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$ZnGa_2O_4$ thin films fabricated by Sol-gel spinning coating process

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Abstract $ZnGa_2O_4$ thin film phosphors have been synthesized on ITO coated glass and soda-lime glass at a firing temperature of 500°C and an annealing temperature of 500°C and 600°C via a chemical solution method using Zinc acetate dihydrate, Gallium nitrate hydrate and 2-methoxiethanol as a solution. XRD patterns of the film phosphors synthesized showed the peaks of $ZnGa_2O_4$ crystalline phases. AFM surface morphologies of the $ZnGa_2O_4$ thin film phosphors revealed marked differences according to an annealing temperature of 500°C and 600°C under an annealing atmosphere (3% H_2/Ar). On the other hand, the sheet resistance of $ZnGa_2O_4$ thin film phosphors, which were measured by four-point probe instrument, was approximately 5.76 Ω/square and 7.86 Ω/square with annealing temperature, respectively. The $ZnGa_2O_4$ thin film phosphors exhibited blue emission spectra with peak wavelength of 434 nm and 436 nm by ultra-violet excitation around 230 nm.

Keywords $ZnGa_2O_4$ · Thin film phosphor · Chemical solution method · Photoluminescence

1 Introduction

Flat panel display (FPD) popularity in global market is greatly increasing with the improvement in quality and affordability of LCDs and PDPs and alternative FPD technologies are applied to manufacture new display products. Field emission displays (FED), sharing many common features with vacuum fluorescent displays (VFDs) or cathode ray tubes (CRTs), are being expected as one of the most promising FPD technologies [1]. The image of FED is made from the light created from phosphor anode. Thus FED technologies should include a formation of high efficient phosphors with high brightness, in particular, the phosphors introduced into low-anode voltage FEDs suffer a severe circumstance of a high-density current, which would induce the degradation of brightness. Despite many researches for low-voltage FED phosphors, there are no suitable candidates available to high brightness. Even though powder phosphors show high brightness and high efficiency, the out-gassing from phosphors in FED operation of high vacuum circumstance would limit display lifetime. In general, thin film phosphors have the merits of good lifetime and chemical stability in high vacuum condition and high density current, although they are generally less efficient than powder phosphors because of internal reflection of the light generated within the film [2]. Thus, the synthesis and selection of suitable phosphors has been important research item in enhancing the low-voltage FED technologies.

Recently, $ZnGa_2O_4$ phosphor has received much attention in its application to low voltage field emission display (FED) and vacuum fluorescent display (VFD), since it has good luminescent characteristics and stability in a high vacuum circumstance and a high current density [3–6]. In addition, $ZnGa_2O_4$ has been expected as a potential candidate among oxide phosphors to substituting sulfide-based phosphors in low-voltage cathode luminescence device [7]. In particular, the phosphors for low voltage FED applications should have low electrical resistance for a reduction of charging effects of electrons and a high luminous efficiency. $ZnGa_2O_4$ has a spinel structure and wide band gap of about 4.4 eV.

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In normal spinel, Zn^{2+} ions occupy the tetrahedrally coordinated A-sites, whereas Ga^{3+} ions occupy the B-sites of octahedra.

$ZnGa_2O_4$ phosphors have been prepared by various methods such as solid-state reactions, sol-gel process, hydrothermal synthesis, combustion synthesis and pulsed laser deposition. The synthesis of $ZnGa_2O_4$ phosphors has utilized mainly a solid-state reaction using metal compounds, but the phosphors prepared through this conventional process are still insufficient to be applied to high-definition, low-voltage FED anode. Generally, a chemical solution method as a sol-gel process has several advantages of a simple and economical process as well as a formation of homogeneous oxides of multi-component films [8].

In this study, we tried to synthesize $ZnGa_2O_4$ thin film phosphors by a chemical solution method and observe surface morphologies of films using FE-SEM and AFM. XRD phase analysis photoluminescence (PL) spectra of $ZnGa_2O_4$ thin film phosphors were examined.

