $a=6.118\,97$ Å, $b=10.3495$ Å, and $c=3.5970$ Å. It exhibits a blue-white emission band that peaks at 485 nm, with a quantum yield of 0.48 ± 0.02 under 254 nm excitation. The luminescence was suggested to originate from a ligand-to-metal Ce^{4+} charge transfer. Jiang *et al.*[6] showed very promising results for Sr_2CeO_4 phosphors in field emission display applications. They prepared Sr_2CeO_4 powder phosphors by a chemical coprecipitation technique. It was reported that the powder has an emission peak at 470 nm (CIE chromacity coordinates $x=0.19$, $y=0.26$) with a luminescence efficiency of 5.4 lm/W at 4 kV and 29.0 lm/W at 10 kV. Despite the relatively complex crystal structure, we have successfully grown epitaxial Sr_2CeO_4 films on single crystal cubic oxide substrates. We report on the growth and luminescent properties of epitaxial Sr_2CeO_4 films, comparing their properties to polycrystalline films.

Sr_2CeO_4 thin-film phosphors were grown using pulsed-laser deposition. Polycrystalline 1 in. diam Sr_2CeO_4 ablation targets were prepared by mixing and pressing $SrCO_3$ [Alfa, 99.994%] and CeO_2 [Alfa, 99.99%] powders, followed by sintering in air at 1260 °C for 24 h. The films were grown using an excimer KrF laser with a wavelength of 248 nm. The laser fluence was approximately 4 J/cm^2 and the repetition rate used was 10 Hz. Approximately 400–500 nm-thick films were grown at temperatures ranging from 600 to 750 °C. The oxygen partial pressure, $P(O_2)$, was varied during deposition from 50 to 800 mTorr. 2-μm-thick films were deposited using a repetition rate of 50 Hz. c-plane Al_2O_3, (100) yttria-stabilized zirconia (YSZ), and (100) $SrTiO_3$ single crystal substrates were used. Once deposited, the Sr_2CeO_4 films were annealed at several temperatures for 1 h in air. Crystal structure was investigated using x-ray diffraction (XRD) with Cu $K\alpha$ radiation (0.154 06 nm wavelength). The PL spectra were measured at room temperature using a broadband incoherent ultraviolet light excitation source with a dominant excitation wavelength of 256 nm. Low voltage cathodoluminescence (CL) was measured with a Plasma Scan PSS-2 spectrometer. CL intensity measurements were taken with an International Light 1700 photometer equipped with a photopic filter.

Figure 1 shows x-ray θ–2θ and ϕ scans of Sr_2CeO_4

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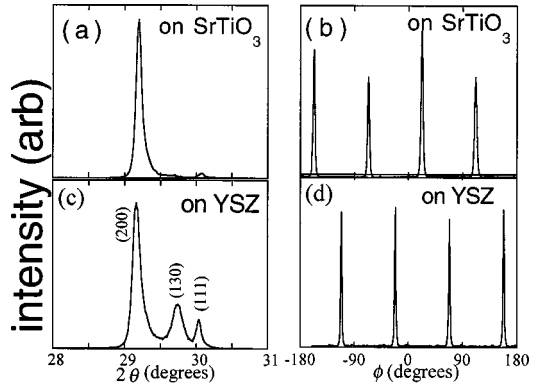

FIG. 1. X-ray (a) θ–2θ and (b) ϕ scans through (110) for Sr_2CeO_4 films deposited on (100) YSZ single crystal substrates and (c) θ–2θ and (d) ϕ scans through (110) for Sr_2CeO_4 films deposited on (100) $SrTiO_3$ single crystal substrates at 760 °C under $P(O_2)$ of 300 mTorr.

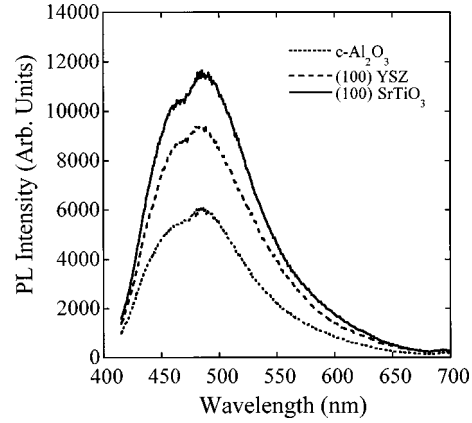

FIG. 2. Comparison of PL emission spectra of Sr_2CeO_4 films grown on various single crystal substrates deposited at 760 °C under $P(O_2)$ of 300 mTorr.

