Structure and Photoluminescence of Optically Transparent $\text{Y}_2\text{O}_3\text{:Eu}$ Thin Films Prepared on Sapphire Substrates by RF Magnetron Sputtering

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ABSTRACT

The $\text{Y}_2\text{O}_3\text{:Eu}$ films were prepared on sapphire substrates by radio frequency magnetron sputtering. The samples were post-annealed in an air ambient at different temperatures. The $\text{Y}_2\text{O}_3\text{:Eu}$ films prior to annealing did not show photoluminescence (PL), however, after annealing, the films became capable of emitting photoluminescent light. The PL spectra were composed of several peaks originating from the transitions between $4f$ energy levels of the Eu^{3+} ion, from 5D_0 to 7F_J where $J = 0, 1, 2, 3$, and 4 . The PL intensity increased upon annealing at higher temperatures, which was due to the higher degree of crystallinity. The PL intensity decreased above 1200°C resulting from the formation of yttrium aluminate phases, such as YAM ($\text{Y}_4\text{Al}_2\text{O}_9$), YAP (YAlO_3), and YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$). The unannealed $\text{Y}_2\text{O}_3\text{:Eu}$ films exhibited a high optical transmittance in the visible to near-infrared wavelength range. The transmittance of the films decreased as annealing temperature increased due to increase in crystallite sizes.

Keywords: Radio frequency magnetron sputtering, Thin films, Sapphire, Annealing, X-ray diffraction

1. Introduction

Y_2O_3 is a material of high importance in a wide variety of applications. Y_2O_3 is suitable as a high-temperature protective coating material in a severely reactive environment due to its thermal stability up to 2325°C and excellent chemical stability coupled with high mechanical strength [1,2]. In addition, Y_2O_3 exhibits high dielectric permittivity, high breakdown strength, and large band gap energy, which makes it useful as a gate oxide for metal-oxide-semiconductor field effect transistors and as a dielectric for metal-insulator-metal capacitors [3,4]. Furthermore, Y_2O_3 is a constituent of a high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) and Y_2O_3 -stabilized ZrO_2 (YSZ) thermal barrier coatings [5–7]. YSZ and Y_2O_3 -doped CeO_2 are solid-state electrolytes in solid oxide fuel cells and solid-state gas sensors [8–10].

Y_2O_3 is also a key material in the field of lighting and display technologies. Y_2O_3 is an excellent host material for doping with rare earth elements, which shows luminescence in various spectral ranges from visible to near-infrared [11–13]. Especially, Y_2O_3 doped with Eu has attracted great interest due to its highly efficient luminescence. $\text{Y}_2\text{O}_3\text{:Eu}$ has been widely used as a red-emitting phosphor in fluorescent tubes and display devices [12, 14]. Besides, $\text{Y}_2\text{O}_3\text{:Eu}$ has been used for biological imaging and temperature sensing applications [11, 15]. Moreover, a recent study has shown that $\text{Y}_2\text{O}_3\text{:Eu}$ could be used as a red-emitting phosphor to generate white light with GaAlN-based UV-emitting light emitting diodes [16].

$\text{Y}_2\text{O}_3\text{:Eu}$ is typically synthesized in the forms of micrometer- and nanometer-sized particles [11, 12, 14, 15]. Thin-film form of $\text{Y}_2\text{O}_3\text{:Eu}$ is also attractive because of its advantages, such as better thermal sta-

bility, more uniform thickness, better adhesion to the substrate, and smaller pixel spot size, i.e. higher resolution [17]. Transparency is another benefit of thin-film form of $\text{Y}_2\text{O}_3\text{:Eu}$ because it provides a smoother surface in comparison to its particle form, thus leading to lower light-scattering loss. Transparent $\text{Y}_2\text{O}_3\text{:Eu}$ has been suggested for use in transparent displays and transparent optical coatings [18]. Thin films of $\text{Y}_2\text{O}_3\text{:Eu}$ have been studied previously [19, 20]. However, data concerning the optical transparency of the $\text{Y}_2\text{O}_3\text{:Eu}$ films are very limited. Therefore, in this work, we aimed to study on the $\text{Y}_2\text{O}_3\text{:Eu}$ films with optical transparency. We focused on the relationship between optical transparency, structure, and photoluminescence of the $\text{Y}_2\text{O}_3\text{:Eu}$ films. Sapphire was chosen as a substrate material because of its high optical transparency as well as high thermal stability and durability.