2 Experimental procedure

$ZnGa_2O_4$ thin film phosphors were prepared by a sol-gel and spinning coating process. The starting materials of Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Junsei), Gallium (III) nitrate hydrate (Ga $(NO_3) \cdot nH_2O$, Aldrich) were dissolved into a mixed solution with 2-methoxiethanol. The atomic ratio of Zn to Ga in the mixed solution was 1:2. The solutions were stirred for 1 h 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 spinning coating procedure of thin film phosphors. The aqueous solutions were coated on ITO-glass substrate and soda-lime glass at 2000 rpm for 30 sec and the thin films coated were dried at 100°C then, fired at 500°C for 30 min (in air) and at annealing temperature of 500°C and 600°C for 30min (in 3% H_2/Ar). Firing and annealing process for thin films coated were carried out with an temperature increment of 5°C/min using quartz tube. Crystalline phases of the film phosphors synthesized were analyzed with X-ray diffraction (XRD, RIGAKU, Japan). Surface morphologies of the film phosphors were observed with field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6340, Japan) and atomic force microscopy (AFM, PSIA, XE-150, Korea). On the other hand, sheet resistance of $ZnGa_2O_4$ thin film phosphors, measured by four-point probe instrument (AIT, CMT-SR2000N, Korea). The photoluminescence (PL, ISS, USA) spectra of $ZnGa_2O_4$ films were examined using a spectrometer with a broadband incoherent ultraviolet (UV, Shimadzu, UV-2450, Japan) light as an excitation source ($\lambda = 232$ nm) at room temperature.

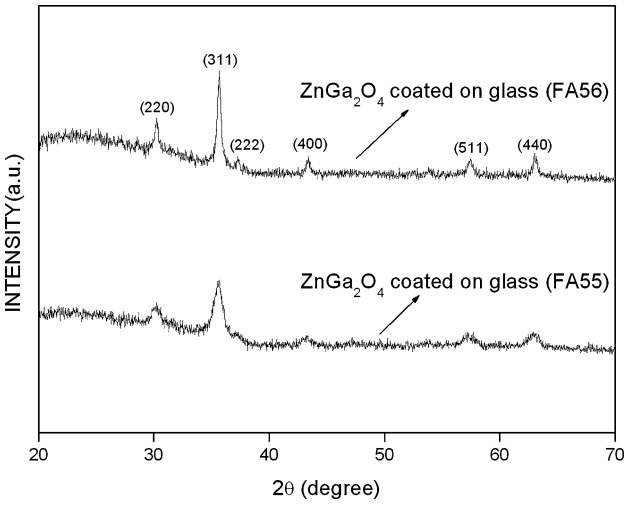

Fig. 1 XRD patterns of $ZnGa_2O_4$ thin film phosphors coated on glass. • FA55 : Firing (500°C, in air), Annealing (500°C, in 3%H_2/Ar). •FA56 : Firing (500°C, in air), Annealing (600°C, in 3%H_2/Ar)

3 Results and discussion

Figures 1 and 2 show XRD patterns of surface of the $ZnGa_2O_4$ thin film phosphors coated on soda-lime and ITO coated glass, respectively. The XRD patterns of the thin film phosphors coated on ITO-glass are nearly similar to those of films formed on soda-lime glass. All specimens showed (311) peak with the highest intensity in the XRD patterns. The thin film phosphors showed the XRD patterns of $ZnGa_2O_4$ crystalline phases composed of (311) peak indicating the standard powder diffraction pattern of $ZnGa_2O_4$ and (220) peak of preferred orientation. The XRD peak intensity of (311) peak, which would contribute largely to PL spectra intensity, was increased with an annealing temperature. However, the thin film phosphor on ITO-glass annealed at 500°C showed two

