Preparation and Luminescent Characteristics of UV-C Emitting ZnAl₂O₄ Phosphor for Sterilization Device

Hiroko Kominami¹, Naoki Sonoda¹, Kazuhiko Hara²

Corresponding author's e-mail address : kominami.hiroko@shizuoka.ac.jp ¹Graduates School of Integrated Science and Technology, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8561, Japan ²Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, 432-8011, Japan Keywords: ZnAl₂O₄, UV emission, Cathodoluminescence, Photoluminescence

ABSTRACT

ZnAl₂O₄ ultraviolet (UV) emitting phosphor has been studied for next-generation ultraviolet emission device. We have been focused ZnAl₂O₄ powder and thin film for UV emitting phosphor to aim for sterilization devices because of the emission around 250 nm. Under electron beam excitation, ZnAl₂O₄ showed strong UV emission, the peak intensity of ~ 60% of P-22G (CRT commercial phosphor : ZnS:Cu,Al). Moreover, the phosphor has the excitation band around 150~180 nm. It indicates that it absorbs and emits excited by 147 nm and 172 nm VUV rays emitted by the discharge of rare gas containing Xe. Former display technologies may help develop UV generation lamps.

1 INTRODUCTION

The global pandemic of COVID-19 has led to frequent disinfection of hands and everywhere they can touch, and the pharmaceutical industry is rapidly developing vaccines. A new lifestyle has been advocated, and it has become necessary not only to wear face masks and secure social distance, but also lifestyle habits including dietary habits that improve immune function are emphasized, and how to protect ourselves from viruses is important. It has become a re-concern in people's lives.

Recently, attention has been focused on the possibility of ultraviolet sterilization in order to remove such harmful bacteria and viruses to the human body. UV-A, which is effective in producing tannins and vitamin D, has a relatively longer wavelength in UV region (320 - 390 nm). There are UV-B (280 - 320 nm), which is used as a medical light source for vitiligo, and UV-C (200 - 280 nm), which is said to be effective for sterilization.

Among these, UV-A is well known as an ultravioletemitting phosphor using 5d-4f transitions such as Eu^{2+} and Ce^{3+} , and one using band-to-band emission and exciton emission such as GaN and ZnO. UV-B has higher energy than that, and it is difficult for phosphors such as d-f transitions that depend on the crystal field. However, the Gd^{3+} -doped phosphor known as the 4f-4f transition luminescent center has emission around 310 nm, and those doped to various host materials are used.

On the other hand, UV-C has a higher photon energy

than UV-A and UV-B, and the energy corresponds to the forbidden gap width of the phosphor. The light in this region constitutes the organism. Since it is larger than the binding energy of carbon – carbon bonds (including double and triple bonds) that it bears, it is possible to break these bonds in a non-contact, and it shows a function as sterilization. So far, 254 nm, which is one of the emission lines of mercury, has been used as the light in this region. It is "fluorescent lamp" without phosphor coating. It is still widely used today because of its simple structure, low production cost, and strong sterilization line. However, concerns remain about the environmental issues of mercury utilization.

In recent years, we have been studying ultraviolet luminescent phosphors. Focusing on zinc oxide-based compound as the host material, we have been verified the detailed characteristics of these structures and the emitting characteristics for the application of sterilization lamps [1-8].

2 EXPERIMENT

2.1 Synthesis of powder phosphors

ZnAl₂O₄ powders were prepared by solid phase synthesis using ZnO (99.999%) and α -Al₂O₃ (99.99%) powders of High Purity Materials Kojundo Chemical Laboratory Co., Ltd. The ratio of source materials (ZnO/ α -Al₂O₃) was changed from 0.90 ~ 1.05 for control the phase and the vacancy. The powders were fired at 1300 °C for 3 hours in air. Below 1300 °C, the source materials were remained in the powder because synthesis temperature was not enough high. On the other hand, above 1300 °C, α -Al₂O₃ was remained in the powder because Zn was removed. Therefore, the optimum firing temperature is 1300 °C. Additionally, the powders were annealed in active carbon, hydrogen and oxygen atmosphere [1-3].

2.2 Preparation of thin films

For ZnAl₂O₄ thin film preparation, we used an RF magnetron sputtering device for deposition of ZnO and α -Al₂O₃ layers on c-plane sapphire substrate. ZnO layer (~300 nm) was deposited at 180 °C for 100 min in the atmosphere of 25%O₂ diluted with Ar. Next, α -Al₂O₃ layer (~10 nm) as a capping layer to prevent re-evaporation of

ZnO film was deposited on ZnO layer. RF powers were kept at 100 W during deposition. After deposition, the films were annealed for $2 \sim 200$ hours at $1000 \,^{\circ}$ C in air. ZnAl₂O₄ films were formed by thermal diffusion of Zn and Al between deposited ZnO film and sapphire substrate [4-8].

