

## Photoluminescence and surface morphologies of ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors deposited by a chemical solution method

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The XRD patterns of zinc gallate (ZnGa<sub>2</sub>O<sub>4</sub>) thin film phosphors, deposited on indium tin oxide (ITO) glass substrates and glass plates using a chemical solution method, indicated that the annealing temperature was a major factor in controlling the crystallization behavior. Thin films of ZnGa<sub>2</sub>O<sub>4</sub>, deposited on the two different substrates, showed the (222), (400), (511) and (440) peaks of the spinel structure as well as the (311) peak indicating a standard powder diffraction pattern. It was also suggested that the presence of the (311) peak of the ZnGa<sub>2</sub>O<sub>4</sub> film phosphor, annealed at 600 °C, could be correlated with embossed morphologies showing surface dots with a regular spacing. Meanwhile, all the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors on ITO glass exhibited blue emission spectra in the wavelength range of 400 nm to 445 nm. In particular, ultraviolet (UV) emission near 363 nm was detected in the case of the phosphor film annealed at 500 °C. It seems that the photoluminescence characteristics of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors are influenced by the crystallization behavior during the annealing process.

**Key words:** ZnGa<sub>2</sub>O<sub>4</sub>, Thin film phosphor, Chemical solution method, Photoluminescence.

### Introduction

Field emission displays (FED), sharing many common features with vacuum fluorescent displays (VFDs) or cathode ray tubes (CRTs), are one of the most promising FPD technologies [1]. FED technologies need to synthesize highly efficient phosphors with high brightness to obtain an image using the light created from the anode side [2]. Practically, thin film phosphors have the merits of good lifetime and chemical stability under a high vacuum condition and a high current density, although they are generally less efficient than powder phosphors because of internal reflection of the light generated within film [3]. Several phosphor materials for FED anode applications have been prepared by synthesis methods such as a solid-state reaction, a sol-gel process, hydrothermal synthesis, a combustion synthesis and pulsed laser deposition [2-9].

Zinc gallate (ZnGa<sub>2</sub>O<sub>4</sub>) phosphor has received much attention for its application as a low voltage field emission display (FED) and a vacuum fluorescent display (VFD) since it has good luminescent characteristics and stability under a high vacuum and a high current density [5-7]. ZnGa<sub>2</sub>O<sub>4</sub> has the spinel structure and a wide band gap of about 4.4 eV. In the normal spinel, Zn<sup>2+</sup> ions occupy the tetrahedrally-coordinated A-sites, whereas Ga<sup>3+</sup> ions occupy the B-octahedral sites [6,

10]. In addition, ZnGa<sub>2</sub>O<sub>4</sub> has been suggested as a potential candidate among oxide phosphors to substitute for sulfide-based phosphors in low-voltage cathode luminescence devices [7].

Many studies have been made on the synthesis of ZnGa<sub>2</sub>O<sub>4</sub> powder phosphors mainly through a solid-state reaction using metal compounds, but the phosphors prepared through this conventional method are unsuitable for application in a high-definition and low-voltage FED anode [11, 12]. A chemical solution method such as a sol-gel process has several advantages of being a simple and economical process as well as forming homogeneous oxides of multi-component films [4, 8].

In this study, the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors were fabricated by a chemical solution method. The surface morphologies of the films were observed by a field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). The X-ray diffraction (XRD) patterns and sheet resistance of the thin film phosphors were investigated. The photoluminescence (PL) characteristics of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors were examined.