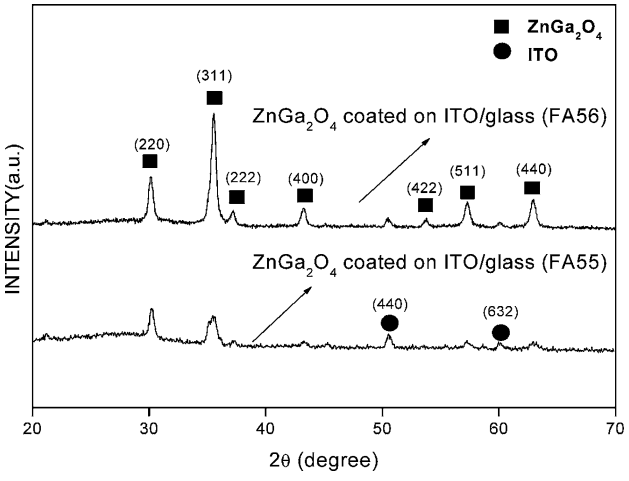

Fig. 2 XRD patterns of $ZnGa_2O_4$ thin film phosphor coated on ITO-glass

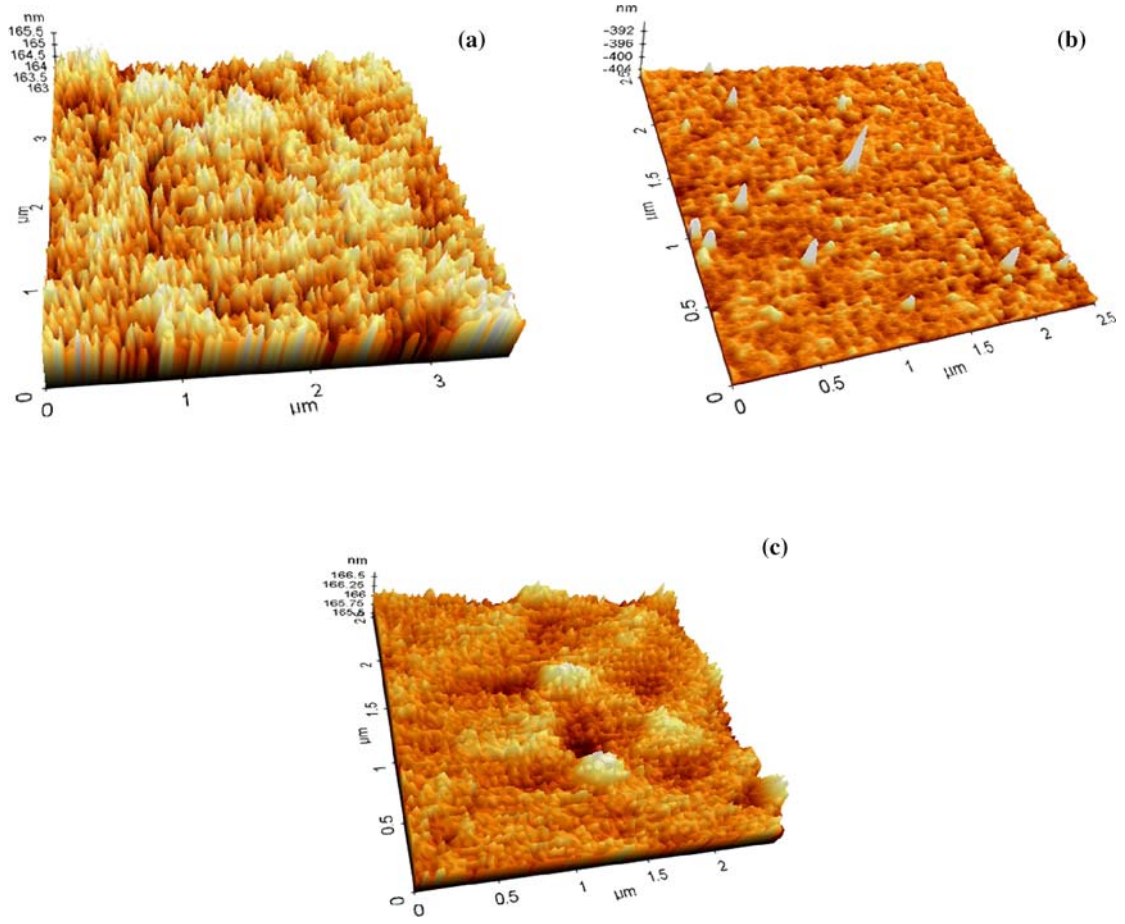

Fig. 3 AFM images of ITO-glass and $ZnGa_2O_4$ film phosphors coated on ITO-glass. (a) ITO-glass, (b) $ZnGa_2O_4$ film (FA55) on ITO-glass (c) $ZnGa_2O_4$ film (FA56) on ITO-glass

large peaks of (220) and (311) plane with nearly equal intensity. It was found in the XRD patterns of film phosphor on ITO-glass annealed at 500°C that the peak intensity of (220) plane was higher than that of film on soda-lime glass. It was suggested that this propensity is due to the presence (222) peak of the ITO-glass introduced to form $ZnGa_2O_4$ thin film phosphor.

