Effect of Substrate Temperature on the Structural and Luminescent Characteristics of RF-Magnetron-Sputtered ZnGa$_2$O$_4$:Dy^{3+} Thin Films

K. Mini Krishna, G. Anoop,* and M. K. Jayaraj[z]

Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi-682 022, India

ZnGa$_2$O$_4$:Dy^{3+} phosphor thin films were deposited on quartz substrates by radio frequency (rf) magnetron sputtering and the effect of substrate temperature on its structural and luminescent properties was investigated. Polycrystalline film could be deposited even at room temperature. The crystalline behavior, Zn/Ga ratio, and surface morphology of the films were found to be highly sensitive to substrate temperature. Under UV illumination, the as-deposited films at and above 300°C gave white luminescence even without any postdeposition treatments. The photoluminescent (PL) emission can be attributed to the combined effect of multicolor emissions from the single luminescence center Dy^{3+} via host-sensitization. Maximum PL emission intensity was observed for the film deposited at 600°C, and the CIE chromaticity coordinates of the emission were determined to be (x,y) = (0.34, 0.31).
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The development of flat-panel display (FPD) technology, such as field-emission displays (FEDs), plasma display panels (PDPs) and thin-film electroluminescent devices (TFELs), require highly efficient phosphor materials. Extensive research has now been triggered in the domain of oxide phosphors due to their excellent chemical stability over conventional sulfide phosphors. It is well known that sulfide phosphors degrade under electron beam exposure, thereby leading to contamination of emission tips and subsequent shortening of device lifetime. However, oxide phosphors exhibit excellent luminescent characteristics and better stability in vacuum without corrosive gas emission under electron bombardment.

Zinc gallate is a promising luminescent oxide material with a characteristic intrinsic blue emission[1] under UV or low-voltage electron excitation.[2] It possesses a cubic spinel crystal structure and a wide energy bandgap of about 4.4 eV, allowing tunability in the infrared-to-ultraviolet range and making it an ideal material for optoelectronic devices including FPDs, optical limiter for UV, and stable gas sensors.[3-8] It can also be used in vacuum fluorescent displays (VFDs) and FEDs as a low-voltage cathodoluminescent phosphor.[9-11] Additionally, ZnGa$_2$O$_4$ phosphor can be suitably doped to develop color-emitting phosphors using either transition metals like Co^{3+} (reddish orange),[12] Cr^{3+} (red),[13] or Mn^{2+} (green)[14] or rare earths (REs) like Eu^{3+} (red)[13] or Tb^{3+} (green).[15]

RE ions serve as excellent activators in modern lighting and display fields due to the abundant emission colors based on their characteristic 4f-4f or 5d-4f transitions. Trivalent dysprosium, a rare-earth activator with 4f^9 electronic configuration, is found to emit in the blue, yellow, and reddish regions of the electromagnetic spectrum.[16,17] Unlike the RE dopants Eu^{3+} and Tb^{3+}, the luminescence of Dy^{3+} cannot be excited using the common fluorescent lamps that have a strong and broad absorption band around 254 nm. This is because the excitation spectrum of Dy^{3+} consists of only narrow f-f transition lines from 300 to 500 nm, whereas its charge-transfer absorption band (CTB) and 4f^9-4f^{8}5d excitation band lie below 200 nm.[18] This drawback of Dy^{3+} luminescence can be overcome either by host sensitization[19,20] or by impurity ion sensitization.[21] Luminescence investigations in Dy^{3+}-doped Ga$_2$O$_3$ and ZnGa$_2$O$_4$ have already been reported.[22-24]

In this study, we have investigated the effect of substrate temperature on the structural and luminescent characteristics of ZnGa$_2$O$_4$:Dy^{3+} thin films grown on fused silica substrates by rf magnetron sputtering. The analysis serves as an initial approach toward the realization of oxide-phosphor-based TFEL devices on low-temperature substrates without any postdeposition treatments.