films deposited on a (100) $SrTiO_3$ single crystal substrate. Two different types of crystal structures have been reported for Sr_2CeO_4. According to the Joint Committee on Powder Diffraction Standards (JCPDS) card, the structure of Sr_2CeO_4 is triclinic.[7] However, Danielson *et al.*[8] reported that Sr_2CeO_4 has an orthorhombic structure. In this study, the Sr_2CeO_4 films were orthorhombic as determined by four-circle XRD. The film on (100) $SrTiO_3$ shows a near singular orientation with a very weak (111) diffraction peak. The ϕ scan through the $Sr_2CeO_4(110)$ also confirmed in-plane aligned structure for the film. The epitaxial relationship between film and substrate was (100) $[010]_{Sr_2CeO_4}//(100)[010]_{SrTiO_3}$. The films deposited on (100) YSZ reveal (200), (130), and (111) diffraction peaks. However, ϕ scans through the $Sr_2CeO_4(110)$ reveal that the (100)-oriented Sr_2CeO_4 grains are well aligned in-plane indicating a partially epitaxial film. The epitaxial relationship between the film and substrate was (100) $[010]_{Sr_2CeO_4}//(100)[011]_{YSZ}$. High-resolution scans with a Ge analyzer crystal gave lattice parameters of the orthorhombic Sr_2CeO_4 film to be $a=6.119$ Å, $b=10.35$ Å, and $c=3.60$ Å on (100) YSZ and $a=6.115$ Å, $b=10.36$ Å, and $c=3.596$ Å on (100) $SrTiO_3$. These values are in good agreement with the values reported by Danielson *et al.*[8] In contrast, the films deposited on c-plane Al_2O_3 single crystal substrates were polycrystalline with (111) and (002) diffraction peaks in the θ–2θ scan and no in-plane alignment.

Typical PL spectra for as-deposited 0.5-μm-thick Sr_2CeO_4 films on various substrates are shown in Fig. 2. As-deposited films exhibit a broadband PL emission with a full width at half maximum (FWHM) of about 100 nm, peaking at about 477–481 nm depending on growth conditions. For instance, films deposited at 300 mTorr exhibit higher PL intensity than films grown at 100 mTorr. In addition, deposition temperatures of 750 °C yielded higher PL intensity than those obtained at 600 °C. The maximum CL intensity was at about 465 nm which is slightly shorter than that for PL. These values are slightly different from the 485 and 472 nm reported by Danielson *et al.*[5] and Jiang *et al.*,[6] respectively. Moreover, the PL spectra seems to be composed of several emission bands. Note also that the epitaxial film deposited on (100) YSZ and $SrTiO_3$ exhibits enhanced PL intensity as compared to the polycrystalline film on c-plane Al_2O_3. The superior PL intensity is likely the result of enhanced intragranular crystallinity and reduced defect density via epitaxy on low energy crystallographic planes. Defect structures associated with polycrystalline materials, such as grain boundaries, point defects, and impurities, act as nonradiative centers and can impact relevant transport and luminescent properties.

The effect of postannealing of the films was also investigated. Figure 3 shows an improvement in PL intensity for Sr_2CeO_4 films deposited on various single crystal substrates by postannealing. Heat treatment in air considerably enhanced the PL intensity of the Sr_2CeO_4 films, while a reduction in PL was observed for the films annealed in inert or reducing atmosphere. The films annealed at 800 °C in air showed extensive enhancement in PL. The postannealing process presumably results in an improved crystallinity, elimination of defects and increased surface roughness. The degree of the improvement in PL for the epitaxial films was much larger than that for polycrystalline deposits. The films grown on c-plane sapphire substrates showed increased PL intensity up to an annealing temperature of 900 °C; emission was lost after annealing at 1000 °C. In the case of films

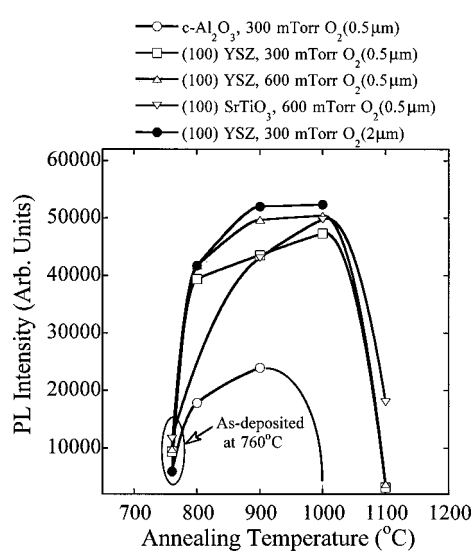

FIG. 3. Postannealing temperature dependence of PL emission spectra for Sr_2CeO_4 films grown on various substrates. Lines are guides for the eye.

