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Preparation and Fluorescence Properties of Amorphous Zn-Ga-O Thin Film with Multilayered Structure

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A greenish blue light emission was observed in the sputtered film which was deposited on 500 °C substrates from a $ZnGa_2O_4$ target. The films prepared were an amorphous and a characteristic multilayered structure with a compositional modulation. In the film with thickness of about 40nm, about 2nm thick of surface layers were Zn-rich and inner layers were Ga-rich. Light emission intensities increased as increasing film thickness and showed a saturation at the film thickness above 50nm. In the case of 40nm thick of films the maximum light emission strength was obtained at acceleration voltage of an electron beam excitement of about 200V. A penetration depth of electrons exited by 200V may be few nm, of which the thickness is same order of the surface layers. It was thought that an enhancement of a light emission intensity took place in the multilayered structure of the Zn-Ga-O films.

Key Words: Zn-Ga-O thin film, amorphous, multilayer, cathodeluminescence, FED

1. Introduction

A Field Emission Display (FED) has been interested in as a new light emissive display with high resolutions and less electricity consumption.[1] Materials of phosphor screen or cathode emitter cones of the FED have been developed for practical applications.

Well known phosphors for a high voltage cathode ray tube are not available for the FED because of their high resistivity and of release of pollution gas. Also since acceleration voltage in a vacuum fluorescent display (VFD) is lower than that in FED, the VFD phosphors are also not optimized for FED operations. Especially blue light emissive phosphors have not been enough developed in comparison with green or red light emissive phosphors.

A thin film type of phosphors have been expected to reduce the impediments about phosphors derived from a high electric resistivity or to increase an efficiency of light emissions instead of conventional phosphors[2]. The purposes of this work are to prepare Zn-Ga-O thin films by sputtering and to evaluate in-situ low voltage electron beam excitation luminescence. An enhancement mechanism of light emission was found in the obtained films with compositionally multilayered structure.

2. Experimental

Since properties of cathodeluminescence strongly depend on phosphor surfaces, it is necessary to investigate latent properties under surface conditions of less contamination. As deposited films must be evaluated without exposing in the atmosphere. A new vacuum system was developed and its details appeared elsewhere [3]. The feature of the system is that the sputtered film can be investigated in-situ just after a film deposition.

The vacuum system was constructed from a transfer system of a specimen film, a film preparation chamber, and a chamber for evaluations of cathodeluminescence or crystal structure.

Since sulfide phosphors emit easily sulfide or oxygen gas and pollute surfaces of emitters for field emission[4], a $ZnGa_2O_4$ oxide is a strong candidate for blue light emissions in FED[5]. In the film preparation chamber, thin films of a Zn-Ga-O system were prepared by rf reactive sputtering.

$Zn_xGa_2O_y$ (x=1, 2) targets used were sintered disks with a diameter of 40mm. The sputtering gas was a mixture of Ar and O_2. A total gas pressure was changed in the range, 10-20 mTorr. The sputtering power was 100-200W. The distance between the target and substrates was about 30mm. The typical deposition rate was very small, about 10nm/hr. A substrate used was a ITO glass. The substrate temperature was varied up to about 500 °C.

In the chamber for evaluations, thermionic electrons emitted from the VFD filaments were accelerated by anode up to 700V. A cathode luminescence generated in the specimen film was guided to a spectrometer (Hamamatsu Photonics K. K., C5966-11) through a hemisphere lens of 2mm diameter and an optical fiber.

The film surface structure was studied in-situ by reflected high energy electron diffraction (RHEED). A crystal structure was also analyzed by reflected X-ray diffraction (XRD) in the atmosphere. The depth profile of the film composition was investigated by X-ray

photoelectron spectroscopy (XPS). The thickness of the film was measured by multiple beam interferometer (MBI) or an atomic force microscope (AFM). The morphology of the film was observed by AFM or a scanning electron microscope (SEM).

3. Results and Discussion

Since Halo pattern by RHEED and no XRD peaks from the film were observed, the films prepared were thought amorphous.

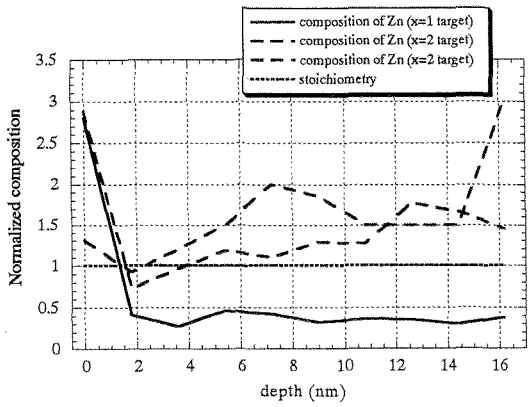

Fig. 1 Depth profile of the Zn composition in the films deposited on 500 ℃ substrates from different two targets with the composition of $Zn_xGa_2O_y$ (x=1 and 2).

