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ZnGa₂O₄ THIN-FILM PHOSPHORS GROWN BY PULSED LASER ABLATION

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ABSTRACT

The growth and properties of undoped and Mn-doped ZnGa₂O₄ thin-film phosphors on (100) MgO and glass substrates using pulsed laser ablation were investigated. Blue-white and green emission were observed for as-deposited undoped and Mn-doped films, respectively. Luminescent properties as well as crystallinity were considerably affected by processing conditions and film stoichiometry. Films with enhanced luminescent characteristics were obtained on single crystal substrates without post-annealing.

INTRODUCTION

The development of efficient oxide thin-film phosphors has received considerable attention for use in field emission displays, thin-film electroluminescent devices, and plasma displays. For these applications, oxide thin-film phosphors offer potential advantages over sulfide-based materials due to their stable luminescent properties in high vacuum and absence of corrosive gas emission under electron bombardment.[1,2] ZnGa₂O₄, with a spinel crystal structure and wide energy band gap of about 4.4 eV, shows green emission when doped with Mn and blue luminescence without doping via transition of a self-activated center.[3] It has been suggested that full-color luminescence could be achieved using ZnGa₂O₄ phosphors by doping various activators like Mn²⁺, Eu³⁺, and Ce³⁺. [4] In addition, ZnGa₂O₄ is also potentially useful as ultraviolet-transparent electroconductive oxide after annealing under a reducing atmosphere at high temperature.[5]

The emission properties for undoped and doped ZnGa₂O₄ is very sensitive to preparation conditions with variations in luminescent behavior reported in the literature. For undoped ZnGa₂O₄, Yu and Lin [6] reported that cathodoluminescence (CL) spectra for ZnGa₂O₄ showed an emission shifting from the ultraviolet(UV) (349 nm) to the blue (457nm) regime as the mixing of ZnO and Ga₂O₃ varied from 1: 1 to 1.3:1. Itoh et al.[3] measured the maximum of the gallate band in the CL spectra to be at 470 nm at room temperature. Hsu et al. [7] showed a broad-band photoluminescence(PL) emission extending from 375 to 700 nm with a maximum emission peak at 470 nm under an excitation wavelength of 254 nm. Fluorescence at 432 nm has also been reported by Jeong et al. [8] In the case of Mn-doped ZnGa₂O₄, emission at 508 and 666 nm were reported for different firing conditions by Yu and Lin [6]. Therefore, an understanding of how processing conditions affect the microstructure and luminescent properties of ZnGa₂O₄ phosphor is essential to obtaining high performance thin-film phosphor materials. Moreover, there has been few reports focusing on the emission

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behavior of ZnGa_2O_4 thin-film phosphors. In this study, we are investigating the growth and luminescent properties of un-doped and Mn^{2+} doped ZnGa_2O_4 thin films using pulsed laser ablation.

EXPERIMENTS

Pulsed-laser deposition (PLD) was used to synthesize the undoped and Mn-doped ZnGa_2O_4 films. Un-doped and doped with 0.5% Mn polycrystalline 1 inch dia. ZnGa_2O_4 ablation targets were prepared by mixing and pressing ZnO [Alfa, 99.9995%] Ga_2O_3 [Alfa, 99.999%] and MnO_2 [Alfa, 99.999%] powders, followed by sintering in air at 1250 °C for 24 hours. Three different types of targets consisting of 1) a single ZnGa_2O_4 and $\text{ZnGa}_2\text{O}_4\text{:Mn}$, 2) the area portion of ZnGa_2O_4 (or $\text{ZnGa}_2\text{O}_4\text{:Mn}$)/ ZnO of 75%/25% (mosaic I) and 3) 50/50% (mosaic II) targets were used.

The films were grown using an excimer KrF laser with a wavelength of 248 nm. The laser fluence was approximately 3.3 J/cm² and the repetition rate used was 10Hz. Approximately 200 – 300 nm thick films were grown at temperatures ranging from 400 to 700 °C with an Ar-O_2 gas mixture. The oxygen content was varied from 0 to 100 vol% with the total chamber pressure ranging from 60 to 100 mTorr. (100) MgO single crystal and Corning 7059 glass were used as substrates. Crystal structure was investigated using x-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation (0.15406 nm wavelength). Compositional analysis was performed by energy dispersive x-ray spectroscopy (EDX). The photoluminescence (PL) spectra were measured at room temperature using a broad band incoherent UV light excitation source with a dominant excitation wavelength of 255 nm.