2. Experimental details

The thin films of $\text{Y}_2\text{O}_3\text{:Eu}$ were prepared on sapphire (0001) substrates by radio frequency (RF) magnetron sputtering of an Eu-doped Y_2O_3 target in argon gas. The Eu concentration of the target was about 1at.%. The sapphire substrates were loaded into the sputtering chamber that was subsequently pumped down to a pressure below 1×10^{-6} Torr. The high-purity argon gas was introduced into the chamber and the gas pressure was maintained at 2×10^{-2} Torr. During deposition, the sapphire substrates were not intentionally heated and the RF power density was kept at $5.92 \text{ W}\cdot\text{cm}^{-2}$. The thickness of the films was about 500 nm. After deposition, the samples were post-annealed in an air

Figure 1. Schematic diagrams of (a) the Y_2O_3 formula unit and (b) the unit cell of cubic bixbyite Y_2O_3 structure. Oxygen ions are denoted by green spheres. Blue and orange spheres represent Y ions at the C_2 and S_6 sites, respectively.

ambient at temperatures from 800 to 1300 °C for 1 h.

The crystallographic phases of the films were investigated by X-ray diffraction (XRD) using a SmartLab Rigaku diffractometer with $\text{Cu K}\alpha$ radiation. For photoluminescence (PL) studies, the PL spectra were measured using a Perkin Elmer LS 55 spectrometer. The PL emission spectra were detected for excitation at 207 nm and the excitation spectra were recorded for the luminescence at 612 nm. The PL spectra were measured at room temperature using a xenon discharge lamp with 20 kW power. The transmittance spectra of the samples were recorded by using a Perkin Elmer Lambda 35 spectrophotometer in the range from 190 to 1100 nm.

3. Results and discussion

Y_2O_3 has a cubic bixbyite crystal structure with a space group of $\text{Ia3}-(T_h^7)$ [21]. The bixbyite Y_2O_3 structure is a modified fluorite-type cubic structure, where one quarter of the total oxygen ions are taken out in order to maintain charge neutrality. As depicted in Fig. 1, the unit cell contains sixteen Y_2O_3 formula units [21]. There are eighty ions with thirty-two yttrium and forty-eight oxygen ions in the unit cell. Oxygen ion is four-fold coordinated ($\text{CN} = 4$) and occupies the center of the cation tetrahedron. Yttrium ion occupies the center of the oxygen cube and is six-fold coordinated ($\text{CN} = 6$) by six neighboring oxygen ions with one quarter of oxygen sites vacant and regularly arranged. This structure results in two symmetry-inequivalent crystallographic yttrium sites, i.e., S_6 and C_2 sites. Orange and blue spheres in Fig. 1 represent yttrium ions at S_6 and C_2 sites, respectively. As can be seen in Fig. 1(a), the S_6 site has a center of inversion resulting from two oxygen vacancies lying on the body diagonal of the cubic cell. But, the C_2 site has non centrosymmetry due to the two oxygen vacancies along face diagonal.

Figure 2 shows the PL emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ films. No PL emission was observed from the unannealed films. After annealing, the films were capable of emitting PL light. The PL spectra are composed of several peaks which originate from the transitions of the Eu^{3+} ion. As labeled in Fig. 2, all the emission peaks are attributed to the transition from $^5\text{D}_0$ to $^7\text{F}_J$ where $J = 0, 1, 2, 3$, and 4. The most intense peak is observed near 612 nm corresponding to the transition from $^5\text{D}_0$ to $^7\text{F}_2$ level. The relatively small peak at 632 nm is also from the transition from $^5\text{D}_0$ to $^7\text{F}_2$ level. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is a symmetry-sensitive and parity-forbidden electric-dipole transition which strongly depends on the local symmetry environment of the Eu^{3+} ions [22]. In cubic-structured Y_2O_3 crystallites, as illustrated in Fig. 1, Y^{3+} ions reside at two different sites, C_2 and S_6 . The C_2 site has non centrosymmetry, but the S_6 site has perfect inversion symmetry. It can therefore be found that the parity-forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_2$ tran-

Figure 2. Photoluminescence emission spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ films.

Figure 3. Variation of the PL peak intensity with annealing temperature.

sition is allowed due to the Eu^{3+} ion occupying at the C_2 site which lacks inversion symmetry. This results in the prominent PL emission peak at 612 nm.

Figure 3 shows the change in the PL emission intensity at 612 nm as a function of annealing temperature. The PL intensity increases with increasing annealing temperature. As discussed below with XRD data, the crystallinity of the $\text{Y}_2\text{O}_3:\text{Eu}$ films is improved and the crystallite size increases with increasing annealing temperature. This suggests that the higher PL intensity of the $\text{Y}_2\text{O}_3:\text{Eu}$ films annealed at higher temperature can be accounted for by increase in the degree of crystallinity of the films. At temperatures above 1200 °C, the PL intensity decreases, which results from the formation of yttrium aluminate phases by the reaction of the film with the sapphire substrate, as confirmed by XRD results below. Figure 4 shows the PL excitation spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ films. The intense band centered near 208 nm is related to the absorption of the Y_2O_3 host. The additional bands at wavelengths between 225 and 280 nm are due to the charge transfer from O^{2-} to Eu^{3+} ion [17].

