

Photoluminescence of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) Thin Films

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Mn-doped $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x$ (M=S, Se) thin film phosphors have been grown using a pulsed laser deposition technique under various growth conditions. The structural characterization carried out on a series of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) films grown on MgO(100) substrates using Zn-rich ceramic targets. Oxygen pressure was varied from 50 to 200 mTorr and Zn/Ga ratio was the function of oxygen pressure. XRD patterns showed that the lattice constants of the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) thin film decrease with the substitution of sulfur and selenium for the oxygen in the ZnGa_2O_4 . Measurements of photoluminescence (PL) properties of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) thin films have indicated that MgO(100) is one of the most promised substrates for the growth of high quality $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) thin films. In particular, the incorporation of Sulfur or Selenium into ZnGa_2O_4 lattice could induce a remarkable increase in the intensity of PL. The increasing of green emission intensity was observed with $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ and $\text{ZnGa}_2\text{O}_{3.925}\text{S}_{0.05}\text{:Mn}^{2+}$ films, whose brightness was increased by a factor of 3.1 and 1.4 in comparison with that of $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$ films, respectively. These phosphors may promise for application to the flat panel displays.

Keywords : Photoluminescence, Thin film, Pulsed laser ablation, $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$

1. INTRODUCTION

For the development of flat panel display devices, such as field emission displays (FEDs), plasma display panels (PDPs), and thin-film electroluminescent devices, highly efficient phosphor materials has been required. Recently, zinc gallate (ZnGa_2O_4) and Mn-doped ZnGa_2O_4 have attracted enormous attention for applications in vacuum fluorescent display (VFD) and field emission display (FED) as a low-voltage cathodoluminescence phosphor[1-4]. ZnGa_2O_4 has a spinel structure with space group of Fd_{3m} and an energy band gap of about 4.4 eV and shows blue photoluminescence without doping via transition of a self-activated center. In normal spinel structure, Zn^{2+} ions occupy the tetrahedrally coordinated sites, whereas Ga^{3+} ions occupy the octahedrally coordinated sites. Jeong et al[5]. did report the new self-activated optical center in ZnGa_2O_4 related to tetrahedrally coordinated Ga-O groups. The emission shifts to green by activation with Mn^{2+} ions in tetrahedral host lattice sites[3]. The green emitting Mn^{2+} site in $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$ is generally accepted as tetrahedrally coordinated, but there are two kinds of ions which are tetrahedrally coordinated where Mn^{2+} ions can be replaced in ZnGa_2O_4 [5]. A given optical center in different host lattice will exhibit different optical properties due to the changes of the direct surroundings of the center. When we substitute

oxygens with sulfurs or selenium in ZnGa_2O_4 , i.e., $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x$ (M=S, Se), we can expect some changes on its optical properties.

Among the several thin film deposition techniques, pulsed laser deposition has been eagerly used for high quality ZnGa_2O_4 thin films[6-8]. Thin film phosphors have several advantages over powders, such as higher lateral resolution from smaller grains, better thermal stability, reduced outgassing, and better adhesion to the solid surface[9]. However, the biggest hindrance in the use of phosphors in thin films form is their low brightness and efficiencies in comparison to those of bulk powder materials.

Although numerous studies have been performed to improve the luminescent intensity of phosphor materials, the fundamental relationship between structural properties and luminescent characteristics in thin film phosphors is not fully understood. In this study, we will investigate the characteristics of luminescence for the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ (M=S, Se) phosphor thin films that are fabricated by pulsed laser deposition (PLD) on MgO (100) substrates. By changing the fabrication conditions and the concentrations of dopants (M=S, Se), we will measure the crystallinity, and surface morphology and PL spectrum and analyze the relationship between the fabrication conditions and characteristics of luminescence. Therefore, we could develop the superior phosphors that improve the luminescent efficiency.

