

Evaluation of Inner Phase of ZnAl₂O₄ Thin Film for Ultra Violet Emission

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ABSTRACT

ZnO films were deposited on sapphire substrates by magnetron sputtering and annealed to produce zinc aluminate (ZnAl₂O₄) deep ultraviolet emitting phosphor thin films by mutual thermal diffusion between film and substrate. Etching was applied to the annealed samples to change the film thickness of ZnAl₂O₄. the samples after etching were subjected to emission characteristics evaluation by cathodoluminescence (CL) and crystal structure analysis by X-ray diffraction (XRD), and elemental mapping by field emission-scanning electron microscope analysis (FE-SEM) to estimate the range where Zn was distributed and the distribution of high quality emitting layer.

1 INTRODUCTION

UV light has high energy and is said to be appropriate for sterilization because it can decompose C=C bonds in cells. The currently used UV light sources, such as mercury lamps and UV LEDs, have problems in terms of cost and the risk of using mercury, and the need for new UV light sources is focused on high efficiency and low cost, low environmental impact. In this study, we focus on ZnAl₂O₄, a deep UV emitting phosphor. [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 addition, application to solid-state devices can be expected by thinning the phosphor. 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 its optical properties for application to solid-state devices such as EL lamps.

2 EXPERIMENT

Fig.1 shows the experimental procedure and conditions for preparing the ZnAl₂O₄ thin film. ZnO layer of 300 nm and α-Al₂O₃ layer of 50 nm as a capping layer to prevent

re-evaporation of ZnO film was deposited on c-plane sapphire substrates by RF magnetron sputtering. Thereafter, films were annealed at 980~ 1100 °C for 40 to 75 hours in air. ZnAl₂O₄ films were formed by thermal diffusion of Zn and Al between deposited ZnO film and sapphire substrate. ZnAl₂O₄ films were etched with hydrogen chloride (HCl) for 20 to 300 minutes to evaluate internal properties. Crystal structure and element distributions of films were evaluated by XRD

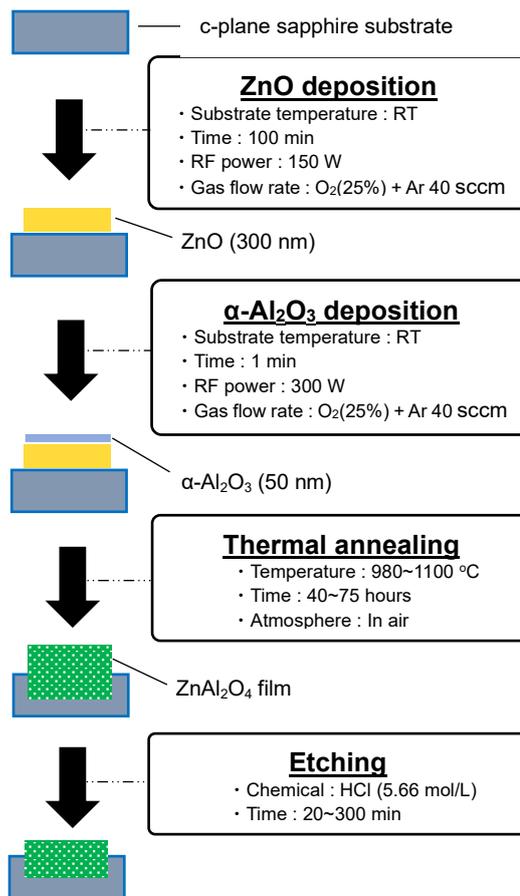


Fig.1 Experimental procedure of preparing ZnAl₂O₄ films.

and FE-SEM, and luminescence property was analyzed by CL.

3 RESULTS AND DISCUSSIONS

The internal properties of the thin film were investigated by comparing the results of FE-SEM, XRD, and CL measurements after etching the samples for 20 to 300 minutes.

Figure 2 shows the elemental mapping image of $ZnAl_2O_4$ thin film before etching process. It was confirmed that the film thickness of $ZnAl_2O_4$ before etching was about 600 nm from the diffusion length of Zn elements.

Figure 3 shows the elemental mapping of Zn at each etching time. It was confirmed that the diffusion length of Zn elements decreased in proportion to the increase in etching time.

Figure 4 shows the relationship between etching time and the diffusion length of Zn elements. The etching rate was about 1.5 nm/min.

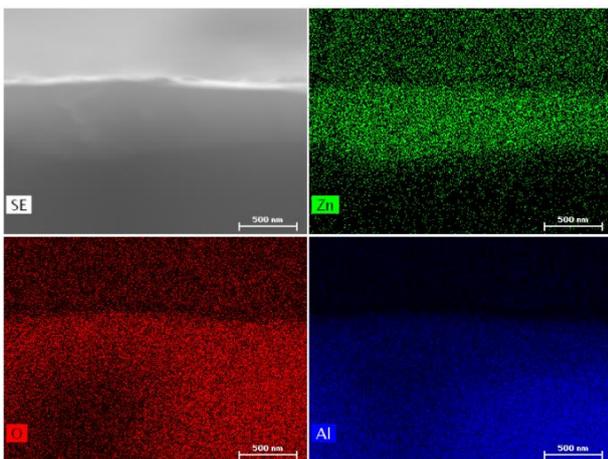


Fig.2 Elemental mapping image of $ZnAl_2O_4$ thin film before etching process.