RESULTS AND DISCUSSION

Cation Stoichiometry

Figure 1 shows the compositional variation of the films deposited using the various types of targets and deposition conditions. Significant Zn loss was observed in films deposited from a stoichiometric single target due to the high vapor pressure of Zn as that of Ga. To compensate for the Zn deficiency in the films, mosaic targets consisting of various ZnGa_2O_4 (or $\text{ZnGa}_2\text{O}_4\text{:Mn}$)/ ZnO surface area ratios were used. For any given target selection, the ratio of Zn/Ga decreased considerably with increasing substrate temperatures. The loss of Zn in the films at elevated temperature has been reported by several researchers. Hsieh et al. [9] obtained rf magnetron sputtered ZnGa_2O_4 films with Zn/Ga ratio of 0.28 at 600 °C. Lee et al. [10] also reported that Mn-doped ZnGa_2O_4 thin film with the ratio of 0.12 was obtained using a stoichiometric target.

Increasing the oxygen partial pressure during deposition significantly reduced the loss of Zn in the films. Ablated species consist of metallic Zn, Ga and Zn-O, Ga-O, and Zn-Ga-O molecules. The metallic Zn is more likely to evaporated from the heated substrate than other species due to its relatively higher vapor pressure. Introduction of additional oxygen content will produce more Zn-O molecules through gas-phase collisions of Zn species with oxygen. This process lessens the probability of desorption of Zn species from the substrate and results in the incorporation of more Zn in the films. Note that near stoichiometric films were

attained at the substrate temperature of 600 °C or higher under $P_{O_2}=60$ mTorr and total pressure of 100 mTorr with the O_2/Ar ratio of 3:1.

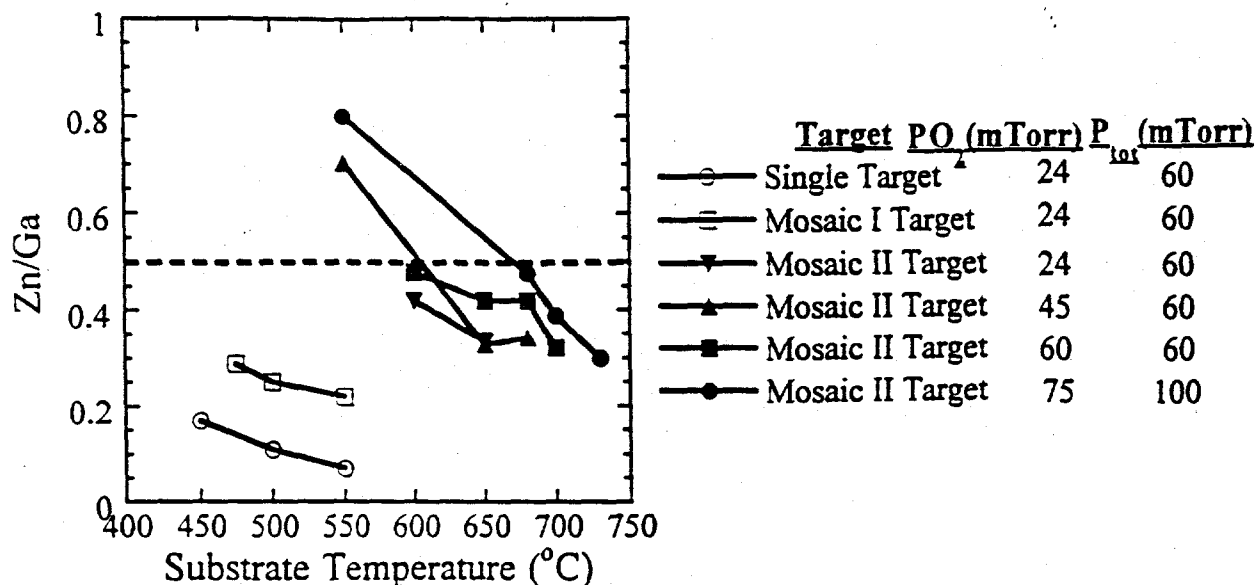


Fig.1. Variation of Zn/Ga ratio in $ZnGa_2O_4$ films with various types of targets and substrate temperatures.

