

Photoluminescent Studies in Co-sputtered ZnGa₂O₄:Mn Phosphor Thin Films

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Abstract: ZnGa₂O₄:Mn thin films have been deposited using RF magnetron co-sputtering technique on quartz substrates. The effect of substrate temperature on structural and optical properties is investigated. Polycrystalline films with preferred (311) orientation of normal spinel ZnGa₂O₄ were grown even at room temperature. The film grown at 600°C showed excellent green luminescence compared to films deposited at various substrate temperatures. The CIE coordinates of the film (x,y) = (0.136, 0.544) are comparable to that of powder phosphors (0.082,0.688). The luminescent behaviour degrades above and below 600°C due to improper substitution of Mn in the host lattice. The thin films can be used as an active layer in ACTFEL devices.

Keywords: Zinc gallate; Photoluminescence; ACTFEL devices.

Introduction

Recently, oxide phosphors are widely being investigated for display applications compared to the conventional sulphide-based phosphors. They are well known for their excellent stability in vacuum under irradiation of electrons and emit fewer harmful gases compared to sulphide phosphors, which makes them potential candidates for host materials in electroluminescent devices and flat panel displays. Zinc gallate (ZnGa₂O₄) is a promising oxide phosphor which serves as an excellent and efficient host material for thin film as well as powder electroluminescent devices [1,2]. Fabrication of multicolor emitting electroluminescent and field emission displays can also be realized by doping it with suitable dopants. The normal spinel structured semiconductor having wide band gap ($\approx 4.5\text{eV}$) is also used as a transparent electrode in optoelectronic devices. ZnGa₂O₄ has tetrahedrally coordinated Zn sites (T_d) and octahedrally coordinated Ga sites (O_h).

Mn doped zinc gallate phosphors give an excellent green emission where Mn²⁺ substitutes Zn²⁺ isoelectronically at tetrahedral sites. The intense green emission at 505nm is assigned to ⁴T₁-⁶A₁ transitions of unshielded 3d⁵ electrons of Mn²⁺.

Thin film phosphors are preferred to powder phosphors whenever high resolution and high contrast are required. Also, they are relatively insensitive to surface contamination compared to powders. Thin films of ZnGa₂O₄ have been deposited employing various methods such as Pulsed laser deposition (PLD) [2-4]. RF magnetron sputtering [5-9] etc.

In the present work, thin films of ZnGa₂O₄:Mn are deposited on quartz substrates using co-sputtering technique.

Experiment

Bulk ZnGa₂O₄ powder phosphor was prepared by mixing constituent oxides namely ZnO (99.99%) and Ga₂O₃ (99.99%) stoichiometrically in ethyl alcohol medium and is calcined at 1350°C for 12hrs. Thin films of ZnGa₂O₄ doped with Mn²⁺ were prepared using RF magnetron co-sputtering technique. The target used was stoichiometric pure ZnGa₂O₄ powder with a small pellet of (CH₃COO)₂Mn of diameter 8mm placed at the erosion area. The films were grown on glass and quartz substrates at room temperature and at higher temperatures in the range 500-700°C. The substrate to target distance was maintained at 4.5cm and the deposition was carried out for 2 hours under argon ambient of 0.02mbar. The rf sputtering power used was 100W. The crystal structures of the powder as well as thin films are identified using Powder X-ray diffractometer (Rigaku) with CuK_α radiation. The photoluminescent emission and excitation spectra of the samples were recorded using Spex-Fluoromax-3 Fluorimeter with 150W xenon lamp. Transmission spectra of thin films are recorded using JASCO V-570 Spectrophotometer.

Results and Discussions

Figure.1 shows XRD patterns of sputtered films on quartz substrates at different substrate temperatures. Thin films of ZnGa₂O₄:Mn with a preferred (311) orientation were deposited even at room temperature and above. As

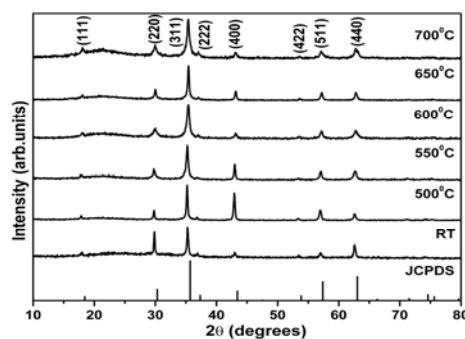


Figure1. XRD patterns of ZnGa₂O₄: Mn films deposited at different substrate temperatures on quartz

the substrate temperature is increased above 550°C, films shows highly preferred orientation along (311) plane. The JCPDS values are also given as reference.

