Zinc Gallate [$ZnGa_2O_4$] thin film phosphors for Field Emission Display application

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ABSTRACT

Thin films of $ZnGa_2O_4$ phosphor with single phase of spinel were synthesized from a mixed solution of zinc acetate dehydrate and gallium nitrate hydrate using 2-methoxiethanol as a solution. Thin films deposited on ITO glass plates showed the (222), (400), (422), (511) and (440) peak of spinel structure as well as the (311) peak indicating a standard powder diffraction pattern. The film phosphor, fired and annealed at 600℃, revealed the domelike shape composed of the fine grain aggregates. The $ZnGa_2O_4$ film phosphors showed the blue emission spectra around 410 nm

Keywords：Field Emission Display (FED), $ZnGa_2O_4$ thin films, Photoluminescence, Blue emission

1. INTRODUCTION

In present, many Flat panel displays (FPD) have been developed together with a rapid improvement in panel fabrication technologies, and are being gradually thinner and lighter, less power consumption compared to previous displays. Field emission displays are most popular in developing their commercial products particularly in world market.[1, 2] For its commercialization and mass production, FED technologies require obtaining stable oxide based phosphors showing a high efficiency under high vacuum operating situation of module, low-voltage condition as well as CNT-array.

$ZnGa_2O_4$ has been expected as a potential candidate among oxide phosphors to substitute sulfide-based phosphors in low-voltage cathode luminescence devices.[3, 4, 5] There were many researches on the synthesis of $ZnGa_2O_4$ powder phosphors mainly through a solid-state reaction using metal compounds, but the phosphors prepared through this conventional method are still insufficient to be applied to a high-definition and low-voltage FED anode. [6] 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. [7]

In this study, the $ZnGa_2O_4$ film phosphors on ITO glass were synthesized by a sol-gel spinning coating method. The surface morphologies of the films were observed by FE-SEM, AFM. XRD patterns of the thin film phosphors were investigated. The PL characteristics of the $ZnGa_2O_4$ thin film phosphors were examined.

2. EXPERIMENTAL DETAILS

The thin film phosphors of $ZnGa_2O_4$ were synthesized through a sol-gel spinning coating method. The solution for the film formation was obtained by mixing 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) with 2-methoxiethanol as solution. The solutions were stirred for 1hr at room temperature in air. The aqueous solutions were coated on ITO glass substrate at 2000 rpm for 30 seconds and the thin films coated were dried at 100℃ then, fired at 500℃, 600℃ for 30 minutes (in air) and at the annealing temperature of 500℃, 600℃ for 30minutes (in 3% H_2/Ar). A firing and annealing process for the thin films coated were carried out with the temperature increment of 5℃/min using 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). The photoluminescence spectra of the $ZnGa_2O_4$ films were examined using a spectrometer (PL, ISS, USA)

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with a broadband incoherent ultraviolet (UV, Shimadzu, UV-2450, Japan) light as an excitation source (λ=232nm) at room temperature.

3. RESULTS AND DISCUSSION

The thin film phosphors with spinel structure were obtained through the spinning coating on ITO glass substrates, and indicated the XRD patterns of the $ZnGa_2O_4$ crystalline phase (Fig.1 and Fig.2). These XRD patterns of the $ZnGa_2O_4$ thin film phosphors showed a (311) peak of the standard powder diffraction pattern and a (220) peak of the preferred orientation of the thin film. In these XRD patterns of the $ZnGa_2O_4$ film phosphors, deposited on ITO glass, the intensities of (220) peaks were higher than those of the (311) peaks. By increasing an annealing temperature of the thin films into the firing temperature of 600℃, the intensity of the (311) peaks increased with compared to the intensity of (220) peak. With an increase of firing and annealing condition, the apparent changes of the peak intensity and peak shape as well as the peak width were observed in their XRD patterns, and the crystallinity was slightly increased.

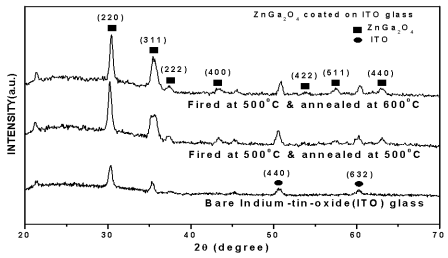

Figure 1. XRD patterns of $ZnGa_2O_4$ thin film phosphors coated on ITO glass.

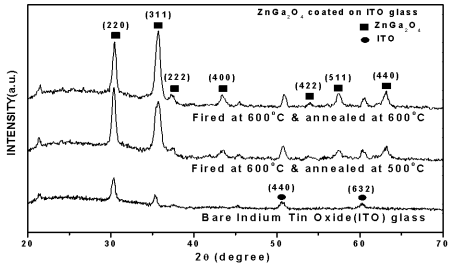

Figure 2. XRD patterns of $ZnGa_2O_4$ thin film phosphors coated on ITO glass.

The AFM images of the $ZnGa_2O_4$ thin film phosphors, formed on ITO glass substrates, are shown in Fig. 3. The film phosphor of $ZnGa_2O_4$, fired and annealed at 500℃ demonstrates the AFM surface morphology composed of sharp-cornered particles and very fine crystalline aggregates. The $ZnGa_2O_4$ thin film phosphor, fired at 500℃ and annealed at 600℃ showed the morphology of the larger grain aggregates with the spherical shape compared to that of film phosphor fired and annealed at 500℃. The surface morphologies of the $ZnGa_2O_4$ thin film phosphors, which were prepared in the firing temperature of 600℃ and subsequently by the annealing temperature of 500℃ and 600℃, indicated the grain clusters larger than those of the specimen fired at 500℃ and annealed at 500℃ and 600℃.