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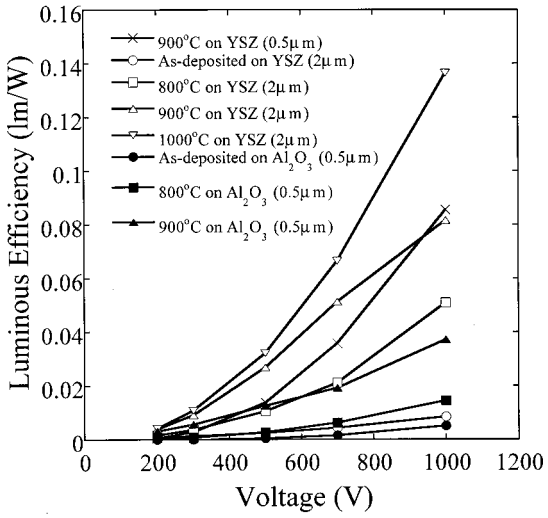

FIG. 4. Variation of CL efficiency for Sr_2CeO_4 films grown on various single crystal substrates, and subsequently postannealed. Anode current density is 22 $\mu A/cm^2$. Lines are guides for the eye.

grown on (100) YSZ and $SrTiO_3$ single crystal substrates, the PL intensity was reduced after heat treatment at 1100 °C. XRD results showed that secondary phases associated with chemical reactions between the substrate and film formed at these temperatures.

Figure 4 shows the CL efficiency versus voltage for Sr_2CeO_4 films deposited on various substrates. Again, the epitaxial film shows superior CL intensity as compared to the polycrystalline deposit. With increasing annealing temperatures up to 1000 °C, enhancement in the CL intensity is observed. A 2-μm-thick film annealed at 1000 °C in air showed the highest luminous efficiency of about 0.14 lm/W at 1 kV and 22 $\mu A/cm^2$. The 2-μm-thick films were grown on (100) YSZ single crystal substrates using a repetition rate of 50 Hz. X-ray θ–2θ scan showed a similar diffraction pattern to that of the thinner films. However, the 2-μm-thick films had higher values of surface roughness and a smaller FWHM (200) rocking curve than that for the 0.5-μm-thick films.

In summary, blue-light-emitting epitaxial Sr_2CeO_4 thin-film phosphors were grown on (100) $SrTiO_3$ and YSZ single crystal substrates. As-deposited films exhibit broadband PL emission, peaking at about 477–481 nm, with a maximum CL intensity at about 465 nm. Enhanced PL intensity was observed for the films deposited on (100) YSZ and $SrTiO_3$ substrates as compared to polycrystalline deposits on *c*-plane sapphire. Postannealing in air significantly enhanced both PL and CL intensities. Luminous efficiencies of 0.14 lm/W were observed for 2-μm-thick films annealed at 1000 °C in air.

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[1] S. L. Jones, D. Kumar, K.-G. Cho, R. Singh, and P. H. Holloway, Display **19**, 151 (1999).
[2] K.-G. Cho, D. Kumar, P. H. Holloway, and R. Singh, Appl. Phys. Lett. **73**, 3058 (1998).
[3] T. Minami, T. Maeno, Y. Kuroi, and S. Takata, Jpn. J. Appl. Phys., Part 2 **34**, L684 (1995).
[4] Y. E. Lee, D. P. Norton, and J. D. Budai, Appl. Phys. Lett. **74**, 3155 (1999).
[5] E. Danielson, M. Devenney, D. M. Giaquinta, J. H. Golden, R. C. Haushalter, E. W. McFarland, D. M. Poojary, C. M. Reaves, W. H. Weinberg, and X. D. Wu, Science **279**, 837 (1998).
[6] Y. D. Jiang, F. Zhang, and C. J. Summers, Appl. Phys. Lett. **74**, 1677 (1999).
[7] JCPDS No. 22-1422.
[8] E. Danielson, M. Devenney, D. M. Giaquinta, J. H. Golden, R. C. Haushalter, E. W. McFarland, D. M. Poojary, C. M. Reaves, W. H. Weinburg, and X. D. Wu, J. Mol. Struct. **470**, 229 (1998).

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