

The Origin of Change in Luminescent Properties of ZnMgS:Mn Thin Film Phosphor with Varying Annealing Temperature

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Abstract

With varying rapid thermal annealing (RTA) temperature, luminescence properties of Zn_{0.75}Mg_{0.25}S:Mn thin film deposited by RF-magnetron sputtering technique were investigated. In this study, Zn_{0.75}Mg_{0.25}S:Mn thin film phosphor showed more red emission than those of the previous studies when annealed around 600 or 650 °C. Although all samples were deposited from identical source composition, a main peak wavelength of photoluminescence spectra of Zn_{0.75}Mg_{0.25}S:Mn shifted toward shorter wavelengths depending upon increase of RTA temperature. The same dependence of wavelength on RTA temperature was also observed in cathodoluminescence as well as electroluminescence measurements. It was revealed that the change of the luminescence properties were originated from structural changes in Zn_{0.75}Mg_{0.25}S:Mn thin film phosphor from cubic to hexagonal phases analyze using conventional Xray pole figure mapping. The phase transition would be the origin of luminescence property changes with respect to RTA temperature.

1. Introduction

Thin film electroluminescent (TFEL) devices have been developed in the last twenty years and become one kind of major flat panel display devices. For recent decade, a few new phosphor compositions have been reported as TFEL phosphor such as CaS:Pb, BaMgAl₂S₄:Eu, GdVO₄:Eu, SrS₂S₄:Eu for red, green, and blue color [1-4]. Among electroluminescent (EL) phosphors ever developed, ZnS:Mn has been the most efficient for TFEL devices [5]. However, it has a limitation to date – its emission color is yellow, and it requires the use of color filters for red and green light to obtain green and blue color. Therefore, it is necessary to improve emission color property of

ZnS:Mn thin film phosphor for high efficient full color TFEL displays.

To acquire high efficient red or green color for full color TFEL displays, it may be a promising way to change the energy band gap of ZnS. For example, R. Inoue et al. presented their work on changing the energy band gaps of the ZnS and Mg-added ZnS thin films determined using optical technique and found to be 3.43 and 3.67 eV respectively [6]. Because MgS has an energy band gap of 4.65 eV, the energy band gap of ZnS can be increased with Mg concentration and it also causes a change of transition energy of activator ion such as Mn²⁺ due to modification of host matrix. Actually, R. Inoue et al. proposed ZnMgS thin film as green color EL phosphor and CIE color coordinates of ZnMgS largely changed with Mg concentration [6-8]. However, most of the literatures concerning ZnMgS:Mn have shown structural and luminescent changes toward green light, only with varying Mg concentration. Unusually, it was reported that ZnMgS is the solid solution composed of ZnS and MgS [7]. Therefore, it is conceivable that changing the band gap can be achieved for not only green but also red light by controlling the Mg concentration in ZnMgS host [8].

In our study, we focused on the observation for luminescence changes toward reddish light of ZnMgS:Mn thin film with process conditions, especially rapid thermal annealing (RTA) temperature. Also, it will be demonstrated that ZnMgS:Mn is a strong candidate material as TFEL phosphor for red light and, in addition, the origin of its red emission is explained.

2. Results and Discussions

Photoluminescence (PL) and cathodoluminescence (CL) spectra were obtained for $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ films annealed with varying temperature from 450 to 800 °C. As shown in PL spectra (Fig. 1), the films annealed even at temperatures as low as 450 and 500 °C showed a weak emission around 600 nm. The emission peak gradually shifted toward shorter wavelength region when annealed at higher temperature. As shown in Fig. 2, similar tendency was observed also in CL spectra. Previously, R. Inoue et al. reported an emission at a wavelength shorter than 590 nm [6]. However, our results were clearly different from ones in their study. The origin of its red emission will be explained on the next page.

To characterize EL properties of $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ phosphor film in this study, the luminance-voltage (L-V) curves of $\text{ZnMgS}:\text{Mn}$ EL devices were measured with the increase of RTA temperature. Two EL devices were fabricated at the same conditions except the annealing temperature. Annealing temperatures were determined considering ITO glass substrate deformation temperature and luminescence characteristics. For comparison, $\text{ZnS}:\text{Mn}$ EL devices were fabricated with having the same structure, but annealed at 600 and 650 °C, respectively.

