

Formation of ZnAl₂O₄ Thin Film for Deep Ultraviolet Emitting Phosphor and Evaluation of Luminescence Properties

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ABSTRACT

ZnAl₂O₄ thin films for deep UV emitting phosphor were prepared by deposition of ZnO on a-sapphire substrate and thermal diffusion process at 1000 °C. The distribution of the emitting layer of thin films was analyzed from the relationship between the penetration depth of electron beam by increasing acceleration voltage and the UV emission intensity by cathodoluminescence. The UV emission intensity of the annealed films tended to saturate at 8 kV against the penetration depth of electron beam, suggesting the possibility of the formation of the emitting layer of 650 nm. From the results of FE-EPMA and SEM, the UV emitting layer were formed at the almost same region of Zn distribution.

1 INTRODUCTION

Currently, mercury lamps are mainly used as the light source for ultraviolet (UV) sterilization, but its use is refrained from the influence on the human body and the natural environment. Therefore, we have focused on ZnAl₂O₄ phosphor, which shows a peak near 250 nm by electron beam excitation as a material for new UV light source [1].

Conventionally, powder samples have been prepared and evaluated [2], but it was difficult to analyze transmittance and refractive index due to the influences of surface scattering, so it would be possible to evaluate these basic physical properties by preparing thin film samples. In this research, ZnO films were deposited on sapphire substrates by sputtering and ZnAl₂O₄ thin films were prepared by thermal diffusion [3, 4]. These films were evaluated the orientation and crystallinity. Quality of thin films were evaluated by relationships between UV emission intensity and penetration depth of electron beam, and also the distribution of Zn and Al was studied using cross sectional FE-EPMA to analyze the emitting layer.

2 EXPERIMENT

Fig.1 shows the experimental procedure and conditions for preparing the ZnAl₂O₄ thin film. ZnO layer of 350 nm and α-Al₂O₃ layer of 50 nm as a capping layer to prevent

re-evaporation of ZnO film was deposited on a-plane sapphire substrates by RF magnetron sputtering. Thereafter, films were annealed at 1000 °C for 5 to 125 hours in air. ZnAl₂O₄ films were formed by thermal diffusion of Zn and Al between deposited ZnO film and sapphire substrate. Crystal structure and element distributions of films were evaluated by X-ray diffraction (XRD) and field emission-electron probe micro analysis (FE-EPMA), and luminescence property was analyzed by cathodoluminescence (CL).

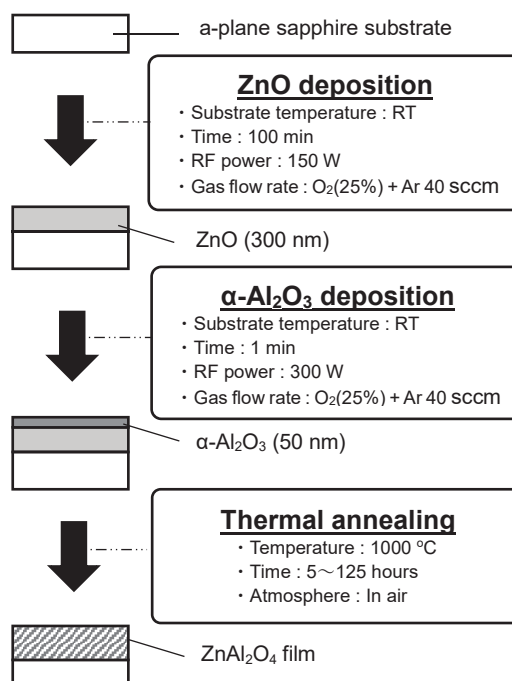


Fig.1 Experimental procedure of preparing ZnAl₂O₄ films.