Figure 1 shows the typical depth profile of the composition of the film by XPS. As a general tendency surface layers of the film were Zn-rich and inner layers Ga-rich, though the composition of Ga changed depending on that of the target. The film deposited on 50 ℃ substrates showed almost the stoichiometry. When the thickness of the thin film was about 40nm, that of Zn-rich layers was about 2nm.

A surface morphology of the film deposited on 500℃ substrates is shown in Fig. 2(a) in comparison with Fig. 2(b) of typical crystal $ZnGa_2O_4$ particles. Both the film and the particle revealed very smooth surfaces. However, many fine particles with a diameter of about 60nm on film surfaces. They were not crystallized and may be anomalously grown grains.

A cathodeluminescence was not observed in the films which were prepared on low temperature substrates, and were sputtered from the target of the composition, $Zn_2Ga_2O_5$ (mixture of ZnO+$ZnGa_2O_4$). The film deposited on 500 ℃ substrates from the $ZnGa_2O_4$ target revealed a greenish blue light emission. The cathode luminescence from thin films was studied by changing the film thickness. Figure 3 shows the cathodeluminescence spectra of the films. As a comparison with them the typical light emissions of $ZnGa_2O_4$ powders and ZnO powders are shown. The spectrum of the film was similar to that of ZnO rather than that of $ZnGa_2O_4$. The half width of the light emission peak of the films was wider than that of ZnO. The emission component at $\lambda \sim$ 500nm increased as increasing the film thickness.

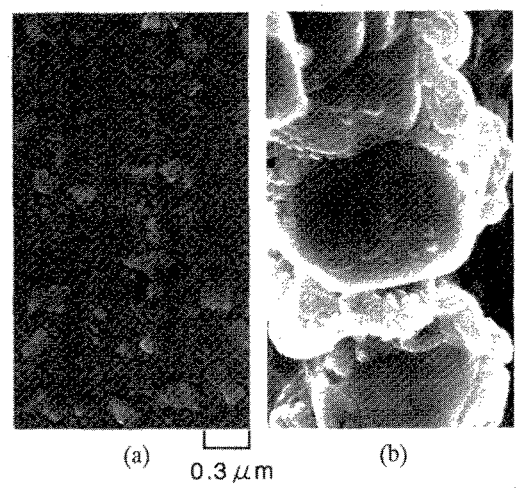

Fig. 2 SEM photographs.
(a) the film surface deposited on 500℃ substrates
(b) $ZnGa_2O_4$ particles.

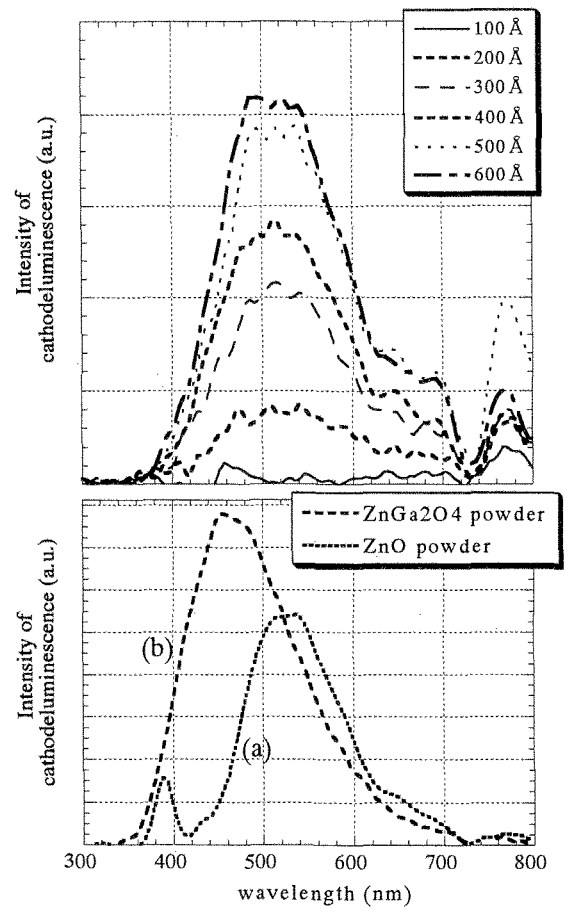

Fig. 3 Cathodeluminescent spectra of Zn-Ga-O films deposited on 500 ℃ substrates with various film thickness, and (a) ZnO and (b) $ZnGa_2O_4$ powder on ITO glasses.

The light emission was observed for the first time in the amorphous Zn-Ga-O thin film with the bilayered compositional modulation, though several groups[6-8] have reported a blue light emission from a $ZnGa_2O_4$ or a green light emission from ZnO.