In the L-V characteristic measurements, it was observed that the threshold voltage (V_{th}) of $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ EL devices was over 220 V as shown in Fig. 3. The EL device annealed at 650 °C showed a steeper increase of luminance in L-V curve than that of one annealed at 600 °C.

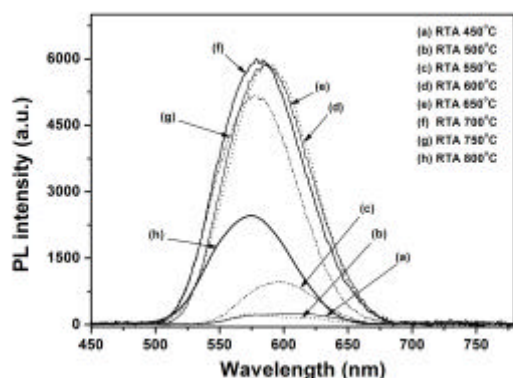


Figure 1. PL spectra of $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ phosphor films as a function of RTA temperature. (ex. 325 nm.)

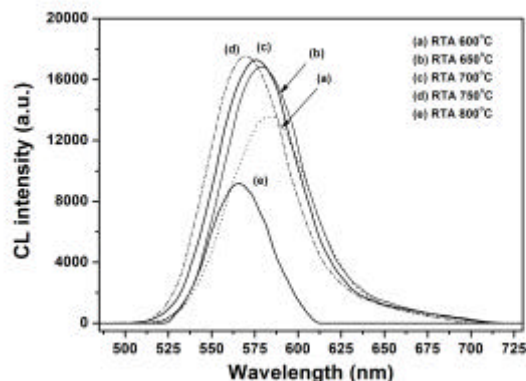


Figure 2. CL spectra of $\text{ZnMgS}:\text{Mn}$ phosphor films as a function of RTA temperature (CL circumstance: 900 V, $60 \mu\text{A}/\text{cm}^2$).

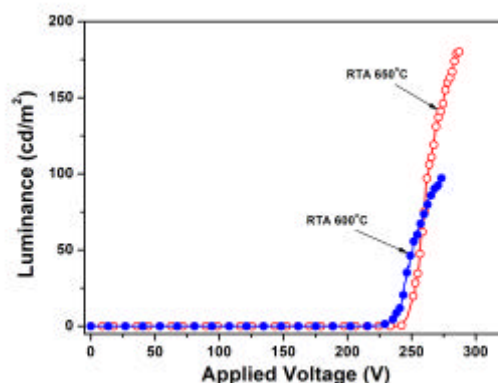


Figure 3. Luminance-voltage (L-V) characteristics of $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ phosphor films : annealed at 600 and 650 °C. (Excitation frequency : 400 Hz).

Compared with $\text{ZnS}:\text{Mn}$ EL device, $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{S}:\text{Mn}$ EL devices annealed at 600 or 650 °C showed that the CIE color coordinates of their emissions moved toward more reddish color. While the color coordinates of emission from $\text{ZnS}:\text{Mn}$ EL device were (0.510, 0.490), those of one from $\text{ZnMgS}:\text{Mn}$ EL devices annealed at 600 or 650 °C were (0.530, 0.470) and (0.515, 0.485), respectively. The EL behavior is in accordance with the above results, that is, shorter wavelength emission at higher RTA temperature in PL and CL measurements shown in Fig. 1 and 2. Although the previous studies of $\text{ZnMgS}:\text{Mn}$ phosphor reported more greenish EL emission than that of $\text{ZnS}:\text{Mn}$ EL device, our results showed more

reddish EL emission, noticeably. Based on the results up to date, it may be suggested that ZnMgS:Mn phosphor film would be a candidate for TFEL red emitting TFEL phosphor.