3 RESULTS AND DISCUSSIONS

Fig. 2 shows the XRD patterns of thin films prepared on a-plane sapphire substrate. Before annealing, any diffraction peaks of ZnAl₂O₄ were not observed, however ZnO (002) peak was confirmed near 34°. After annealing, diffraction peak of ZnAl₂O₄ (333) appeared, and selective growth was confirmed. In Fig.3, FWHM of diffraction peaks of ZnAl₂O₄ (333) decrease according to

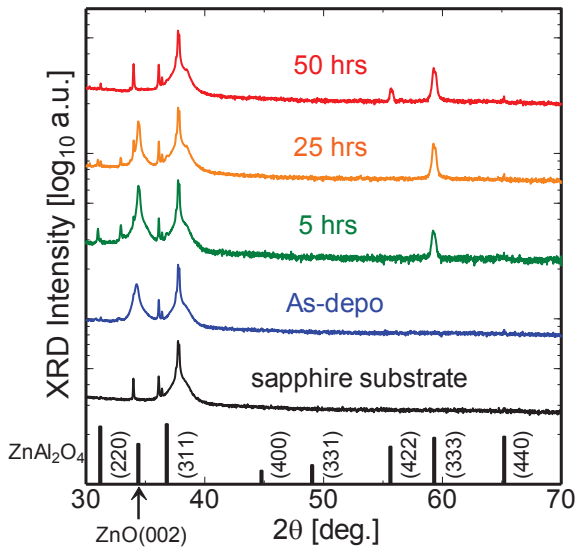


Fig.2 XRD patterns of films on a-plane sapphire substrate before and after annealing for several hours.

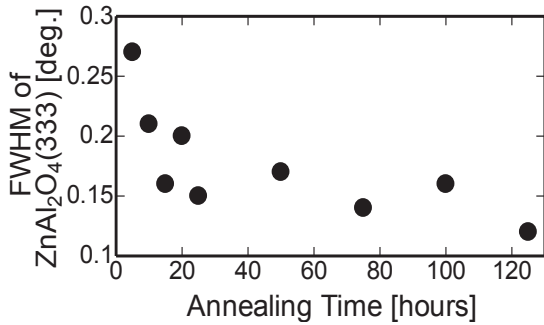


Fig.3 FWHM of ZnAl₂O₄ (333) on a-plane sapphire substrates depending on annealing time.

increase of annealing time, so the crystallinity was improved by longer annealing. The diffraction peak of ZnO (002) disappeared after annealing above 50 hours. From this result, it is considered that all deposited ZnO reacted with the sapphire substrate, and ZnO on the surface not involved in the formation of ZnAl₂O₄ sublimated.

Fig. 4 shows CL spectra for several acceleration voltage (V_A) of films annealed for 125 hours. The UV emission near 250 nm caused from ZnAl₂O₄, the green emission of 510 nm caused from ZnAl₂O₄:Mn, and the deep red emission of 700 nm caused from Cr in sapphire substrates were observed. The intensity of UV emissions were clearly increased according to the V_A .

Fig.5 shows the peak position of UV emission of ZnAl₂O₄. The peak of films annealed for 25 hours or less were around 240 nm, and films annealed 50 hours were around 250 nm. In our previous work, it was confirmed that the peak of Zn-poor ZnAl₂O₄ shows shorter wavelength (235 nm), the peak of Zn-rich ZnAl₂O₄ shows longer (260 nm), and the peak of stoichiometric ZnAl₂O₄ shows middle (250 nm) [2]. It indicates that the Zn-poor ZnAl₂O₄ phase was formed by annealing for less than 25

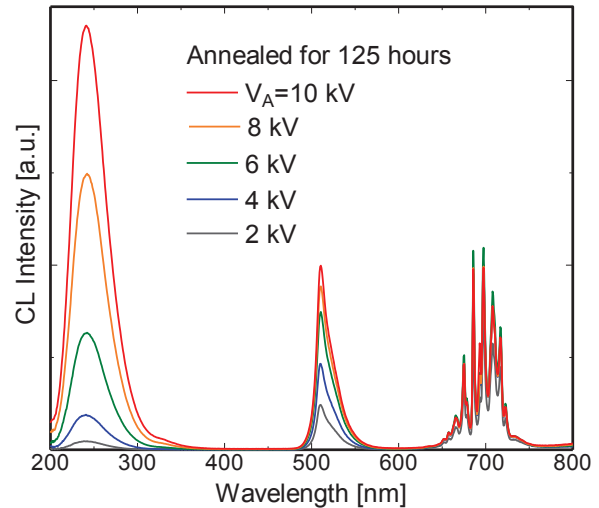


Fig.4 CL spectra of films annealed for 125 hours excited by electron beam.