2. EXPERIMENTAL

Zn-rich $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) powder samples ($2\text{ZnO} + 1.5\text{Ga}_2\text{O}_3$) were synthesized through solid state reactions of ZnO [Alfa, 99.999%], Ga_2O_3 [Alfa, 99.999%], elemental sulfur or selenium and MnO in the evacuated quartz tube at 1000°C for 12 hours in an electric furnace. To compensate for the loss of Zn ions during the deposition, the Zn-rich powder samples were used. The doping mole fraction of Mn^{2+} in the Zn-rich $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x$ ($\text{M}=\text{S}, \text{Se}$) powder was fixed at 0.02, and the x value in $\text{ZnGa}_2\text{O}_{4-x}\text{S}_x$ and $\text{ZnGa}_2\text{O}_{4-x}\text{Se}_x$ was 0.05 and 0.075, respectively. The films were grown by pulsed laser ablation using an excimer ArF laser with a wavelength of 193 nm. The beam of excimer laser was focused on the surface of Zn-rich $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) ceramic targets (with 1 inch diameter, and hot pressed and thermally annealed) with a spot size of about $1\text{ mm} \times 2.5\text{ mm}$. The distance between target and substrate was kept at about 40 mm. The laser fluence was approximately 3.5 J/cm^2 and repetition rate used was 5 Hz. The oxygen growth pressure was varied from 50 to 200 mTorr. A variety of characterization techniques were employed to study various properties of the as-grown $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films, including a x-ray diffraction (XRD) for film structure, atomic force microscope (AFM) for surface morphology and roughness. The PL spectra were measured at room temperature using a broadband incoherent ultraviolet (UV) light excitation source with a dominant wavelength of 232 nm.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns as-grown $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$, $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}:\text{Mn}^{2+}$ and $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$ films deposited on MgO (100) substrates at oxygen pressure 100 mTorr and substrate temperature 600°C . The $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films were perfectly crystallized. ZnGa_2O_4 has a spinel cubic structure ($a = 0.8335\text{ nm}$) and the lattice mismatch is less than 1 % with MgO ($a = 0.4211\text{ nm}$). Epitaxial films were certainly obtained on MgO (100) substrates under certain deposition conditions due to the low lattice mismatch. The x-ray θ - 2θ scan in Fig. 1 shows the crystalline orientation for epitaxial films grown on (100) MgO at 600°C . The XRD patterns of films reveal a (400) ZnGa_2O_4 diffraction peak at 44° with an additional diffraction peak near 30° , which is likely associated with a (400) Ga_2O_3 phase. As can be seen from this figure, Zn loss was observed in the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films deposited using a Zn-rich $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) ceramic targets due to the relatively high vaporization pressure of Zn. The shift of (400) ZnGa_2O_4 peaks are observed. In the case of $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$ film, the (400) ZnGa_2O_4 diffraction peaks

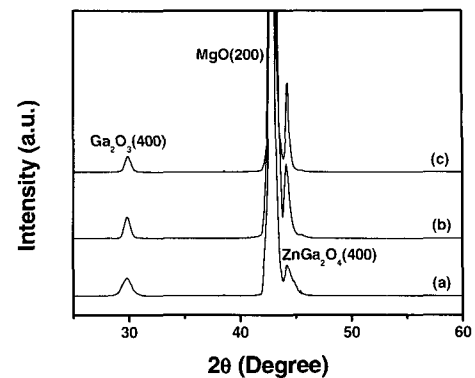


Fig. 1. A comparison of XRD patterns in as-grown (at 600°C) $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) thin films (a) $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$, (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}:\text{Mn}^{2+}$, (c) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$.

shift toward larger angles. Also a very small change in lattice constant is observed and the lattice constant of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) decrease when oxygen is substituted with sulfur (S) or selenium (Se) in ZnGa_2O_4 films. This observation is in contradiction to the ionic radius argument. This result indicates that the substitution of S or Se increases the covalency of ions and then reduces the lattice constant. Two possible variations of the lattice constants occur in the tetrahedral sites in the ZnGa_2O_4 when S, Se and Mn are added. One possibility of the variation is the substitution of oxygen with S or Se in forming tetrahedrons. Another possible change is the sites where the Mn^{2+} ions are located in tetrahedrons, i.e. ZnO_4 or GaO_4 [5].