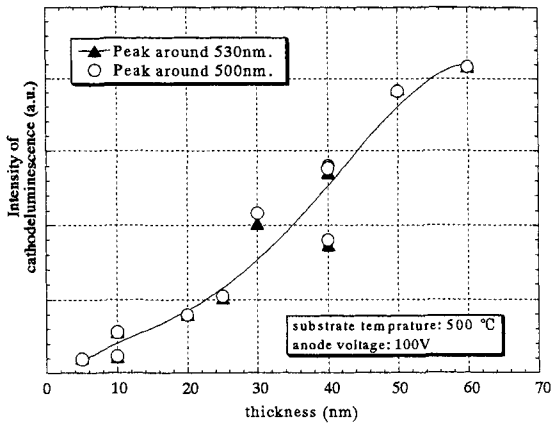

Fig. 4 The maximum peak intensity of cathode-luminescence vs. film thickness.

Figure 4 shows the maximum light emission peak intensities of the film as a function of a film thickness at acceleration voltage Va of 100V. They increased as increasing film thickness and revealed a saturation at thickness above 50nm. This result indicated that an electron penetration depth was at most about few nm.

Figure 5 shows the changes of the light emission spectra depending on an acceleration voltage Va. The light emission intensity attained the maximum at about 200V and decreased as increasing Va as shown in Fig. 6. The penetration depth at Va of 200V may be very small , the order of 1nm. Generally a penetration depth of incident electrons become large as increasing energy of the electrons. The enhancement of the light emission took place, however, in the bilayered structure as a function of Va.

These obtained results revealed that the light emissive region was strongly restricted near the surface layers. Here additional enhancement mechanism for light emission should be considered. When the band gap of surface layers is comparatively smaller than that of inner layers, a quantum potential well structure is formed. It is expected that carriers concerning with the light emission are enclosed and then the efficiency of the emission increases in the potential well.

4. Conclusion

Greenish blue light emission was observed in amorphous films deposited on 500°C ITO substrates from the $ZnGa_2O_4$ target. The composition was Zn-rich in surface layers and Ga-rich in inner layers. The cathodeluminescence from such the film was studied by changing the film thickness and acceleration voltage Va. When a penetration depth of excitation electrons was same order to the thickness of the Zn-rich surface layers, the maximum light emission was obtained. Conclusively the greenish light emission observed in this work was originated and enhanced in ZnO-based ultra thin layers near the surface of the Zn-Ga-O thin film.

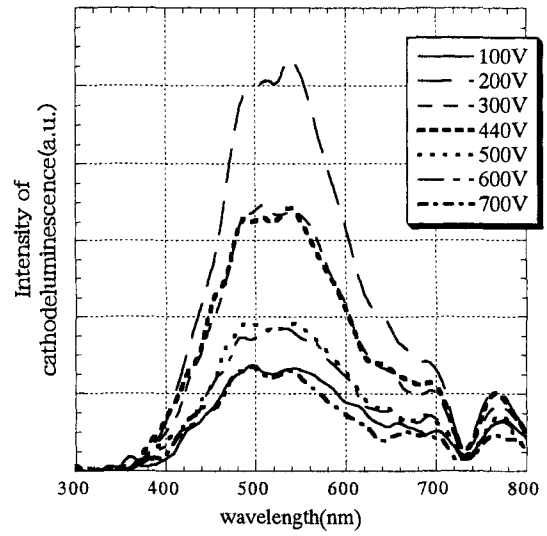

Fig. 5 Cathodeluminescent spectra observed at various acceleration voltage Va in the films with the thickness of about 40nm.

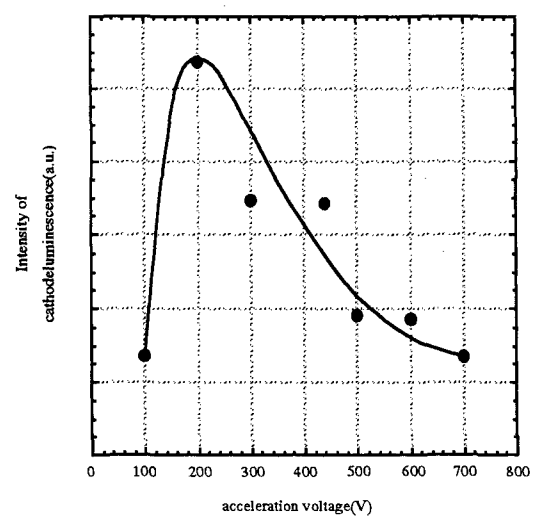

Fig. 6 The maximum peak intensity of cathode-luminescence vs. acceleration voltage Va.

Acknowledgements

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