### Experimental Procedure

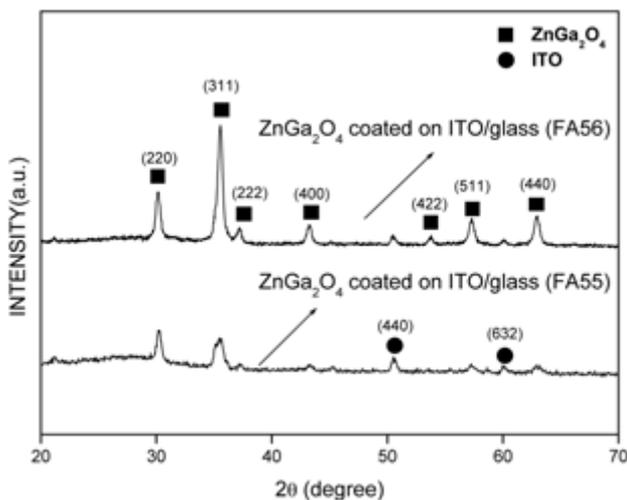
In the preparation of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors through a sol-gel spinning coating method, the starting materials of zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Junsei), gallium (III) nitrate hydrate (Ga(NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O, Aldrich) were dissolved into a mixed solution with 2-methoxyethanol. The atomic ratio of Zn to Ga of the mixed solution was 1:2. The solutions were stirred for

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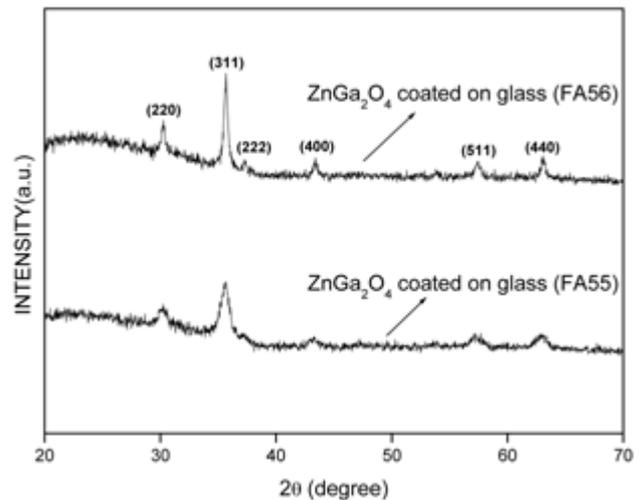
1hr at room temperature in air. Indium-tin-oxide (ITO) coated glass plates (3 cm × 3 cm) and soda-lime glass were used as substrates for spin coating with the thin film phosphors. The aqueous solutions were coated on ITO glass substrates and soda-lime glass at 2000 rpm for 30 seconds and the thin films coated were dried at 100°C then, fired at 500°C for 30 minutes (in air) and at the annealing temperature of 500°C and 600°C for 30 minutes (in 3% H<sub>2</sub>/Ar). The firing and annealing processes for the thin films coated were carried out using a quartz tube. The crystalline phases of the film phosphors annealed were analyzed with XRD patterns (RIGAKU, Japan). Surface morphologies of the film phosphors were observed with FE-SEM (JEOL, JSM-6340, Japan) and AFM (PSIA, XE-150, Korea). In addition, the sheet resistance of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors was measured by a four-point probe instrument (AIT, CMT-SR2000N, Korea). The photoluminescence spectra of the ZnGa<sub>2</sub>O<sub>4</sub> films were examined using a spectrometer (PL, ISS, USA) with a broadband incoherent ultraviolet (UV, Shimadzu, UV-2450, Japan) light as an excitation source ( $\lambda = 232$  nm) at room temperature.

## Results and Discussion

The XRD patterns of the thin film phosphors, formed on soda-lime glass and ITO coated glass, showed ZnGa<sub>2</sub>O<sub>4</sub> crystalline phases with the spinel structure (Fig. 1 and Fig. 2). In these XRD patterns, a (311) peak corresponding to the standard powder diffraction pattern of ZnGa<sub>2</sub>O<sub>4</sub> phase and a (220) peak showing the preferred orientation of the thin film were detected [6, 13]. The intensity of the (311) peak increased with an increase of annealing temperature. It was inferred that the (311) peak contributes largely to the photoluminescence behavior or intensity of the ZnGa<sub>2</sub>O<sub>4</sub> film phosphors.