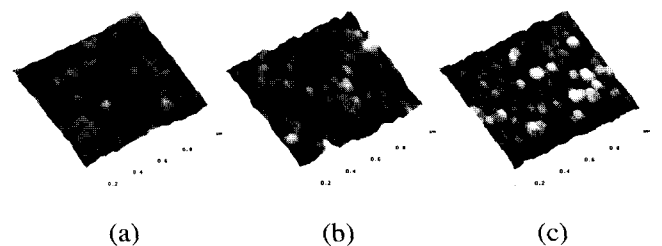


Fig. 2. A comparison of AFM images in as-grown (at 600°C) $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) thin films (a) $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$, (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}:\text{Mn}^{2+}$, (c) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$.

Figure 2 shows the atomic force microscope (AFM) images of as-grown (at 600°C) thin films (a) $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$, (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}:\text{Mn}^{2+}$, (c) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$. Surface morphologies of the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films revealed by an AFM images on a surface area of $1\mu\text{m} \times 1\mu\text{m}$. As one can see from these pictures, the variations in morphology are evident for the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films grown with the substitution of S or Se for oxygen in

ZnGa_2O_4 lattice. The surface roughness is very related to the crystallinity and average grain size of the films. According to the results of Fig. 1, when we substituted oxygens with sulfur or selenium, the intensity of (400) diffraction peak increased. The average grain size and roughness are increased due to the improved crystallinity of the films by S or Se doping. Films with different roughnesses were obtained by substituting oxygen with S or Se and the values of root mean square (rms) roughness of $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$ and $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ measured by AFM, were found to 3.25 nm, 5.43 nm and 10.92 nm, respectively. Roughness of the $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films had a strong effect on the PL response of the films.

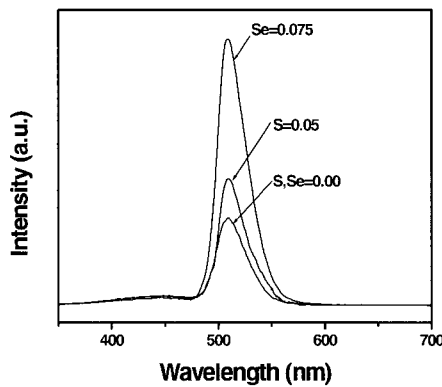


Fig. 3. A comparison of PL spectra in as-grown (at 600 °C) $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) thin films (a) $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$, (c) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$.

The photoluminescence (PL) spectra of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x\text{:Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films are shown in Fig. 3. The films exhibit a broad band emission extending from 470 to 550 nm, peaking at 509 nm. The emission band can be primarily attributed to the transition ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ of the 3d electrons in the Mn^{2+} ion. When we substitute oxygens with S or Se in ZnGa_2O_4 , we can expect some changes on its optical properties. A given optical center in different host lattice will exhibit different optical properties due to the changes of the direct surroundings of the center. The emission intensity of the $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ films exhibits the strongest among the samples studied in this work. The peak intensity of PL of the $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ films is about a factor of 3.1 times brighter than that of the $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$ films and enhanced about a factor of 2.1 times in comparison with that of $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$ films. Thus, since the environment change of the GaO_4 tetrahedron into the $\text{Ga}_2\text{O}_{4-x}\text{M}_x$ ($\text{M}=\text{S}, \text{Se}$) enhances the Ga^{3+} absorption, the emission intensity consequently increases. The oscillation strength of the $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$ and $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ films in the absorption of both Ga^{3+} and Mn^{2+} is stronger than that of the $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$ film. This trend that

occurs in the absorption leads to the enhancement of the emission intensity[10].

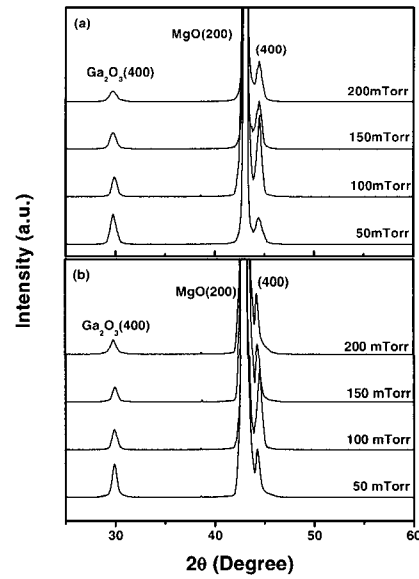


Fig. 4. XRD patterns of (a) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ and (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$ films as a function of oxygen pressure.