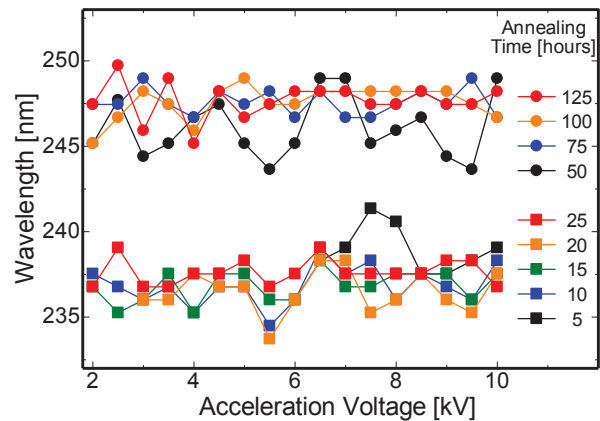


Fig5. UV peak position of films as a function of annealing time (5~125 hours).

hours, and the stoichiometric ZnAl₂O₄ phase was prepared by annealing for above 50 hours. These results correlates with the disappearance of the ZnO (002) diffraction peak in XRD measurement of thin film annealed for 50 hours as shown in Fig.2.

Fig.6 shows the CL intensity of ZnAl₂O₄ and Cr emission peaks as a function of V_A . From Fig.6(a), the emission of ZnAl₂O₄ and Cr were observed around 6.0 kV. It is thought the ZnO layer was remained on the surface and prevented the electron beam penetration. According to Feldman's equation, the ZnAl₂O₄ was formed at the depth of about 350 nm, interface between ZnO and substrate. From Fig.6(b), the emission of Cr increased according to increasing of V_A , whereas from Fig.6(c) it saturated. Therefore, Zn was sufficiently diffused to the substrate from 25 to 50 hours, suggesting that Cr in the substrate may have reached the film surface. In addition, the UV emission intensity was greatly improved, and the above considerations are consistent with the disappearance of the diffraction peak

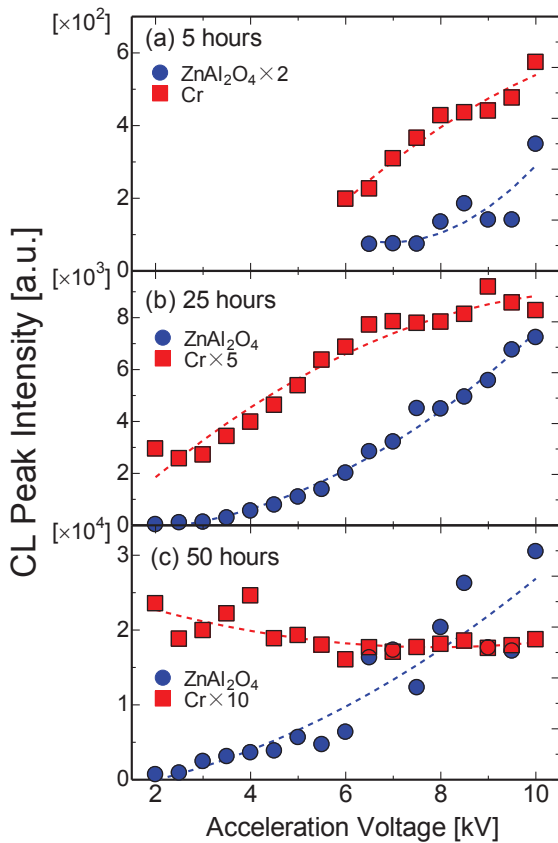


Fig.6 CL intensity of ZnAl₂O₄ and Cr as a function of annealing time (a) 5, (b) 25 and (c) 50 hours ($V_A=2\sim 10$ kV).

of ZnO (002) and the improvement of crystallinity due to the decrease of FWHM from XRD results.