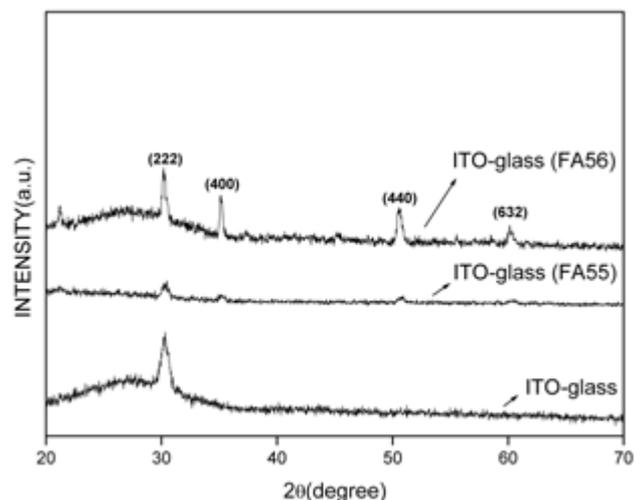
**Fig. 1.** XRD patterns of ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors coated on ITO glass. [Fired at 500°C and annealed at 500°C (FA55), 600°C (FA56)]



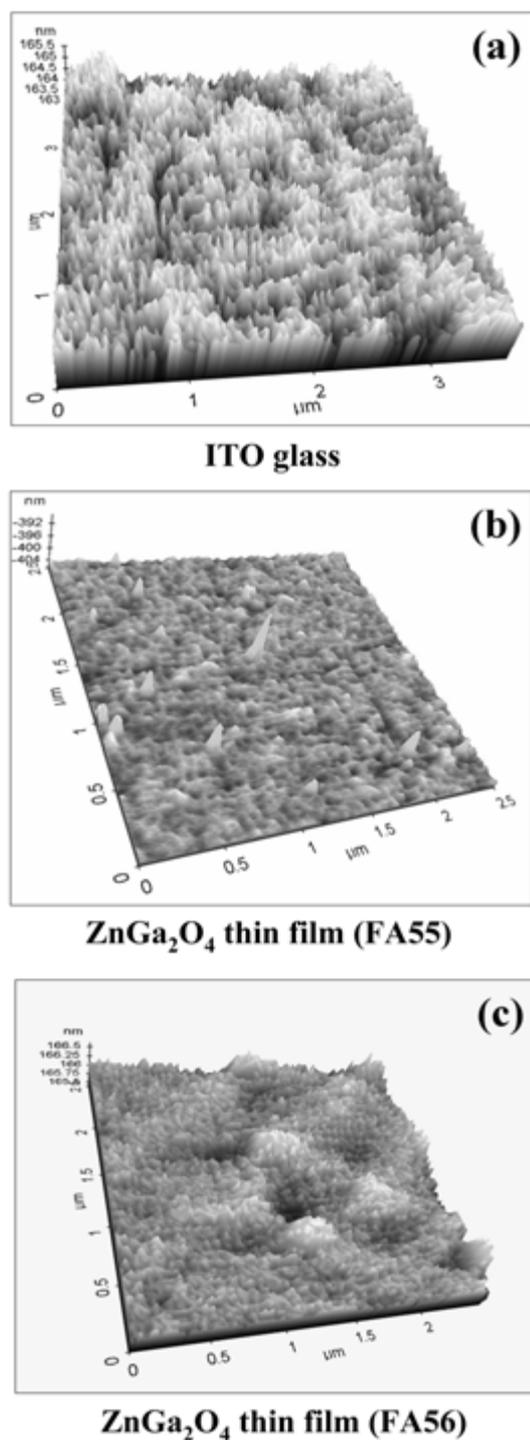
**Fig. 2.** XRD patterns of ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors coated on soda lime glass. [Fired at 500°C and annealed at 500°C (FA55), 600°C (FA56)]

The weak peaks from the (222), (400), (422), (511) and (440) planes are shown in the XRD patterns of the film phosphors annealed at 600°C (Fig. 2). Meanwhile, the thin film phosphor on ITO coated glass, annealed at 500°C, showed two peaks from the (220) and (311) planes with similar intensity. The (222), (400) peaks of the as-received or heated ITO coated glass substrates have similar positions to the (220), (311) peaks of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors (Fig. 3). Thus it seemed from the XRD pattern of the samples on ITO coated glass that this substrate has substantial influence upon the diffraction patterns of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors.