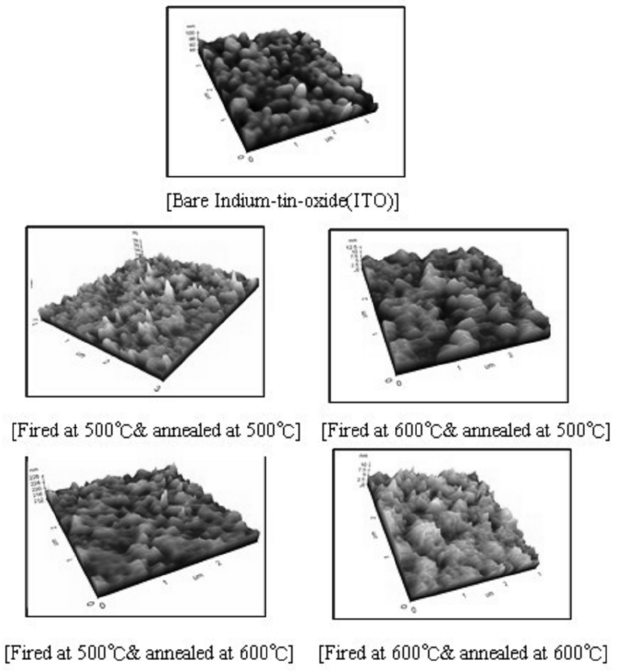

Figure 3. AFM surface morphologies of $ZnGa_2O_4$ thin film phosphors coated on ITO glass.

The formation of the dome or dot pattern of the surface morphology in the film phosphors were observed mainly at the annealing temperature of 600℃ after the firing step of 500℃, and would be related directly to the crystallization behavior of the film phosphors during firing and annealing process. It seemed that the annealing

temperature was an important factor in controlling the surface morphologies of the film phosphor.

The photoluminescence spectra of the $ZnGa_2O_4$ thin film phosphors are shown in Fig. 4. The blue emission peak around 410 nm was observed in the photoluminescence spectrum of the $ZnGa_2O_4$ thin film phosphors. In this study, the blue emission spectra of the film phosphors were detected as the relatively broad and weak peaks around 410 nm. The intensity in the PL spectra of the film phosphors increased with the annealing temperature. It is known that the emission behavior in the $ZnGa_2O_4$ phase is caused by an excitation of the Ga^{3+} ions of Ga-O group. [5, 8]

The presence of the broad emission spectra overlapping bands has been explained as a shift or splitting of the 3d orbital energy levels by the Ga^{3+} excess condition or the Zn loss (the changes of chemical composition) in the $ZnGa_2O_4$ spinel structure which might be induced by increasing the annealing temperature. It seemed that the 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 410 nm of the $ZnGa_2O_4$ phosphor is based on the presence of the Ga^{3+} ion of the regular octahedral site. However, the ultraviolet (UV) emission band, which was observed near 366 nm, would indicate the presence of the Ga^{3+} ions of the distorted octahedral sites in the $ZnGa_2O_4$ spinel structure.[8]

It was supposed that the UV luminescence band is due to an incomplete crystallization of the film phosphors. In this study, the UV peaks were detected mainly in the PL spectra of the film phosphors, fired and annealed at the lower temperature. Thus it was found that the self-activated emission bands of the $ZnGa_2O_4$ thin films depend strongly upon the primary factors causing the distortion in its spinel structure. The shift of the PL emission peak of the film phosphors would be due to the increase of annealing temperature or the resultant chemical composition changes. Also, it is inferred that the intensity changes of the PL spectra of the film phosphors are related to the differences of the grain shape and size of the surface morphologies..As a result, it could be concluded that the PL emission spectra and AFM surface morphologies are controlled by the crystallization of the film phosphors during firing and annealing process.

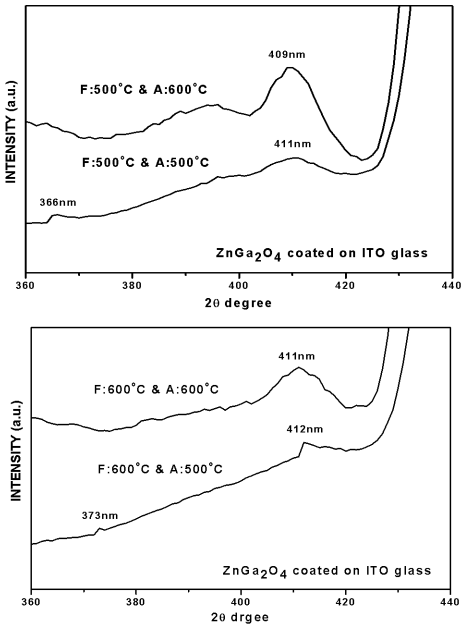

Figure 4. Photoluminescence spectra of $ZnGa_2O_4$ thin film phosphors coated on ITO glass. [Fired at 500℃, 600℃ and annealed at 500℃, 600℃]

4. CONCLUSION

The film phosphor of $ZnGa_2O_4$ were coated on ITO glass by a sol-gel spinning method and fired at 500℃ and 600℃, subsequently annealed at 500℃ and 600℃. The surface morphologies of the $ZnGa_2O_4$ thin films showed the sharp-cornered particles or the spherical type particles and the prominent change in the constituent grain size or grain aggregate shape according to the firing and annealing temperature. The $ZnGa_2O_4$ film phosphors exhibited the broad blue emission bands around 410 nm as well as an ultraviolet (UV) emission

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band near 366 nm. The introduction of the different ITO glass for phosphor coating caused the unique PL spectrum characteristics of the film phosphors.

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6. References

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