Figure 4 shows the XRD patterns of the as-grown (a) $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ and (b) $\text{ZnGa}_2\text{O}_{3.95}\text{S}_{0.05}\text{:Mn}^{2+}$ films deposited on $\text{MgO}(100)$ substrates at the fixed substrate temperature 600 °C with the different oxygen pressures. The oxygen pressure significantly influenced formation of the both films. The films grown under low oxygen pressure reveal a (400) ZnGa_2O_4 peaking at 44 ° with an additional diffraction peak near 30 °, which is likely associated with a Ga_2O_3 phase. The variation of Zn/Ga ratio in the films also depends on the oxygen pressure during deposition. Reduced Ga_2O_3 diffraction peak intensity was observed with an increasing oxygen pressure in both films. Introduction of additional oxygen will produce more ZnO molecules through gas-phase collisions of Zn species with oxygen. Increased oxygen pressure reduces the probability of vaporization of Zn species from the heated substrates and results in the incorporation of more Zn in the both films.

Shown in Fig. 5 are the plots of PL intensity and rms roughness of $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ thin films as a function of oxygen pressure. Note that initially the PL intensity and rms roughness of $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}\text{:Mn}^{2+}$ films increase linearly with oxygen pressure, while the initial increase on both quantities decreases as the oxygen pressure increases from 100 to 200 mTorr. Maximum PL intensity was observed at an oxygen pressure of 100 mTorr, which relates to the ratio of Zn/Ga and surface roughness of the films. The reduction in PL intensity with reduced $\text{P}(\text{O}_2) = 50$ mTorr correlates with the too much formation of the Ga_2O_3 phase due to the severe Zn deficiency and lower surface roughness.

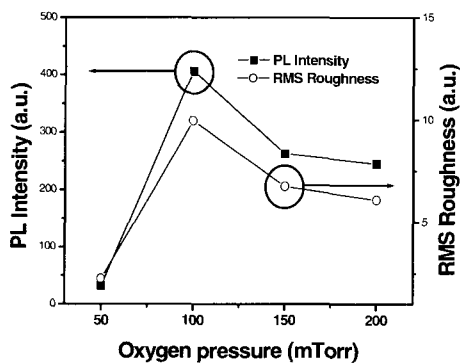


Fig. 5. PL intensity and rms roughness of $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$ films as a function of oxygen pressure.

4. CONCLUSIONS

High quality $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) phosphor thin films have been deposited on $\text{MgO}(100)$ single crystal substrate using a pulsed laser deposition technique. Zn-rich ceramic targets have been prepared to compensate the Zn loss due to the relatively high vaporization pressure of Zn. The variation of the Zn/Ga ratio in the films depends on the oxygen pressure during deposition. The shift of (400) ZnGa_2O_4 peaks are observed as S or Se substituted the oxygen. For the case of $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) thin film, the (400) ZnGa_2O_4 diffraction peaks shift toward larger angles. A small change in lattice constant is observed and the lattice constant is shortened in $\text{ZnGa}_2\text{O}_{4-x}\text{M}_x:\text{Mn}^{2+}$ ($\text{M}=\text{S}, \text{Se}$) films. The all films exhibit a broad band emission extending from 470 to 550 nm, peaking at 509 nm. The PL intensity is highly dependent on the crystallinity, surface morphology and a kind of dopant. Especially, the incorporation of S or Se into ZnGa_2O_4 lattice could induce enhanced crystallinity, rougher surface, and a remarkable increase in the intensity of PL. The emission intensity of the $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$ films exhibits the strongest among the samples studied in this work. The peak intensity of PL of the $\text{ZnGa}_2\text{O}_{3.925}\text{S}_{0.075}:\text{Mn}^{2+}$ films is enhanced about a factor of 3.1 times in comparison with that of the $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$ films. Growth of as-deposited $\text{ZnGa}_2\text{O}_{3.925}\text{Se}_{0.075}:\text{Mn}^{2+}$ thin films with such a high brightness is very encouraging for the application of thin-film phosphors in display technologies.

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