Figure 3 shows AFM surface morphologies of ITO-glass and $ZnGa_2O_4$ thin film phosphors coated on ITO-glass. The $ZnGa_2O_4$ thin film phosphors were formed on ITO-glass through firing (500°C) and subsequently annealing (500°C and 600°C). The roughness and surface morphologies of the $ZnGa_2O_4$ thin films showed somewhat different propensity according annealing temperature. In particular, the $ZnGa_2O_4$ film, which was annealed at 600°C, revealed embossed surface or indented morphology. Sheet resistance of ITO-glass was 5.33 Ω/square. The sheet resistance of $ZnGa_2O_4$ thin film coated on ITO-glass, which was fired at 500°C, was approximately 5.76 Ω/square and 7.87 Ω/square according to annealing temperature of 500°C and 600°C, respectively.

Figure 4 shows the photoluminescence spectra of $ZnGa_2O_4$ thin film phosphors annealed at different temperature. The emission spectra on an excitation of UV light ($\lambda = 232$ nm) revealed several bands between 400 nm and 445 nm in which the main peak wavelength was located at 434 nm and 436 nm according to annealing temperatures, respectively. Generally, it is known that the emission behavior

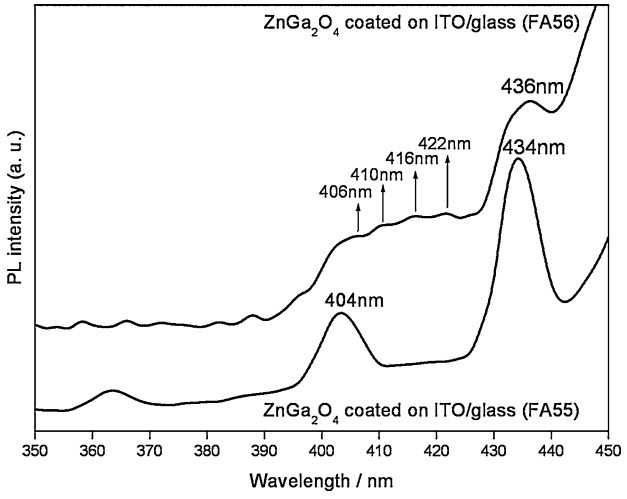

Fig. 4 PL spectra of $ZnGa_2O_4$ thin film phosphors coated on ITO-glass

in $ZnGa_2O_4$ phase is caused by an excitation of Ga^{3+}ions of Ga-O group. The presence of multiple peaks in emission spectrum (FA56 in Fig. 4) can be explained as a shift or splitting of 3d orbital energy levels by the Ga^{3+} excess condition of spinel $ZnGa_2O_4$ structure, which might be induced by increasing an annealing temperature [4]. It seemed that the Ga^{3+} ion excess state is related to the distortion of the spinel structure.

4 Conclusions

$ZnGa_2O_4$ thin film phosphors were coated on ITO-glass and soda-lime glass by sol-gel spinning coating method and fired at 500°C, subsequently annealed at 500°C and 600°C. XRD intensity of (311) plane was increased with an annealing temperature. AFM surface images of the $ZnGa_2O_4$ thin films showed somewhat differences related to roughness and morphological features according annealing temperature. The $ZnGa_2O_4$ thin film, which was annealed at 600°C, showed a rugged pattern in surface morphology. The $ZnGa_2O_4$ film phosphors exhibited blue emission spectra with peak wavelength at 434 nm and 436 nm and wide emission band in the wavelength region of 400 nm to 445 nm.

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