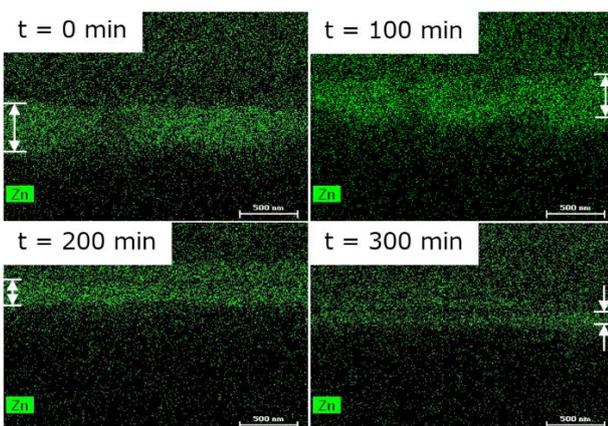


Fig.3 Elemental mapping of Zn at each etching time.

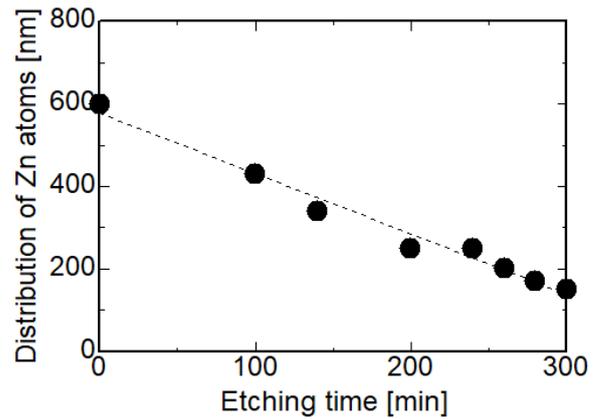


Fig.4 Relationship between etching time and the diffusion length of Zn elements.

Figure 5 shows the XRD measurement results for each etching time. (220) and (311), (400), (333) peaks of $ZnAl_2O_4$ were confirmed in all the samples, indicating that polycrystalline $ZnAl_2O_4$ was formed. Moreover, even if the film thickness was changed by etching, the peak did not disappear, and it is considered that the polycrystal was formed with the same kind of orientation from the surface to about 500 nm.

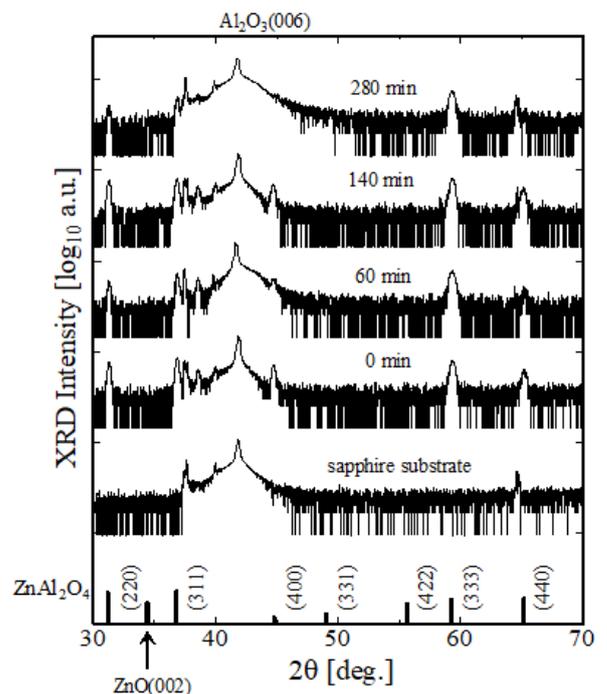


Fig.5 Etching time variation and XRD diffraction pattern.

Figure 6 shows the relationship between etching time and the intensity ratio of each $ZnAl_2O_4$ peak. The intensity ratio between (333) and (400) was relatively large, and it was confirmed that the intensity ratio of (333) increased sharply at around 260 minutes of etching.

This part corresponds to the initial stage of the reaction, and the predominant growth of (333) was observed. In addition, the intensity ratio of (400) tended to increase as it approached the surface, suggesting that the growth of (400) became dominant as the reaction progressed.

