Thin-film structure and fluorescence properties of sol-gel-synthesized $Y_{2-x}Eu_xO_3$ phosphors

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Eu-doped yttria ($Y_{2-x}Eu_xO_3$) thin-film phosphors were prepared using a sol-gel process with post-annealing at 900°C. The $Y_{2-x}Eu_xO_3$ samples showed cubic bixbyite structure with a gradual increase in the lattice constant ($\leq 0.5\%$) as x increases (≤ 0.22). The Eu-doped films exhibited strong photoluminescence (PL) near 2 eV at room temperature with well-resolved fluorescence peaks being ascribed to spin-flip f-f transitions, $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4, 6$), within trivalent $Eu^{3+}(f^6)$ ion. Among the six fluorescence lines, the intensity of the strongest 2.03-eV line ($J = 2$) varies significantly with the Eu content and its optimum value for the maximum PL strength is likely to be near $x = 0.1$. The Eu-doped films on the Al_2O_3 substrates exhibited significantly higher PL intensities than those on the Si substrates despite no significant difference in structural properties between the two species being observed. It can be understood by comparing the change of complex refractive index for the $Y_{2-x}Eu_xO_3/Al_2O_3$ and $Y_{2-x}Eu_xO_3/Si$ optical systems.

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1. Introduction

Yttria (Y_2O_3) has been under a great deal of attention recently due to a wide range of applications to microelectronics,¹⁾ optoelectronics²⁾ and luminescence technologies.³⁾⁻⁵⁾ Y_2O_3 crystallizes in a cubic bixbyite (Mn_2O_3) structure (body-centered-cubic unit cell) and is known to have a large band-gap energy (>5 eV), thus, is transparent in a wide optical frequency range.^{4),6)} Along with high thermal conductivity and crystallographic stability at high temperatures, Y_2O_3 has a large real-part of the dielectric constant ($\kappa \sim 16$ near DC regime), which is about 4 times larger than that of SiO_2 .⁷⁾ Due to such high- κ character, film-deposition of Y_2O_3 on Si substrates have been drawing interest for its possible replacement of amorphous SiO_2 as the transistor gate dielectric in ultra large-scale integrated circuits. With the optical transparency and large κ values, thin-film Y_2O_3 can be a proper waveguide in optoelectronic devices.

Y_2O_3 can be an excellent host for accommodating rare-earth (RE) ions such as Ce^{3+} and Eu^{3+} due to a large ionic radius of Y^{3+} comparable to those of the RE ions. Eu-doped Y_2O_3 compound is a phosphor material that has been under special attention due to its efficient red-fluorescence with the lifetime of several milliseconds³⁾ when the Eu^{3+} ion is excited by ultraviolet and electron-beam irradiation. Such RE-doped yttria materials are applicable for display and lighting devices and a number of candidates for red-green-blue phosphors have been developed in powder form. For these applications, physical and chemical properties of thin-film phosphors are also important but have not been so intensively studied as those of powder phosphors. For flat-panel-display devices, phosphor films have advantages in uniformity, thermal conductivity and spatial resolution compared to phosphor powders.⁸⁾ There were reports in which $Y_2O_3:Eu$ thin films exhibited luminescence intensity comparable to its powder samples.^{9),10)}

This work reports how Eu-doped Y_2O_3 ($Y_{2-x}Eu_xO_3$) thin-film phosphors are successfully deposited on substrates such as sapphire and silicon via a sol-gel method with post-annealing temperature (900°C) significantly lower than the melting temperature of bulk Y_2O_3 (2400°C).

As one of the methods feasible for depositing metal-oxide thin films on crystalline substrates, sol-gel spin-coating technique has advantages of simplicity and short performance time. The present sol-gel prepared $Y_{2-x}Eu_xO_3$ films exhibit intensive ~ 2 eV photoluminescence (PL) at room temperature comparable to those prepared by vapor-phase methods such as pulsed-laser deposition¹¹⁾⁻¹⁴⁾ and metallorganic chemical-vapor deposition.⁸⁾ The observed PL spectra contain well-resolved peaks that are identified as fluorescent transitions between different electronic configurations of the $4f^6$ system of Eu^{3+} ion. The effects of increasing Eu^{3+} content on the PL properties of the phosphor films have been investigated.