The variation of FWHM and grain size at different substrate temperatures is shown in the figure 2. FWHM is found to decrease for the film grown at 500°C in

comparison to that deposited at room temperature. But as the temperature is increased FWHM increases rapidly, reaches a maximum for films grown at 600°C and then again decreases. Grain size was calculated using Scherrer's formula and it exhibits a variation in accordance with the inverse relation with FWHM. Since ZnGa₂O₄ powder has been fired at a high temperature, the powder phosphor will itself be Zn deficient. During sputtering, lighter atoms will scatter more and therefore Zn will get scattered more compared to Ga. As the substrate temperature increases, more Zn evaporation will take place. Therefore usually films grown will be Zn deficient resulting with high Ga/Zn ratio. As substrate temperature goes beyond 500°C, Mn starts replacing Zn at tetrahedral site which will result in broadening of peak. The film grown at 600°C exhibits a maximum FWHM and reduced grain size. But again when substrate temperature goes beyond 600°C, Mn starts re-evaporation which will reduce the FWHM and increase the grain size.

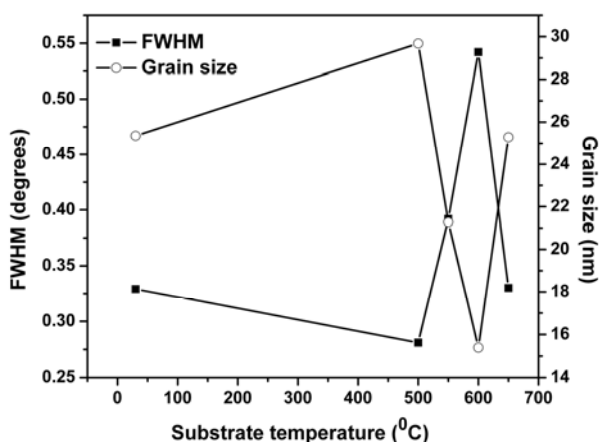


Figure 2. Variation of FWHM and grain size with substrate temperature

Even though all the films show orientation along (311) plane, only films grown at 600°C, 650°C and 700°C show PL emission at 508nm similar to that observed in powder phosphors. The room temperature photoluminescent spectra for films are shown in figure 3. The emission can be attributed to the crystal field perturbed ⁴T₁-⁶A₁ transitions of 3d⁵ electrons of Mn²⁺. The PL excitation spectrum was obtained for emission at 508nm. The PL excitation peak was observed at 290nm which is the direct excitation of Mn²⁺. We couldn't observe band to band excitation at 254nm observed by other authors due to the experiment limitation. It is known that if the excitation light has lower energy than the band gap energy of the host and is resonant with one of the excited states of 3d⁵ multiplet, direct light absorption is dominant [11]. Moreover, ZnGa₂O₄ being a low voltage phosphor, the simultaneous presence of best PL characteristics and reduced grain size can be accounted for [5].

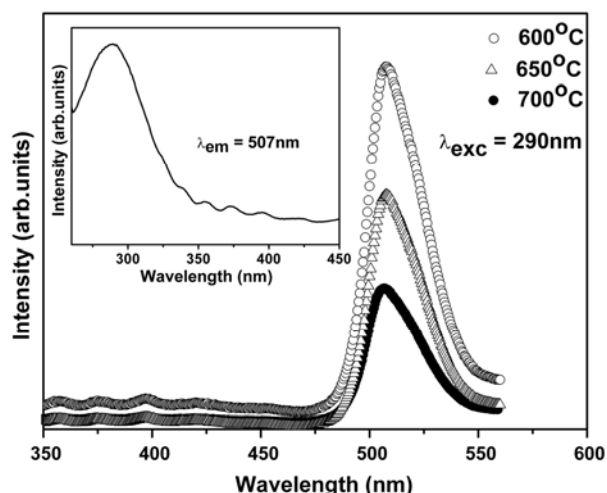


Figure 3. PL spectra of ZnGa₂O₄:Mn films grown at different substrate temperatures excited at 290nm. Inset shows corresponding excitation spectra

The basic mechanism involving PL emission is by non-radiative energy transfer. This is observed when incident photon is absorbed by the host lattice creating electron hole pair and through charge migration, trapping and recombination luminescence results. Here charge transfer to Mn²⁺ occurs via Ga³⁺ centers which act as sensitizer. Here maximum PL intensity is occurred for films grown at 600°C. It can be inferred that Mn²⁺ ions is successfully incorporated in to the lattice only at this temperature. As the temperature is increased, Mn²⁺ ions is re-evaporated and number of luminescent centers decreases which results in the reduction of luminescent intensity. The green emission band of ZnGa₂O₄:Mn thin film deposited at 600°C is compared with that of bulk in figure 4. The film is found to have a wider FWHM than the bulk. The film, being Zn deficient, is expected to possess more vacancies that effectively perturb the spinel arrangement and the crystal field associated with Mn²⁺ ions in the film. Consequently, the transition levels