* Electrochemical Society Student Member.
[z] E-mail: mkj@cusat.ac.in

Experimental

Thin films of ZnGa$_2$O$_4$:Dy^{3+} were deposited on quartz substrates by rf magnetron sputtering. The target used was ZnGa$_{1.95}$O$_4$:Dy$_{0.05}$ powder prepared by the solid state reaction of constituent oxides. The starting materials, namely ZnO (99.99%, Alfa Aesar), Ga$_2$O$_3$ (99.99%, Alfa Aesar), and Dy$_2$O$_3$ (99.99%, Indian Rare Earths, Ltd.), were mixed stoichiometrically in ethanol medium and then fired at 1350°C for 12 h. The doping concentration was fixed at 2.25 atom %. The deposition was carried out at the substrate 4.5 cm away from the target in an Ar ambient of 0.015 mbar at an rf power of 125 W for 2 h. The substrate temperature was varied between room temperature and 700°C. The thickness of the samples was measured using Dektak 6M stylus profiler and the average growth rate was found to be 0.2 nm/s. The crystal structure of the films was analyzed using a Rigaku X-ray diffractometer using Cu Kα radiation (1.5414 Å). The transmission spectra were recorded using Jasco V-570 spectrophotometer. Room temperature photoluminescence (PL) emission and excitation spectra (PLE) were recorded using Jobin Yvon Fluoromax-3 spectrometer equipped with a 150 W xenon lamp. The cation composition ratio and surface morphology of the films were analyzed by X-ray fluorescence (XRF) and atomic force microscopy (AFM), respectively.

Results and Discussion

The X-ray θ-2θ diffraction patterns of ZnGa$_2$O$_4$:Dy^{3+} films (Fig. 1) match well with the standard reflections of the bulk. Highly adhesive thin films with (311) preferred orientation could be grown even at room temperature. The broadening of the (311) peak with substrate temperature may be attributed to the strain induced in the films by the uniform incorporation or substitution of dopant ions into the host lattice. The decline in crystalline nature may also be due to the increase in Ga/Zn ratio with substrate temperature, as evident from XRF studies. Also, it was observed that nucleation of grains with (311) plane as preferred orientation subdues with substrate temperature and the film growth is promoted along other planes like (440), (511), and (400). This is because surface energy plays a crucial role in film texturing, the surface-area-to-volume ratio being large in thin films. So higher substrate temperatures provide sufficient thermal energy to promote film growth thermodynamically along the densest direction.[25]

The variation of full width at half-maximum (fwhm) and lattice constant with substrate temperature is shown in Fig. 2. The lattice constant is found to decrease with substrate temperature. As the temperature of the substrate is increased, one should expect higher vacancy concentration in the deposited films due to the loss of Zn. The subsequent lowering of crystallinity in the films is quite evident from the increase in fwhm with substrate temperature. Minami et

Figure 1. XRD patterns of $ZnGa_2O_4:Dy^{3+}$ films on quartz substrates varying the substrate temperature.

Figure 3. (Color online) AFM images of films deposited at substrate temperatures (a) 200, (b) 400, and (c) 600°C. (d) Zn/Ga ratio with substrate temperature.

al.[7] have reported that such reduction in grain size favors the luminance properties in low-voltage phosphors because of their large surface area per unit volume. But as the temperature is raised to 700°C, the fwhm drastically rises, collapsing the crystallinity, which in turn is found to affect the luminescent properties adversely. This can also be attributed to the partial formation of the binary compound β-Ga_2O_3 in the film, Zn/Ga ratio being very low as evident from XRF data.