XRD Results for $ZnGa_2O_4$ Thin Films

Epitaxial films were obtained on (100) MgO single crystal substrates under proper growth conditions. The lattice mismatch between $ZnGa_2O_4$ ($a=0.8335$ nm) and MgO ($a=0.4211$ nm) is about 1%. The x-ray $\theta-2\theta$ scan in Fig.2 (a) shows the crystalline orientation for an epitaxial films grown on (100) MgO at 700 °C using a mosaic II target under P_{O_2} of 60 mTorr. Randomly-oriented polycrystalline films with poor crystallinity were obtained on glass substrates under similar conditions (Fig.2 (b)).

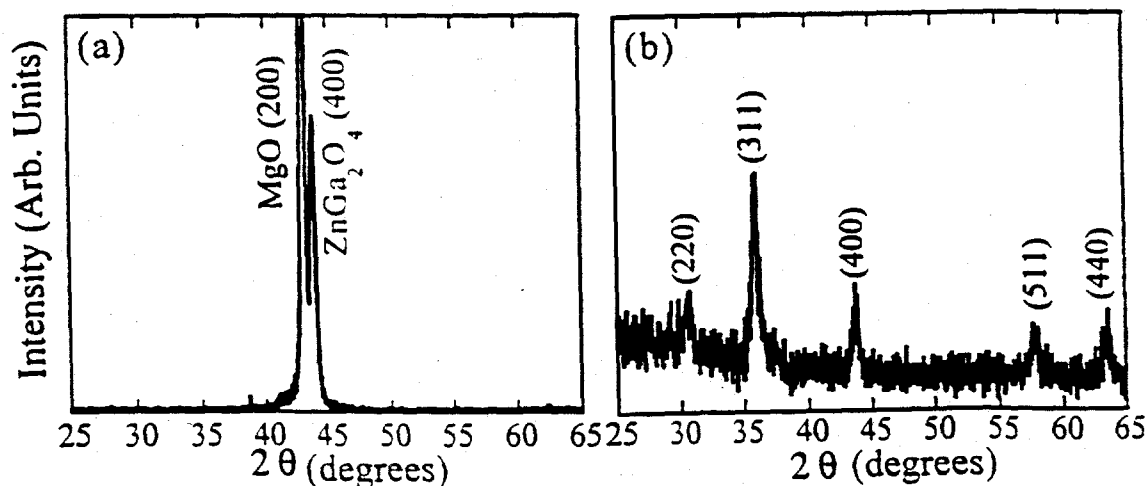


Fig. 2. X-ray $\theta-2\theta$ scans $ZnGa_2O_4$ films deposited on (a) (100) MgO single crystal and (b) glass substrate.

Photoluminescence of ZnGa_2O_4 Thin Films

Typical PL spectra for ZnGa_2O_4 powder, as-deposited epitaxial films on (100) MgO, and randomly-oriented polycrystalline films on glass substrates are shown in Fig. 3. Different PL characteristics was observed for the different types of materials. The powder, epitaxial, and polycrystalline film emissions appear blue, blue-white, and green-white, respectively. Powders exhibit a broad-band emission extending from 415 to 700 nm, peaking at 436 nm while the epitaxial film reveals a more broad-band emission extending from 415 to 700 nm with a maximum emission peak at 479 nm under the excitation wavelength of 255 nm. The emission for the polycrystalline films on glass substrate shows much lower PL intensities. This appears to be related to crystallinity, although a chemical reaction between the glass and film can not be ruled out. Emissions lower than 415 nm could not be measured due to the limitation of the measuring system. These results differ somewhat from that previously reported in the literature. It is reported that CL spectra of ZnGa_2O_4 reveal a peak at 457 nm[6] or 470 nm[3,9] while the PL peak is located at 432 nm[8], 450nm[11] or 470 – 490 nm[3,7]. A peaking at about 436 nm is ascribed to the $^4\text{T}_2 \rightarrow ^4\text{A}_2$ transition in the octahedral structure.[6] The shift in emission to about 450 and 470 nm is not clearly understood. The PL spectra for the films on (100) MgO substrates appears to be composed of several overlapping emission bands. Preliminary deconvolution reveals three peaks at wavelength of about 436, 457 and 480 nm.