Crystal structure and element distributions of films were evaluated by X-ray diffraction (XRD) and field emissionelectron prove micro analysis (FE-EPMA), and luminescence property was analyzed by cathodoluminescence (CL) and photoluminescence (PL, PLE) using deuterium (D2) lamp.

3 RESULTS and DISCUSSION

3.1 Cathodoluminescence Properties

Figure 1 shows CL spectra of ZnAl₂O₄ phosphors by changing the ratio from 0.90-1.05, excited by electron beam at anode voltage of 10 kV and current density of 30 μ A/cm². Interestingly, there is no emission from the source materials in all powders in spite of remain of ZnO at higher ratio. At lower Zn ratio, CL intensity was strong and FWHM of spectra was narrow. However, according to increasing Zn ratio, the emission peaks were shifted to lower energy, and CL intensity decreased. Additionally, FWHM of the spectra became wider from 0.78 eV to 0.84 eV. It is thought that the emission mechanism of ZnAl₂O₄ was changed between higher and lower Zn ratio.

The CL intensity of the powder synthesized at the ratio of Zn 0.95, and 1300 °C firing showed about 60 % against at the CL intensity of ZnS:Cu,Al that is used for CRT green phosphor. It indicates that the efficiency of ZnAl₂O₄ emission is comparable with CRT phosphors.

Previously, a research on Field Emission Displays (FEDs) was actively conducted as one of the display technologies. Research on the phosphors for electron beam excitation and the fabrication of field emission arrays (FEAs) has progressed to a level close to commercialization, however, unfortunately it was



Fig.1 CL spectra of ZnAl₂O₄ (ZnO / α -Al₂O₃ = 0.90 - 1.05) powders fired at 1300 °C, excited by electron beam at anode voltage of 10 kV and current density of 30 μ A/cm² [2].

overwhelmed by other display technologies. Currently, it is very difficult to commercialize the FEDs, but it may be a commercial product as a lamp.

This UV emitting phosphor shows high efficiency. The process of painting RGB phosphors like a display is not necessary, just make a phosphor screen uniformly, and there is no need to worry about the adjustment slight deviations in display creation. Therefore, the possibility of practical use as an UV lamp for sterilization is fully considered.

3.2 Photoluminescent Properties

Figure 2 shows PL and PLE spectra of ZnAl₂O₄ phosphors excited by 160 nm and monitored at each PL peak wavelength. From PLE spectra, there are absorption bands around 180 nm. According to increasing Zn ratio, the absorption edge was shifted to lower energy. It is thought that the bandgap of ZnAl₂O₄ became narrower or was formed another energy level as Zn ratio increase. From PL spectra, all emission peaks showed lower energy than absorption band. Therefore, it indicates that oxygen vacancy or another energy level was formed in the bandgap of ZnAl₂O₄.

From PLE spectra shown in Fig,2, it can be seen that ZnAl₂O₄ has an excitation band in the 150-180 nm region. In other words, it means that it absorbs and emits excited by 147 nm and 172 nm VUV rays emitted by the discharge of rare gas containing Xe. It is possible to manufacture the UV lamps using the principle of plasma display panels (PDPs) that apply Xe-containing rare gas discharge to displays. An UV lamp using a UV-B emitting phosphor has actually been produced [6], and it is considered that an ultraviolet lamp having a shorter wavelength can be produced by optimizing the material of the device.



Fig.2 PL and PLE spectra of ZnAl₂O₄ (ZnO / α -Al₂O₃ = 0.90 - 1.05) powders fired at 1300 °C, excited by 160 nm and monitored at each PL peak wavelength [2].

3.3 Properties of Thin film Phosphor

To analyze the basically optical properties, it is difficult to evaluate because it is the influence of surface scattering. We thought that it is possible to evaluate these fundamental properties by thinning ZnAl₂O₄. Figure 3 shows CL spectra of the prepared thin films, as-deposited and annealed for 2 ~ 200 hours, under excitation by anode voltage of 2 kV. Some emissions in ultraviolet (UV), nearultraviolet (NUV), green and near infrared (NIR) region were obtained. These emissions were originated from ZnAl₂O₄, ZnO exciton, ZnAl₂O₄:Mn and Cr in sapphire, respectively. After 2 hours annealing, UV emission from ZnAl₂O₄ and NUV emission from ZnO were obtained. According to increase annealing time, UV emission became stronger because the formation of ZnAl₂O₄ phase was promoted by annealing. After 100 hours annealing, UV emission was the strongest. The emission became poor and green emission from ZnAl₂O₄:Mn was observed from 200 hour-annealed film. It is thought that reevaporation of Zn from ZnAl₂O₄ was occurred, and Mn doping was occurred from the furnace contamination. The absorbed energy was transferred to Mn, then the green emission was obtained. From X-ray diffraction patterns, ZnAl₂O₄ phase was appeared after 2 hours annealing. Interestingly, the diffraction of ZnAl₂O₄ (333) plane became stronger according to increase of annealing time [4][7].