Additionally, to clarify the origin of red color emission with RTA temperature, typical X-ray diffraction (XRD) was conducted. M.K. Jayaraj showed a strong peak of (111) diffraction of ZnMgS:Mn cubic structure and its intensity decreased with the increase of Mg concentration [10]. In our study, only one peak, which is expected as the peak of (111) diffraction, was detected and its intensity was not changed with the increase of RTA temperature. It might result from the fixed Mg concentration. Since wurtzite {0002} and zinc blende {111} planes have almost the same interplanar distance, their diffraction peaks are superimposed on cubic (111) scattering information [11]. However, although M.K. Jayaraj and R. Inoue reported that the structure of ZnMgS:Mn thin film is cubic in their studies, it is very difficult to distinguish one from another. Therefore, for more definite structural analysis, X-ray pole figures were mapped using a high resolution multi-function four-circle X-ray diffractometer.

Especially, we used the pole figure of specified plane, {10 $\bar{1}$ 0} plane in hexagonal because the wurtzite {10 $\bar{1}$ 0} lattice spacing is different from that of zinc blende [12]. Figure 4 shows a {10 $\bar{1}$ 0} pole figure of ZnMgS:Mn phosphor film annealed at 600 °C. The

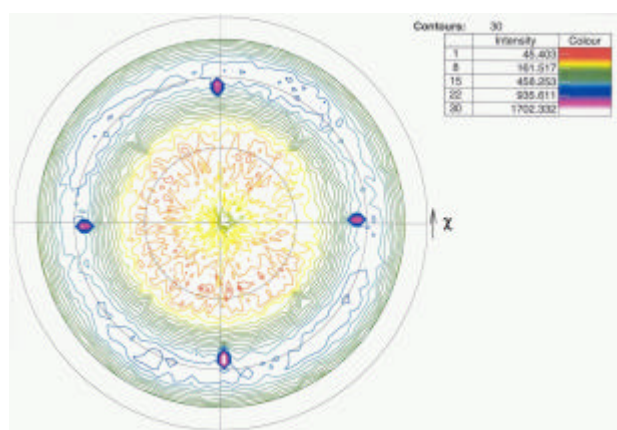


Figure 4. Wurtzite {10 $\bar{1}$ 0} pole figures of RTA-treated phosphor films annealed at 600 °C.

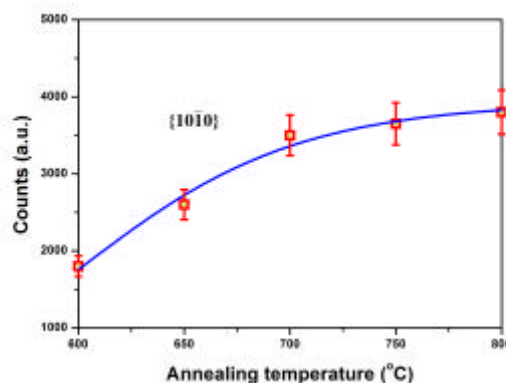


Figure 5. Intensity changes of wurtzite {10 $\bar{1}$ 0} diffraction pole of phosphor films with a function of RTA temperatures.

positions of their diffraction peaks were close to each other at $\theta = 54.74^\circ$ and exhibited four fold symmetry and the scattered intensities in it were all generated from the hexagonal phases. Since the wurtzite {10 $\bar{1}$ 0} diffracted spots appeared at the positions of {112} spots in the standard pole figure of cubic lattice structure, it could be concluded that the {10 $\bar{1}$ 0} planes of hexagonal phase were generated in cubic phase.

Moreover, the diffraction peak intensity in pole figures was changed with the increase of RTA temperature. As shown in Fig. 5, {10 $\bar{1}$ 0} diffraction peak intensity increased with the increase of RTA temperature and it would be originated from growing up of hexagonal phase in Zn_{0.75}Mg_{0.25}S:Mn film. It is concluded that the hexagonal phase gradually grows up from the cubic phase in Zn_{0.75}Mg_{0.25}S:Mn films with the increase of RTA temperature and this may cause the emission property changes, especially red emission.

4. Acknowledgements

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5. References

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