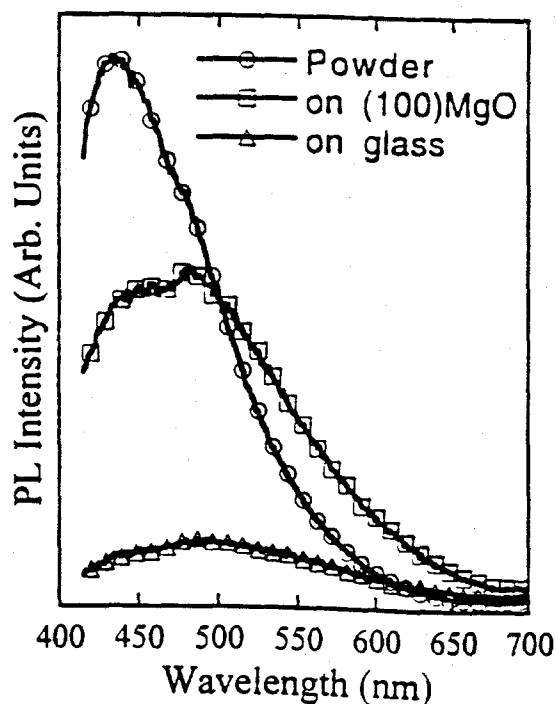


Fig. 3. PL emission spectra of undoped ZnGa_2O_4 powder, epitaxial film on (100) MgO single crystal, and polycrystalline film on glass substrates. Powder intensity divided by factor of 10.

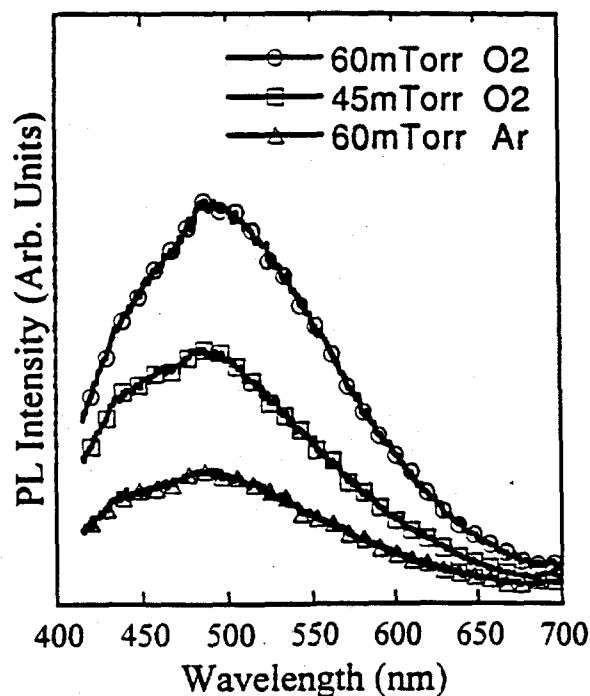


Fig. 4. PL emission spectra for ZnGa_2O_4 films on (100) MgO substrates at 650 °C using a mosaic II target under different P_{O_2} . $\text{P}_{\text{tot}} = 60\text{mTorr}$

Fig. 4 shows the PL emission spectra of ZnGa_2O_4 films on (100) MgO substrates at 650°C using a mosaic II target under different P_{O_2} . By decreasing the ratio of O_2/Ar , the PL intensity at 436 nm become comparable to that of 480 nm and the emissions shift to shorter wavelength with reduced integrated PL intensities. This behavior might be ascribed to Zn deficiency in the films with decreasing oxygen partial pressure. Similar behavior has been reported by Yu and Lin[6]. They report that the emission from ZnGa_2O_4 thin films shifts to shorter wavelength gradually from 470 to 360 nm with decreasing Zn/Ga ratio in the films. The reduced integrated PL intensities result from the formation of Ga_2O_3 in the films. We observed a weak diffraction peak of Ga_2O_3 in the films deposited at $\text{P}_{\text{O}_2}/\text{P}_{\text{Ar}}=3:1$ and 2:3 with $\text{P}_{\text{tot}}=60\text{mTorr}$. The relative intensity of the Ga_2O_3 phase increased with decreasing $\text{P}_{\text{O}_2}/\text{P}_{\text{Ar}}$, correlating with Zn deficiency in the films. Note that the emission at 480 nm is predominant over that at 436 nm in the spectra for the films deposited at 680 °C or lower. The film grown at 700 °C has a PL spectrum composed of comparable emission bands at 436 nm and 480 nm. This result indicates that brighter and more bluish luminescence can be attained through controlling the substrate temperature and oxygen content precisely. In this study, the film deposited at 700 °C or higher and oxygen pressure of 100 mTorr reveals enhanced blue-white photoluminescence as shown in Fig. 5. To compare the spectrum, the emission for the films deposited at 650 °C under P_{O_2} of 60 mTorr is inserted.