2. Experimental procedure

In the present sol-gel process, the precursor solution was prepared by first dissolving $Y(NO_3)_3 \cdot 6H_2O$ powders in 2-methoxyethanol. Then $Eu(NO_3)_3 \cdot 6H_2O$ powders were added and stirred at 60°C for 1 h. The substrates, $Al_2O_3(0001)$ and $Si(100)$ wafers, were spin-coated with the precursor solution at 2000 rpm for 20 s and then heated at 320°C for 80 s at each deposition step in order to remove the organic substances. This process was repeated until the desired film thickness was attained. The precursor films were then annealed in air at 900°C for 1 h to obtain the present $Y_{2-x}Eu_xO_3$ ($x = 0.01, 0.03, 0.05, 0.10, 0.17, 0.22$) films. The film thickness that can be achieved by one spin-coating cycle of the present sol-gel process was ~ 50 nm. Eu contents (x) of the $Y_{2-x}Eu_xO_3$ films were determined by energy-dispersive X-ray spectroscopy.

3. Results and discussion

As shown in the scanning-electron-microscopy images in Fig. 1, $Y_{2-x}Eu_xO_3$ ($x \leq 0.22$) thin films could be well deposited

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Fig. 1. Scanning-electron-microscopy top-view images of (a) $\text{Y}_2\text{O}_3/\text{Si}(100)$, (b) $\text{Y}_{2-x}\text{Eu}_x\text{O}_3/\text{Si}(100)$ ($x = 0.10$), (c) $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3(0001)$, (d) $\text{Y}_{2-x}\text{Eu}_x\text{O}_3/\text{Al}_2\text{O}_3(0001)$ ($x = 0.10$) films.

Fig. 2. X-ray diffraction patterns of (a) $\text{Y}_{2-x}\text{Eu}_x\text{O}_3/\text{Al}_2\text{O}_3(0001)$ and (b) $\text{Y}_{2-x}\text{Eu}_x\text{O}_3/\text{Si}(100)$ thin films.

on $\text{Si}(100)$ and $\text{Al}_2\text{O}_3(0001)$ substrates by using the present sol-gel deposition process. Uniform and crack-free films were produced by post-annealing the precursor films at 900°C . The present films with thicknesses of ~ 200 nm are fine-grained with the average grain size of ~ 30 nm. It is seen that the Eu-doped samples contain some larger grains (created by merger of neighboring grains) than those in the undoped ones. As shown by the XRD patterns in Figs. 2(a) and 2(b), pure and Eu-doped polycrystalline yttria films with the bixbyite structure (JCPDS 88-1040) were produced by the sol-gel process on $\text{Al}_2\text{O}_3(0001)$ and $\text{Si}(100)$ substrates, respectively. All the samples are seen to contain no secondary phases such as Eu_2O_3 and monoclinic Y_2O_3 crystallites. Most of the Eu ions in the $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ films are expected to keep the trivalency (Eu^{3+}) that those in the raw material $[\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ have and to occupy octahedral Y^{3+} sites (with C_2 or C_{3i} point symmetry) in the Y_2O_3 bixbyite lattice. Such Eu^{3+} substitution of Y^{3+} can take place with slight lattice distortion ascribed to the difference in ionic radius between Eu^{3+}

Fig. 3. PL spectra of $\text{Y}_{2-x}\text{Eu}_x\text{O}_3/\text{Al}_2\text{O}_3(0001)$ thin films. In the inset, PL spectrum of $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ ($x = 0.10$) film on $\text{Al}_2\text{O}_3(0001)$ substrate is compared to that on $\text{Si}(100)$ substrate.

(0.1087 nm) and Y^{3+} (0.1040 nm). The lattice constant of the $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ samples on Si (Al_2O_3) substrates estimated from the (440) peak position gradually increases from 1.059 (1.060) nm for $x = 0$ (in good agreement with 1.060 nm in JCPDS 88-1040) to 1.064 (1.065) nm (increase of 0.5%) for $x = 0.22$. The increase of the lattice constant with increasing Eu content is ascribed to the larger ionic radius of Eu^{3+} ion (by 4.5%) than that of Y^{3+} ion. However, the lattice constants of $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ nanoparticle samples (diameter ~ 5 nm) were reported to decrease from that of bulk Y_2O_3 .³⁾ The reason for such discrepancy between the film and nanoparticle samples is unclear at present.