The AFM surface morphologies of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors coated on ITO glass are shown in Fig. 4. The FE-SEM images of surface morphologies of the ZnGa<sub>2</sub>O<sub>4</sub> thin film phosphors are shown in Fig. 5. From the AFM surface morphologies, it was found that



**Fig. 3.** XRD patterns of the heated ITO glass substrates. [Fired at 500°C and annealed at 500°C (FA55), 600°C (FA56)]



**Fig. 4.** AFM surface morphologies of  $\text{ZnGa}_2\text{O}_4$  thin film phosphors coated on ITO glass. [Fired at  $500^\circ\text{C}$  and annealed at  $500^\circ\text{C}$  (FA55),  $600^\circ\text{C}$  (FA56)]

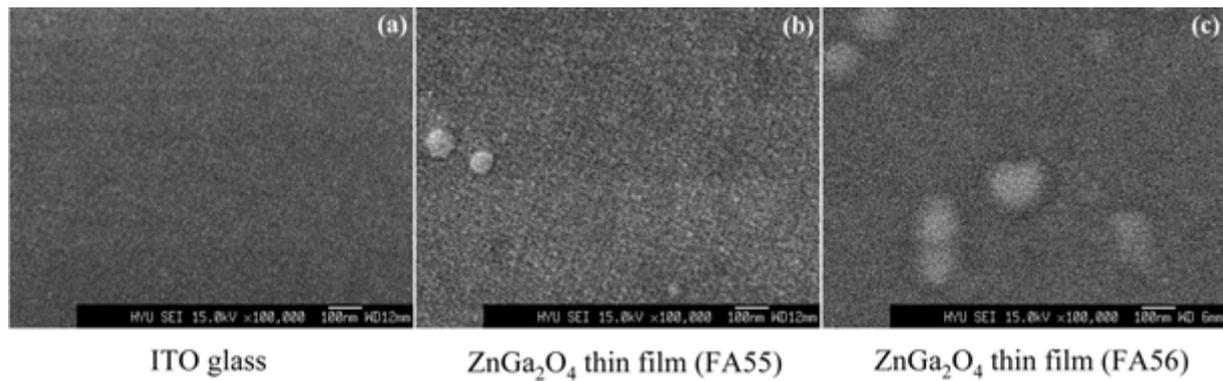
the  $\text{ZnGa}_2\text{O}_4$  thin films showed distinctive characteristics as a function of the annealing temperature, which was an important factor in controlling the surface morphologies of the phosphor film. The embossed surface morphology showing surface dots with a similar size and a regular spacing was observed in the  $\text{ZnGa}_2\text{O}_4$  film annealed at  $600^\circ\text{C}$ . It may be assumed that this

peculiar pattern composed of surface dots has an influence on the peak intensity of the (311) plane in the XRD patterns as well as the photoluminescence spectra of the phosphor films. The sheet resistance of the ITO glass was 5.33 ohms/square. The sheet resistance of the  $\text{ZnGa}_2\text{O}_4$  thin film coated on ITO glass, which was fired at  $500^\circ\text{C}$ , was approximately 5.76 ohms/square and 7.87 ohms/square according to the annealing temperature of  $500^\circ\text{C}$  and  $600^\circ\text{C}$ , respectively.