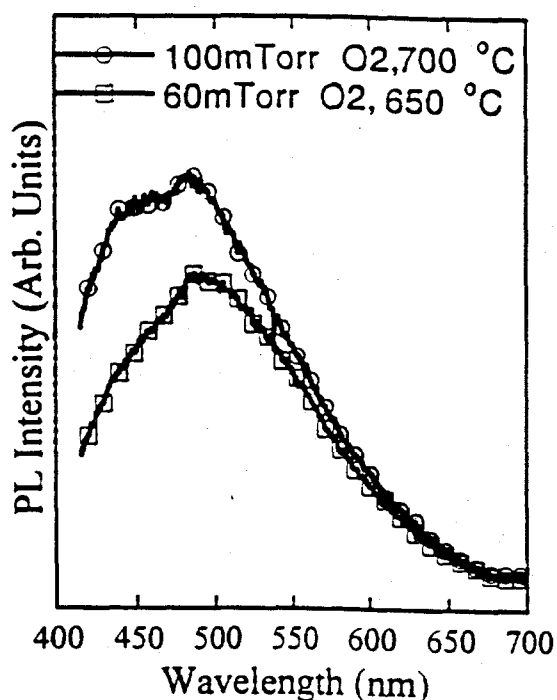


Fig. 5. PL emission spectra for ZnGa_2O_4 films on (100) MgO substrates.

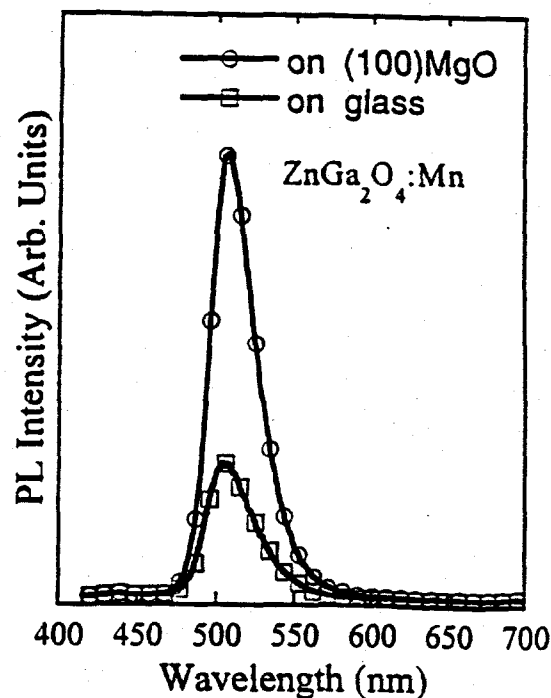


Fig. 6. PL emission spectra for 0.5% Mn doped ZnGa_2O_4 films on (100) MgO and glass substrates.

Photoluminescence of Mn-doped ZnGa_2O_4 Thin Films

Figure 6 shows PL spectra for Mn-doped ZnGa_2O_4 thin films on (100) MgO and glass substrates. The films exhibit a narrower band emission extending from 470 to 580 nm, peaking

at about 506 nm. The emission band is primarily attributed to the transition ${}^4T_1 \rightarrow {}^6A_1$ of the 3d electrons in the Mn^{2+} ion which occupies the fourfold coordinated Zn position in the host material lattice.[12] The full-width-half-maximum(FWHM) of the spectrum was about 35 nm, compared to that of undoped $ZnGa_2O_4$ at about 180 nm.

CONCLUSIONS

Luminescent undoped and Mn-doped $ZnGa_2O_4$ thin-film phosphors were synthesized on (100) MgO and glass substrates using pulsed laser ablation. The emission for $ZnGa_2O_4$ thin films exhibits a broad-band emission extending from 415 to 700 nm, peaking at about 436, 457, and 480 nm dependent on growth conditions. Mn-doped $ZnGa_2O_4$ shows a narrower emission band ranging from 470 to 580nm, peaking at 506 nm. The Zn/Ga ratio governs both crystallinity and luminescent characteristics, and was significantly affected by substrate temperature and oxygen pressure. Epitaxial films with good luminescence properties were obtained on single crystal substrates without post-annealing by controlling the processing conditions precisely.

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