The luminescence properties of the Eu-doped samples were investigated by PL measurements at room temperature using a He-Cd laser beam (wavelength $\lambda = 325$ nm) being incident 45° from the normal direction of the sample plane and the results are shown in Fig. 3. Distinct emission structures were observed in the red region (~ 2 eV) denoted as A, B, C, D, E and F in Fig. 3 with the most intense one (C) being peaked at 2.03 eV ($\lambda = 611$ nm). These emission lines in the $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ films are ascribed to the fluorescence originating from the electronic transitions within the $4f^6$ configuration of Eu^{3+} ion substituting Y^{3+} lattice sites of Y_2O_3 .^{3),15)} The fluorescence properties from Eu^{3+} ion as well as other rare-earth ions are known to be critically dependent on the symmetry of the host crystal.¹⁶⁾

The intermediate coupling scheme ($2S+1L_J$) has been successful in expressing a free-ion state of lanthanide elements having partially-filled $4f$ shells under strong spin-orbit interaction.¹⁵⁾ Thus, the ground and first-excited states of $\text{Eu}^{3+}(f^6)$ ion are represented by 7F_J ($0 \leq J \leq 6$) and 5D_J ($0 \leq J \leq 5$), respectively, with the energy being higher for larger J . When Eu^{3+} ion substitutes the Y^{3+} sites in the bixbyite Y_2O_3 lattice, the crystal field imposed by the octahedral O^{2-} ions induces a mixing between these f^6 configurations. The electric-dipole transitions between 7F_J and 5D_J manifolds are possible due to such crystal-field-induced mixing.

The observed fluorescence structures A, B, C, D, E, and F in Fig. 3 are ascribed to the $^5D_0 \rightarrow ^7F_J$ transitions.^{3),15)} Such spin-flip transitions are possible due to the relaxation of the spin-selection rule by strong spin-orbit interaction in Eu^{3+} ion. When the J-selection rule is adopted for the possible electric-dipole transitions,¹⁵⁾ the transitions to 7F_J with $J = 2, 4, 6$ are allowed,

Fig. 4. Comparison of 2.03-eV fluorescence intensities of $Y_{2-x}Eu_xO_3$ thin films deposited on $Al_2O_3(0001)$ and $Si(100)$ substrates.

while those with $J = 0, 1, 3, 5$ are forbidden. However, in actual materials, spectral lines due to the transitions that violate the J-selection rule are sometimes observed.¹⁵⁾ Thus, as the electric-dipole allowed transitions, the $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_4$, and $^5D_0 \rightarrow ^7F_6$ transitions are identified as the origin for the 2.03-eV (C), 1.91-eV (E), and 1.75-eV (F) peaks, respectively. The observed increase in the energy spacing between successive 7F_J states agrees with theoretical predictions.¹⁷⁾

The relative intensities of these transitions tend to depend strongly on the site symmetry of the substituting Eu^{3+} ion in the crystal structure of the Y_2O_3 host. The observed strongest emission intensity of the $^5D_0 \rightarrow ^7F_2$ line compared to the others might imply that the substituting Eu^{3+} ions prefer the C_2 site without inversion symmetry to the C_{3i} site with inversion symmetry in the bixbyite lattice. The fluorescence structure A peaked at 2.14 eV is assigned to the $^5D_0 \rightarrow ^7F_0$ transition. It is known to be possible by borrowing the intensity mainly from the $^5D_0 \rightarrow ^7F_2$ transition by the J-mixing effect.¹⁸⁾ The structure B consists of 3 peaks at 2.07, 2.09, and 2.11 eV that are equally spaced. It is assigned to $^5D_0 \rightarrow ^7F_1$ transition having a magnetic-dipole character. The intensity of such magnetic-dipole transition is insensitive to the site symmetry. The structure D peaked at 1.97 eV is assigned to $^5D_0 \rightarrow ^7F_3$ transition.