Fig.7 shows the relationship between the emission intensity and the electron beam penetration depth as a function of V_A . The Y-axis and R-axis represent the CL intensity and the penetration depth of electron beam, respectively, and the two axes were plotted so as to have the same intensity ratio of magnitude. The thin film annealed for 25 hours showed the different slope against the penetration depth at lower V_A . It is thought that ZnO film remaining on the surface prevented the electron beam penetration into ZnAl₂O₄. The slope became almost the same as the medium V_A region, and became moderate above 8 kV. From these results, although the intensity was lower, it is thought that the uniform ZnAl₂O₄ layer was formed inner region of the film of about 100 to 650 nm depth.

The thin films annealed for 50 and 75 hours showed higher intensity than the others, and the slope of the intensity and the penetration depth were almost the same below 8 kV. It is considered that the ZnAl₂O₄ layer of around 650 nm with good uniformity and high quality was obtained. Thin films annealed for 100 hours and more showed the almost same slope as the penetration depth, but the CL intensity decreased than the film of 75 hours.

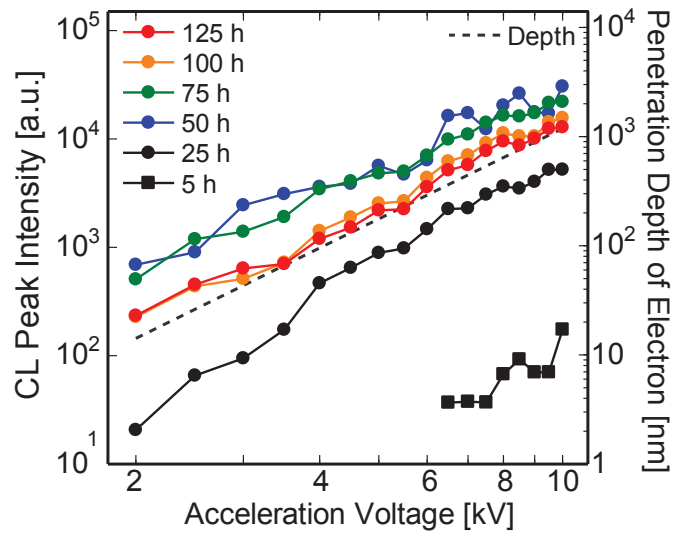


Fig.7 Relationship between emission intensity and electron beam penetration depth of thin film annealed at 1000 °C for 5 to 125 hours .

UV emission of ZnAl₂O₄ was caused from oxygen defects as same as ZnO and ZnGa₂O₄. Oxygen defects are reduced by excess annealing time, then the CL intensity decreased because of less oxygen defects. The result of FWHM as shown in Fig.3 indicates that the crystallinity was improved by longer annealing time, which is consistent with the above considerations.

Fig.8 shows SEM images, and Zn and Al distribution by FE-EPMA measurement. The film annealed for 25 hours, the Zn distribution were observed at the surface region rather than the Al distribution, which is consistent with the observation that the ZnO film remains on the surface from the XRD and CL measurement results. Films annealed for 50 to 125 hours which ZnAl₂O₄ was formed clearly showed Zn and Al distributions were coincided with each other.

Fig.9 shows thickness of the ZnAl₂O₄ crystallized layer measured from SEM image and Zn distributed layer measured from FE-EPMA observation. The thickness of the crystallized layer reduced after above 50 hours thermal annealing. It is considered that the reason of reduction of ZnAl₂O₄ layer caused by re-evaporation of Zn from the film due to longer annealing. The crystallized layer was about 400 nm at the maximum, and the Zn was distributed inner about 600 nm from the surface. From Fig.7, the thickness of the UV emitting layer was estimated at 650 nm. Therefore, the emitting layer is considered to exist thicker than the crystallized layer and at the almost same region as Zn distribution.