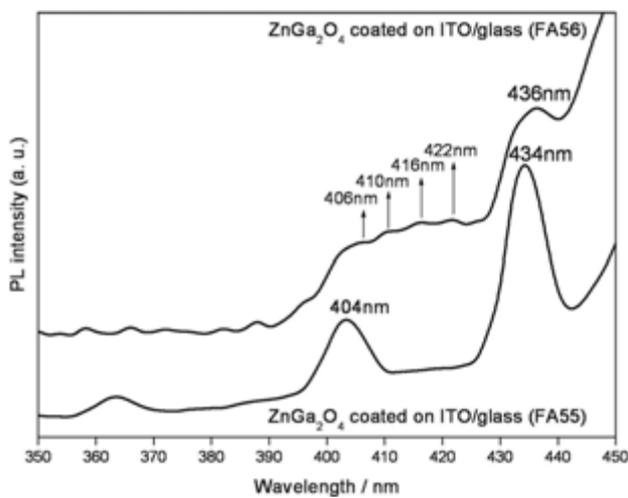
The photoluminescence spectra of the  $\text{ZnGa}_2\text{O}_4$  thin film phosphors are shown in Fig. 6. The blue emission spectra with main peaks at 434 nm and 436 nm were observed in the photoluminescence spectra of the  $\text{ZnGa}_2\text{O}_4$  thin film phosphors. The wide blue emission spectrum including the multiple bands throughout 400 nm to 445 nm was revealed in the case of the film annealed at  $600^\circ\text{C}$ . Generally, it is known that the emission behavior in the  $\text{ZnGa}_2\text{O}_4$  phase is caused by an excitation of the  $\text{Ga}^{3+}$  ions of the Ga-O group [10, 14]. The presence of multiple peaks in the emission spectrum (FA56 in Fig. 6) has been explained as a shift or splitting of the 3d orbital energy levels by the  $\text{Ga}^{3+}$  excess condition or the Zn loss in the  $\text{ZnGa}_2\text{O}_4$  spinel structure, which might be induced by increasing the annealing temperature [6]. It seems that the  $\text{Ga}^{3+}$  ion excess status is related to the distortion of the spinel structure. On the other hand, it is well known that the self-activated blue emission around 430 nm of the  $\text{ZnGa}_2\text{O}_4$  phosphor is based on the presence of the  $\text{Ga}^{3+}$  ion in a regular octahedral site. However, the ultraviolet (UV) emission band, which was observed at 363 nm, would indicate the presence of the  $\text{Ga}^{3+}$  ions in distorted octahedral sites in the  $\text{ZnGa}_2\text{O}_4$  spinel structure [14]. This UV luminescence behavior was observed in the case of the  $\text{ZnGa}_2\text{O}_4$  phosphor film annealed at  $500^\circ\text{C}$ . It was supposed that this UV luminescence band is due to an incomplete crystallization of the phosphor films. Thus it was found that the self-activated emission bands of the  $\text{ZnGa}_2\text{O}_4$  thin films depend strongly upon the primary factors causing the distortion in its spinel structure.

## Conclusions

The  $\text{ZnGa}_2\text{O}_4$  thin film phosphors were coated on ITO glass and soda-lime glass by a sol-gel spinning coating method and fired at  $500^\circ\text{C}$ , subsequently annealed at  $500^\circ\text{C}$  and  $600^\circ\text{C}$ . The crystalline phase of the  $\text{ZnGa}_2\text{O}_4$  thin film phosphors was confirmed from the XRD patterns with a (311) peak of the powder diffraction pattern and a (220) peak of the preferred orientation of the thin film. The weak peaks such as a (222), (400), (422), (511) and (440) appeared in the XRD pattern of the film phosphor annealed at  $600^\circ\text{C}$ . It was found that the surface morphologies of the  $\text{ZnGa}_2\text{O}_4$  thin films have a strong dependence upon the annealing temperature. In particular, the  $\text{ZnGa}_2\text{O}_4$  thin



**Fig. 5.** FE-SEM surface images of  $\text{ZnGa}_2\text{O}_4$  thin film phosphors coated on ITO glass. [Fired at  $500^\circ\text{C}$  and annealed at  $500^\circ\text{C}$  (FA55),  $600^\circ\text{C}$  (FA56)]



**Fig. 6.** Photoluminescence spectra of  $\text{ZnGa}_2\text{O}_4$  thin film phosphors coated on ITO glass. [Fired at  $500^\circ\text{C}$  and annealed at  $500^\circ\text{C}$  (FA55),  $600^\circ\text{C}$  (FA56)]

film, which was annealed at  $600^\circ\text{C}$ , showed regular dots in its surface morphology. The  $\text{ZnGa}_2\text{O}_4$  film phosphors exhibited multiple blue emission bands with peak wavelengths at 434 nm and 436 nm as well as an ultraviolet (UV) emission band at 363 nm.

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