The AFM images of films deposited at substrate temperatures 200, 400, and 600°C are shown in Fig. 3. The AFM images reveal that the films exhibit a granular-shaped microstructure. The surface roughness of the films was found to be highly dependent on the substrate temperature and had a strong effect on the PL response of the films. The variation in Zn/Ga ratio of the films with substrate temperature is also shown in Fig. 3. Reduction in Zn/Ga ratio with substrate temperature is due to the re-evaporation of Zn at higher substrate temperatures, with the vapor pressure of Zn being higher compared to Ga.[10] Lee et al.[26] reported that control of Zn/Ga stoichiometry requires the use of mosaic $ZnGa_2O_4$/ZnO targets to compensate for Zn los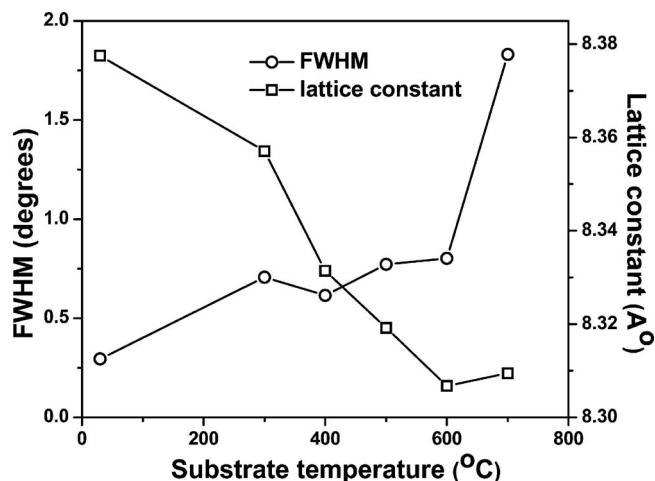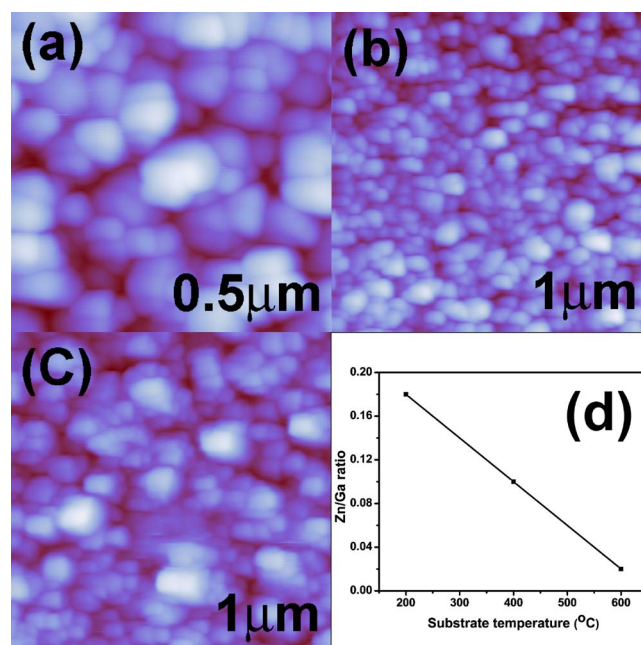s due to evaporation. These excess Ga atoms act as sensitizing sites in the host, influencing the luminescent properties positively.[27]

The transmission spectra of the film coated at a substrate temperature of 600°C is shown in Fig. 4. Almost 95% transparency is observed in the visible region and a strong absorption occurs around the bandedge of the host. The bandgap of the sample was determined to be 4.66 eV from the $[\alpha h\nu]^2$ vs $h\nu$ curve (inset of Fig. 4). All the deposited films exhibited similar characteristics and the bandgap values lie in the range 4.4 ± 0.3 eV.[2]

Figure 5 compares the room-temperature PL emission and excitation spectra of bulk $ZnGa_2O_4$ phosphor and $ZnGa_2O_4:Dy^{3+}$ film deposited at 600°C. The bulk sample exhibits a strong blue emission

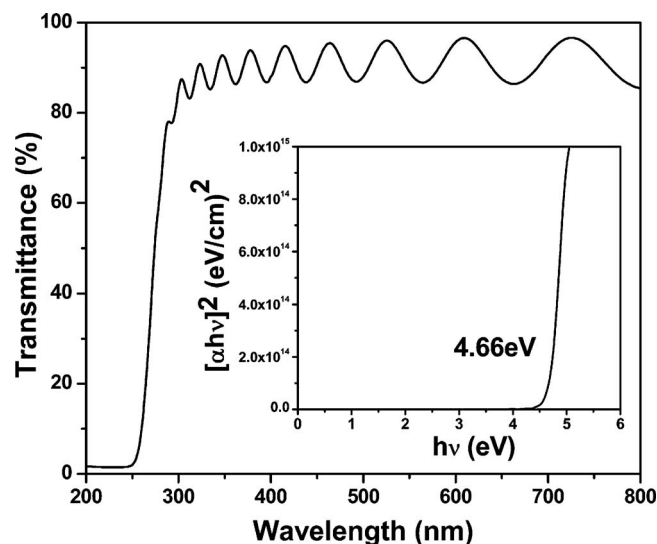**Figure 2.** Variation of fwhm and lattice constant of $ZnGa_2O_4:Dy^{3+}$ films with substrate temperature.