Figure 4 shows FE-SEM observation and crosssectional atomic distributions of the films annealed for (a) 100 hours (left) and (b) 200 hours (right). In Fig.3(a), it is confirmed that Zn was diffused in the substrate and formed ZnAl₂O₄ phase. The thickness of ZnAl₂O₄ was about 1000 nm, it is good agreement with penetration depth property from CL measurements. On the other hand, ZnAl₂O₄ layer



Fig.3 CL spectra of the films as-deposited and annealed for $2 \sim 200$ hours, under anode voltage of 2 kV excitation [7].



Fig.4 FE-SEM observations and cross-sectional atomic distributions of the films annealed for (a) 100 hours (left) and (b) 200 hours (right).[7]

became thinner in 200 hour-annealed film. That is the reason of the saturation of UV emission by CL measurement.

From these results, the optimum annealing time is around 100 hours. If it becomes possible to form a high-quality $ZnAl_2O_4$ thin film, it can be applied to thin film devices. For example, if an insulating layer is formed on the $ZnAl_2O_4$ emitting layer to form a double insulating structure, it may be possible to obtain the electro-luminescence emission.

4 CONCLUSIONS

ZnAl₂O₄ UV emitting phosphor has been studied for next-generation ultraviolet emission device. We have been focused ZnAl₂O₄ powder and thin film for UV emitting phosphor to aim for sterilization devices because of the emission around 250 nm. Under electron beam excitation, ZnAl₂O₄ showed strong UV emission, the peak intensity of ~ 60% of P-22G (CRT commercial phosphor : ZnS:Cu,Al). Moreover, the phosphor has the excitation band around 150~180 nm. It indicates that it absorbs and emits excited by 147 nm and 172 nm VUV rays emitted by the discharge of rare gas containing Xe. Former display technologies may help develop UV generation lamps. The know-how cultivated as a display manufacturing technology may be refocused as an ultraviolet light emitting device.

REFERENCES

- H.Kominami, Y.Nakanishi, Proc. of International Vacuum Nanotechnology Conference 2009, pp.67-68 (2009).
- [2] T.Iguchi, H.Kominami, Y.Nakanishi, K.Hara, A.Ohnishi, M.Kitaura, "Structural and cathodoluminescent properties of ZnAl₂O₄ phosphor for UV emission", Proc. IDW '10, pp.1023-1026 (PHp1-10) (2010).
- [3] T.Ishinaga, T.Iguchi, H.Kominami,K.Hara, M.Kitaura, A.Ohnishi, "Luminescent property and mechanism of ZnAl₂O₄ ultraviolet emitting phosphor", Phys. Status Solidi C, 12/6, pp.797-800 (2015).
- [4] T.Ito,H.Kominami, Y.Nakanishi, K.Hara, "Preparation and Luminescent Properties of Ultra Violet Emitting

ZnAl₂O₄ Thin Film by Thermal Diffusion", Proc. IDW '15, pp.552-553, (PHp1-11L) (2015).

- [5] T.Ito, H.Kominami, Y.Nakanishi, K.Hara, "Preparation of deep UV emitting ZnAl₂O₄ thin film by thermal diffusion of α-Al₂O₃ / ZnO multilayers", Proc. IDW '16, pp.639-640 (PH2-8L) (2016).
- [6] K.Awamoto, H.Hirakawa, B.Guo, T.Shinoda, "Current Status of the Flexible Surface Light Source Development using LAFi Technology", Proc. IDW '15, pp.619-620, (FED3-4L) (2015).
- [7] K.Kijima, T.Ito, H.Kominami, Y.Nakanishi, K.Hara,
 "Atomic Distribution of ZnAl₂O₄ Thin Film Prepared by Thermal Diffusion of ZnO on Sapphire Substrate", Proc. IDW '17, pp.659-660 (PHp1-8L) (2017).
- [8] K.Imagawa, H.Kominami, Y.Nakanishi, K.Hara, "Formation of ZnAl₂O₄ Thin Film for Deep Ultraviolet Emitting Phosphor and Evaluation of Luminescence Properties", Proc. IDW '19, pp.796-799 (PHp1-5L) (2019).