The variation of the 2.03-eV fluorescence intensity with the Eu content of the oxides was monitored for any practical applications to lighting devices. As shown in Fig. 4, the peak intensity of the 2.03-eV line is seen to be the highest at $x = 0.10$ and to decrease as x increases further. The observed decrease in the PL intensity for $x > 0.1$ implies an optimum Eu content near $x = 0.1$ for the maximum fluorescence strength in $Y_{2-x}Eu_xO_3$. The fluorescence strength of $Y_{2-x}Eu_xO_3$ is dominated by the electric-dipole $^5D_0 \rightarrow ^7F_2$ transition (2.03 eV) which is sensitive to the symmetry of the host crystal. The increase in the Eu content in the oxide must cause an increased disorder in the host crystal structure as well as an increase in the repulsive Coulomb interaction between neighboring Eu^{3+} ions. The reduction of the fluorescence intensity in $Y_{2-x}Eu_xO_3$ for $x > 0.1$ is mainly attributable to these two factors that reduce the f-f electric-dipole transition strength by affecting the symmetry of the f-states.

The fluorescence intensities of the $Y_{2-x}Eu_xO_3$ films on the Al_2O_3 substrates are compared with those on the Si substrates. As shown in Fig. 4, the fluorescence intensities of the Eu-doped films on the Al_2O_3 substrates are larger than those on the Si

substrates. Considering the observed identical PL structure of the $Y_{2-x}Eu_xO_3$ films on Al_2O_3 and Si substrates as shown by the inset of Fig. 3, the difference in the PL intensities can be understood in terms of the difference in the dielectric properties of the two substrates. Firstly, the real part of refractive index ($n \approx \kappa^{1/2}$) of Al_2O_3 and Si compared to that of the yttria is expected to affect the path length of the incident laser beam within the film layer. The refractive indices of Y_2O_3 , Al_2O_3 and Si for the photon energy ($E = 3.8$ eV) of the He-Cd laser are 2.0, 1.8 and 4.0, respectively.¹⁹⁾ Therefore, the $Y_{2-x}Eu_xO_3/Al_2O_3$ system is expected to allow more internal reflections of the laser-beam flux within the yttria film layer compared to the $Y_{2-x}Eu_xO_3/Si$ system. Thus, the former is expected to allow longer path length of the laser beam through multiple internal reflections, leading to a higher Eu^{3+} excitation rate than the latter. Secondly, Si has high absorption coefficient $\alpha = 4\pi k/\lambda$ (k = imaginary part of refractive index) in the visible-ultraviolet range, while it is negligible for Al_2O_3 . So, both the incident laser (3.8 eV) and the emitted fluorescence (~ 2 eV) intensities are expected to be reduced by the Si substrate. Thus, the difference in the PL intensity between the two phosphor systems can be understood mainly in terms of these two factors related to the dielectric properties of the substrates. The difference in grain size of the films may affect the observed PL intensity through the difference in their surface roughness.¹²⁾ But the small difference in grain size between the $Y_{2-x}Eu_xO_3$ films on Al_2O_3 and Si substrates as can be seen in the SEM pictures (Fig. 1) is not likely to affect the present PL result significantly.

4. Conclusions

Polycrystalline $Y_{2-x}Eu_xO_3$ ($x \leq 0.22$) phosphors were successfully prepared as thin films on Si and Al_2O_3 substrates by using a sol-gel process in which post-annealing of the precursor films were performed at 900°C, being significantly lower than the melting temperature of bulk Y_2O_3 . The $Y_{2-x}Eu_xO_3$ films have cubic bixbyite structure with the lattice constant gradually increasing with increasing x (0.5% for $x = 0.22$). The $Y_{2-x}Eu_xO_3$ films show strong PL in the red region with well-resolved fluorescence lines at room temperature. A number of spin-flip f-f transitions within Eu^{3+} ion, $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4, 6$), are identified from the PL spectra. The strongest fluorescence line at 2.03 eV, assigned to the electric-dipole transition to 7F_2 , implies that the Eu^{3+} ions favor the C_2 sites with no inversion symmetry in the bixbyite lattice. The fluorescence intensity of the Eu-doped films is expected to be maximized near $x = 0.1$. The $Y_{2-x}Eu_xO_3$ films deposited on the Al_2O_3 substrates showed significantly stronger PL intensity than those on the Si substrates. By comparing the change of real part of refractive index seen by the incident laser beam for the $Y_{2-x}Eu_xO_3/Al_2O_3$ and $Y_{2-x}Eu_xO_3/Si$ waveguide systems, the former is expected to allow a longer beam-path length and subsequently a higher Eu^{3+} excitation rate than the latter. The large absorption coefficient of Si also contributes to the difference between the two systems.

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