Figure 4. Transmission spectra of $ZnGa_2O_4:Dy^{3+}$ film deposited on quartz substrate at 600°C. Inset shows the $(\alpha h\nu)^2$ vs $h\nu$ curve for determining bandgap.
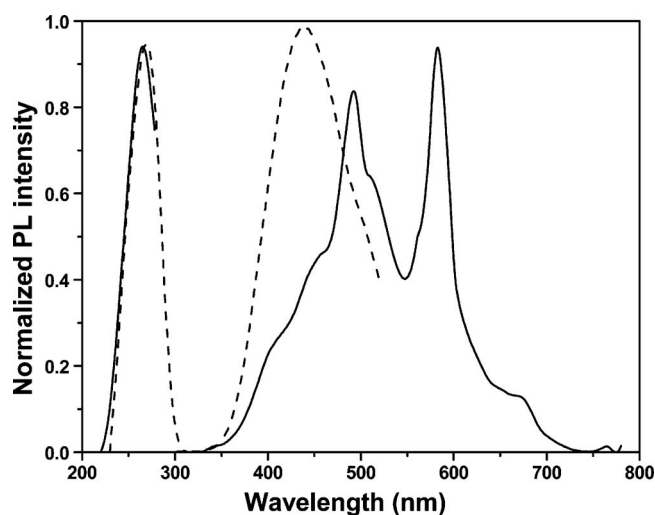
Figure 5. PL emission and excitation spectra of bulk $ZnGa_2O_4$ (dotted) [λ_{exc} = 270 nm and λ_{em} = 437 nm] and $ZnGa_2O_4$:Dy^{3+} film deposited at 600°C (solid) [λ_{exc} = 266 nm and λ_{em} = 583 nm].
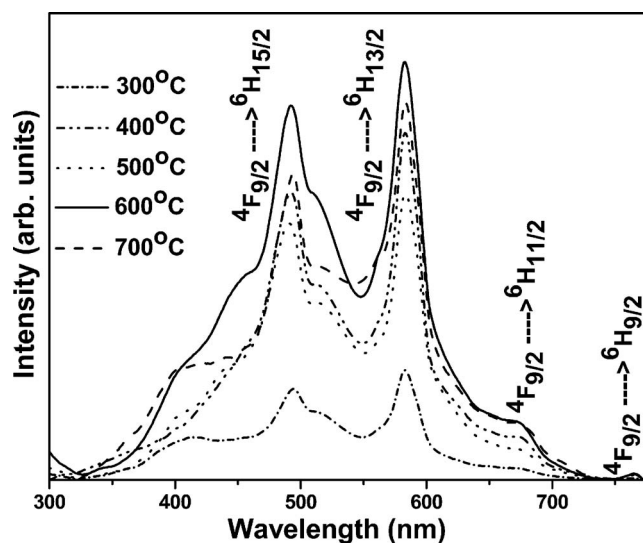

Figure 6. PL emission spectra of $ZnGa_2O_4$:Dy^{3+} films deposited at various substrate temperatures, λ_{exc} = 266 nm.

band peaking at 437 nm attributed to the self-activated transition of regular O_h Ga-O groups.[1] The film exhibits characteristic fluorescence transitions $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2, 9/2) of dopant ions along with a less-intense emission band of the host extending from UV to blue. The characteristic lines of the Dy^{3+} emission spectra fall in the blue, yellow, and red regions of the electromagnetic spectrum, with their peak maxima at 494, 583, 676, and 765 nm, respectively. The dominant emission is the one corresponding to the spectral transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$. The excitation spectrum of the film, recorded at the dominant emission wavelength of 583 nm, gave a broad intense band with a maximum at 266 nm. This was quite similar to the broad band (peak maximum at 270 nm) exhibited by the host excitation spectra recorded at an emission wavelength of 437 nm. Such excellent overlap between the two excitation spectra suggests that the film strongly absorbs at the host bandedge.[15] Moreover, the host emission is greatly suppressed in the Dy^{3+}-doped film and the fluorescent emission of the dopant is found to dominate the spectrum. All these facts strongly support an efficient energy transfer from the host lattice to the dopant ions in $ZnGa_2O_4$:Dy^{3+} films.

The PL emission spectra of films deposited on quartz substrates at various substrate temperatures is shown in Fig. 6 for an excitation wavelength of 266 nm. No luminescence was exhibited by the film deposited at room temperature. The films deposited at 100 and 200°C gave extremely weak emissions due to the improper incorporation of the Dy^{3+} ions. However, at and above 300°C, the films exhibited a white emission due to the simultaneous characteristic fluorescence transitions $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2, 9/2) of Dy^{3+} ions along with a less intense emission band of the host. The weak host emission band was found to blueshift with substrate temperature. This is suggestive of the fact that the substrate heating has resulted in the migration of Ga^{3+} ions to the tetrahedral sites[1] in the Zn-deficient films. The PL emission intensity was observed to be a maximum for the substrate temperature of 600°C. The PL intensity of the film deposited at 700°C falls due to the simultaneous effect of reduced crystallanity and low Zn/Ga ratio.