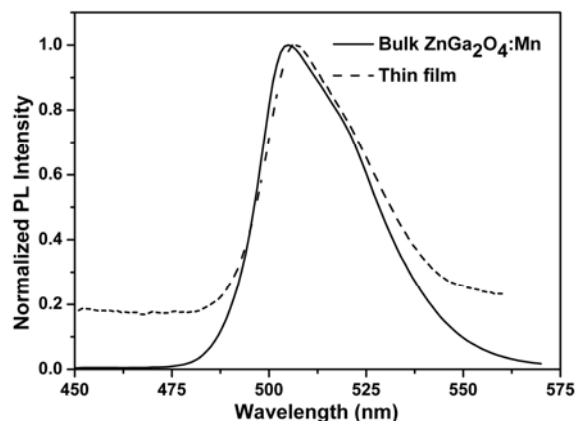


Figure 4. Emission spectra of bulk ZnGa₂O₄:Mn and the film grown at 600°C

of the optically active electrons in Mn²⁺ ions spreads out leading to broader emission bands.

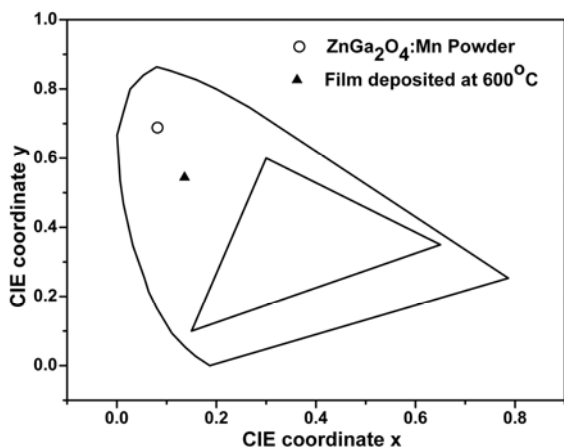


Figure 5. CIE values of $\text{ZnGa}_2\text{O}_4:\text{Mn}$ powder phosphor and thin film deposited at 600°C

The commission Internationale d'Elairage (CIE) values for powder as well as thin film deposited at 600°C is shown in the figure 5. The CIE coordinate shows the inferior nature of films to powder phosphor in terms of the purity of emission. This could be due to the interstitial Mn^{2+} or Mn^{2+} on a Zn^{2+} site with slightly distorted tetrahedral symmetry.

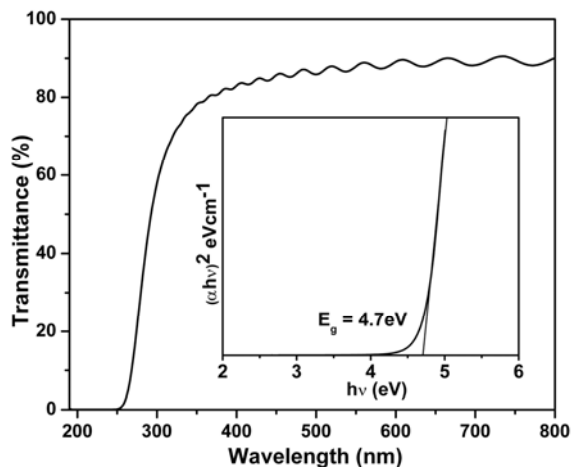


Figure 6. Transmission spectrum of $\text{ZnGa}_2\text{O}_4:\text{Mn}$ film deposited at 600°C . Inset shows its $(\alpha h\nu)^2$ Vs $h\nu$ plot

The transmission spectra of the $\text{ZnGa}_2\text{O}_4:\text{Mn}$ film deposited at 600°C is shown in the figure 6. The film shows a transparency of about 90% in the visible region. The band gap calculated from the $(\alpha h\nu)^2$ vs $h\nu$ plot was found to be 4.7eV (calculated by extrapolating the linear

portion of the curve) which is comparable with the powder phosphor which is 4.5eV.

Conclusions

Polycrystalline $\text{ZnGa}_2\text{O}_4:\text{Mn}$ thin films with preferred (311) orientation have been deposited using RF magnetron co-sputtering technique on quartz substrates at room temperature. The film grown at a substrate temperature of 600°C exhibits excellent green luminescence compared to films deposited at various substrate temperatures. The luminescent behaviour degrades above and below 600°C due to improper substitution of Mn in the host lattice. The thin films can be used as an active layer in ACTFEL devices.

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