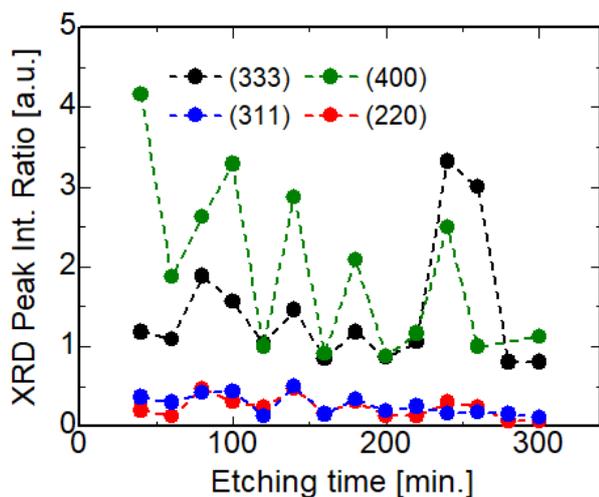


Fig.6 Relationship between etching time and the intensity ratio of each ZnAl_2O_4 peak.

Figure 7 shows the CL spectra before and after etching. The ultraviolet emission intensity reached a maximum after 80 minutes of etching, and then gradually decreased as the film thickness decreased. It is believed that the unetched sample had a lower strength due to the influence of the capping layer. It is known that the alumina of the capping layer deposited by sputtering is amorphous with no fixed orientation unlike the substrate. In the reaction on the substrate side, the (333) phase of sapphire and ZnAl_2O_4 is thought to grow predominantly due to the hexagonal symmetry of aluminum atoms, but the surface side of the thin film reacts with the amorphous layer, making it worse crystallinity than the inside structure. It is believed that this layer partially inhibited the penetration of electron beams and reduced the ultraviolet emission intensity.

In contrast to the previous trend, the film thickness decreased by more than 400 nm after etching for 260 minutes or more, and the ultraviolet emission intensity decreased sharply. From this result, in the range of 600 nm where Zn was distributed, the high quality emitting layer was formed at 400 nm on the surface side of the thin film, and the emitting layer was not sufficiently formed at 200 nm on the substrate side of the thin film, It is considered that the reaction is in the initial stage.

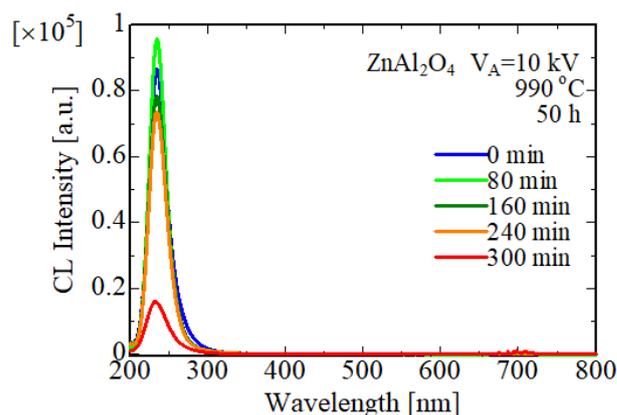


Fig.7 Relationship between etching time and CL spectrum of ZnAl_2O_4 .

Fig. 8 shows the relationship between etching time and the ultraviolet emission intensity, the ultraviolet emission peak wavelength. After etching for 260 minutes or more, the ultraviolet emission peak wavelength shifted to the shorter side corresponding to the rapid decrease in the ultraviolet emission intensity. ZnAl_2O_4 is known to shift the ultraviolet emission peak wavelength to the shorter side when the ratio of Zn is small. This also suggested that the diffusion of Zn and the formation of ZnAl_2O_4 on the substrate side of the sample were insufficient.

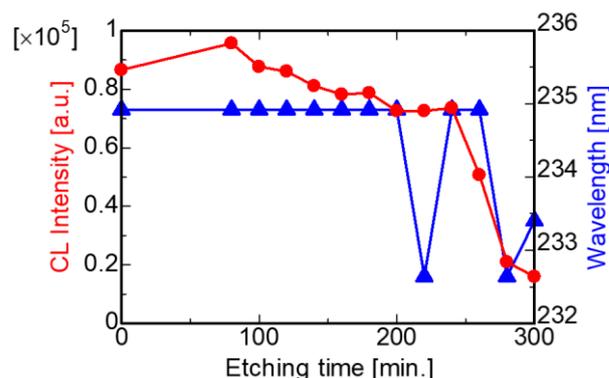


Fig.8 Relationship between etching time and the ultraviolet emission intensity, the ultraviolet emission peak wavelength.

4 CONCLUSION

The fabricated samples were subjected to etching treatment, the film thickness of ZnAl_2O_4 was changed, and the crystal structure analysis by XRD and the emission characteristics by CL, elemental mapping by FE-SEM were evaluated. From the XRD measurement results, it was found that multiple ZnAl_2O_4 phases were formed independently of specific parts of the emitting layer. In the UV emission intensity measurement by CL measurement, it is considered that the penetration of electron beams was inhibited due to the influence of the

film quality near the surface. In addition, from the film thickness where ultraviolet emission intensity decreased sharply and, the ultraviolet emission peak wavelength shifted to the shorter side, we were able to clarify the range where Zn is distributed and the distribution of high quality emitting layer.

5 REFERENCES

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