The $^4F_{9/2}$-$^6H_{13/2}$ spectral transition is more intense in comparison to $^4F_{9/2}$-$^6H_{15/2}$ in the PL emission spectrum of the films. This spectral property of Dy^{3+} provides some information on the site occupation of Dy^{3+} in the host lattice. The $^4F_{9/2}$-$^6H_{13/2}$ transition of Dy^{3+} ions is a hypersensitive transition with $\Delta J = 2$ and is strongly influenced by the crystal field environment. The ($^4F_{9/2}$-$^6H_{13/2}$) transition becomes dominant in the emission spectrum when Dy^{3+} ions are

located at a low-symmetry local site (without an inversion symmetry center).[23] Here, in the host lattice, Zn^{2+} ions occupy tetrahedral sites (T_d point symmetry without inversion center) and Ga^{3+} ions occupy octahedral sites (O_h point symmetry with inversion center). The ionic radii of Zn^{2+}, Ga^{3+}, and Dy^{3+} ions for six-coordination are, respectively, 0.074, 0.062, and 0.0912 nm. But Dy^{3+} ions rarely substitute Zn^{2+} due to charge imbalance. Also, a constant yellow-to-blue (Y/B) intensity ratio[28] (1.12 ± 0.05) of the films is suggestive of the fact that Dy^{3+} replaces Ga^{3+}. Because Zn-deficient films are being deposited at high substrate temperatures, Ga^{3+} ions have a strong tendency to occupy tetrahedral sites[16] or vacant interstitial sites without an inversion center. The replacement of these Ga^{3+} ions by the dopant Dy^{3+} ions therefore enhances its $^4F_{9/2}$-$^6H_{13/2}$ spectral transition.

The CIE coordinates of all the films deposited at various substrate temperatures lie in and around the position of achromatic white in the coordinate diagram (Fig. 7). The CIE chromaticity coordinates of the film deposited at 600°C which gives the maximum PL emission intensity was determined to be (x,y) = (0.34, 0.31).
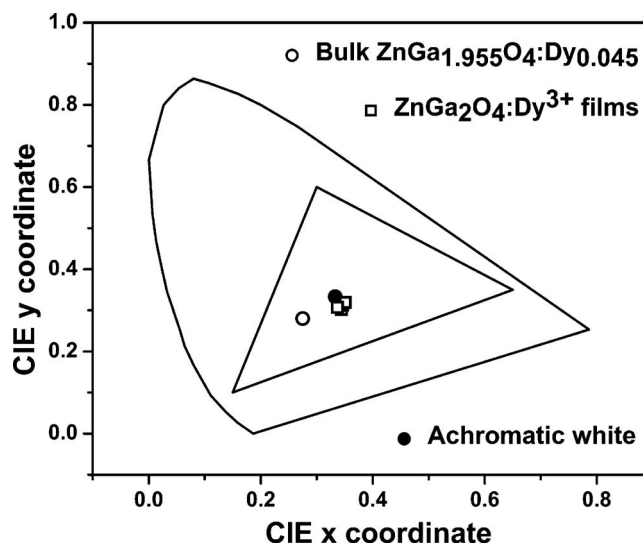

Figure 7. CIE color coordinate diagram $ZnGa_2O_4$:Dy^{3+} films, the CIE coordinates of bulk $ZnGa_2O_4$:Dy^{3+}, and achromatic white shown for reference.

The chromaticity coordinates of the $ZnGa_{1.95}O_4{:}Dy_{0.05}$ powder target with 2.25 atom % Dy content was found to be (0.27, 0.28).[24]

Conclusion

Thin films of $ZnGa_2O_4{:}Dy^{3+}$ could be grown on quartz substrates by rf magnetron sputtering at and above room temperature. The crystal structure, Zn/Ga ratio, and surface morphology of the films were found to be highly sensitive to substrate temperature. No luminescence was observed for the as-deposited film at room temperature that exhibited spinel-phase growth. But the films deposited at and above a substrate temperature of 300°C exhibited white luminescence even without any postdeposition annealing treatments. The emission from the single luminescence center Dy^{3+} is the result of host-sensitization. The film deposited at a substrate temperature of 600°C exhibited the maximum PL intensity. $ZnGa_2O_4{:}Dy^{3+}$ can therefore act as an active layer in ACTFEL displays. The work also suggests the use of low-temperature substrates other than the conventional ceramic substrates for device fabrication.

Acknowledgments

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