Figure 5 presents the optical pictures of $\text{Y}_2\text{O}_3:\text{Eu}$ films prepared on a sapphire substrate under room light and ultraviolet (UV) light excitation at a wavelength of 254 nm. These pictures were taken after annealing the sample at 1000 °C for 1 hour in an air ambient. As shown in Fig. 5(a), the transparency of the $\text{Y}_2\text{O}_3:\text{Eu}$ films is sufficient to allow the easy reading of the underlying letters. Under UV excitation, as seen in Fig. 5(b), the $\text{Y}_2\text{O}_3:\text{Eu}$ films emit strong PL light.

Figure 6 shows the optical transmittance obtained from the $\text{Y}_2\text{O}_3:\text{Eu}$ films deposited on sapphire substrates. For comparison purpose, the transmittance spectrum measured from a bare sapphire substrate is

Figure 4. PL excitation spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ films.

Figure 5. Optical pictures of the $\text{Y}_2\text{O}_3:\text{Eu}$ film deposited on a sapphire substrate taken under (a) room light and (b) ultraviolet light.

Figure 6. Optical transmittance obtained from the $\text{Y}_2\text{O}_3:\text{Eu}$ films deposited on sapphire substrates.

also displayed in Fig. 6. The transmittance edge around 210 nm could be originated either from Y_2O_3 or $\text{Y}_2\text{O}_3:\text{Eu}$. It can be found that the unannealed $\text{Y}_2\text{O}_3:\text{Eu}$ films show a high transmittance in the visible to near-infrared wavelength region. The transmittance of the unannealed $\text{Y}_2\text{O}_3:\text{Eu}$ films at 612 nm is 0.842, which is very close to the transmittance of the sapphire substrate alone (0.860). The transmittance of the films decreases as annealing temperature increases, which can be explained by the light scattering due to increase in crystallite sizes.

The XRD patterns of the $\text{Y}_2\text{O}_3:\text{Eu}$ films are shown in Fig. 7. The unannealed films exhibited a low degree of crystallinity as evidenced by broad and weak diffraction peaks in Fig. 7(b). The diffraction peaks

Figure 7. XRD patterns of (a) a bare sapphire substrate, (b) as-deposited $\text{Y}_2\text{O}_3:\text{Eu}$ films, and the films annealed at (c) 800 °C, (d) 1000 °C, (e) 1200 °C, and (f) 1300 °C.

associated with cubic and monoclinic crystal structures of Y_2O_3 were detected from the unannealed films. The peaks denoted by Miller indices are identified as the cubic phase according to the Joint Committee on Powder Diffraction Standards (JCPDS) No. 43-1036. The peaks from the monoclinic Y_2O_3 phase are marked with the symbol (♦) according to the JCPDS No. 47-1274. This XRD pattern indicates the presence of a cubic Y_2O_3 phase mixed with a monoclinic phase in the unannealed films. After annealing at 800 °C, only the cubic Y_2O_3 phase is present. As the annealing temperature increased, the intensities of the XRD peaks were increased and the widths of the peaks became narrower. This indicates that the sizes of the crystallites in the films were increased with increasing the annealing temperature. The diffraction peaks of secondary phases were detected after annealing at 1200 °C and became more prevalent at 1300 °C. The peaks at about 18.9°, 29.6°, 30.6°, and 43.8° correspond to YAM (monoclinic yttrium aluminate, $\text{Y}_4\text{Al}_2\text{O}_9$) phase (JCPDS No. 34-0368). The peaks at 24.1°, 26.9°, 34.3°, 34.6°, 42.6°, and 49.0° arise from YAP (yttrium aluminate perovskite, YAlO_3) phase (JCPDS No. 33-0041). The peaks at 18.1°, 36.6°, 72.1°, and 73.0° correspond to YAG (yttrium aluminate garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$) phase (JCPDS No. 33-0040). These yttrium aluminate phases were possibly formed through the reaction between the film and the sapphire substrate as described below [23].

4. Conclusions

Optically transparent thin films of $\text{Y}_2\text{O}_3:\text{Eu}$ were prepared and the relationship between their optical transparency, structure, and photoluminescence was investigated. No luminescence was observed from the unannealed $\text{Y}_2\text{O}_3:\text{Eu}$ films. After annealing, the films exhibited strong PL emission. The PL spectra were composed of several peaks which originated from the transitions in Eu^{3+} ion, from 5D_0 to 7F_J ($J = 0, 1, 2, 3$, and 4). The intensity of PL emission was increased with increasing annealing temperature, which was due to the higher degree of crystallinity of the $\text{Y}_2\text{O}_3:\text{Eu}$ films. The PL intensity reduced above 1200 °C because yttrium aluminate phases, such as YAM, YAP, and YAG, were formed. The unannealed $\text{Y}_2\text{O}_3:\text{Eu}$ films were highly optically transparent. The transmittance decreased as annealing temperature increased due to increase in crystallite sizes.

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