4 CONCLUSION

ZnAl₂O₄ thin films for deep UV emitting phosphor prepared by deposition of ZnO on a-sapphire substrate and thermal diffusion process.

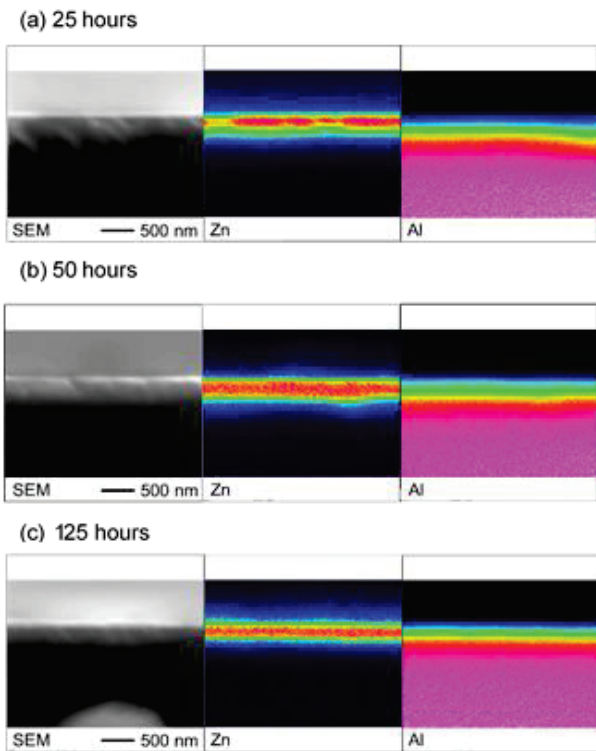


Fig.8 FE-EPMA observations of the films annealed for (a) 25 hours, (b) 50 hours and (c) 125 hours.

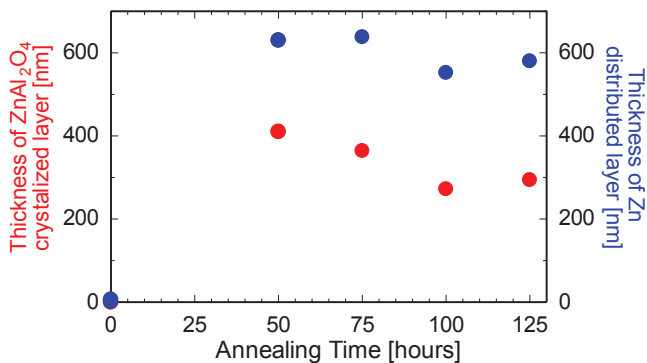


Fig.9 Thickness of crystallized ZnAl₂O₄ films measured from SEM image and thickness of Zn distributed layer measured from mapping of Zn.

The diffraction peak of ZnAl₂O₄ (333) was observed, and the crystallinity was improved by longer annealing from XRD measurement.

The UV emission caused by ZnAl₂O₄ and the deep-red emission caused by Cr in the substrates were observed from CL measurement. The UV peak of films annealed for 25 hours or less were around 240 nm, and films annealed 50 hours above were around 250 nm. It indicates that the former was formed Zn-poor ZnAl₂O₄ phase, and the latter was formed stoichiometric ZnAl₂O₄ layer. Also, it was confirmed that UV intensity was increased by improvement of crystallinity in the process of longer annealing.

The UV emission intensity saturated above 8 kV from relationship between the emission intensity and the penetration depth of electron beam, so the emitting layer of ZnAl₂O₄ was estimated about 650 nm. From SEM image and Zn distribution by FE-EPMA, the thickness of crystallized layer was about 400 nm, and Zn distribution layer was about 600 nm. Therefore, it is thought that the emitting layer exist thicker than the crystallized layer and at the almost same region as Zn distribution.

5 REFERENCES

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