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

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We constructed a new type of a vacuum system in which sputtering preparations of Zn-Ga-O films and in-situ evaluations of low voltage electron beam excitement luminescence can be performed. An emission of greenish blue light was observed in the film which was deposited on about 500℃ substrates from a $ZnGa_2O_4$ target. The obtained films were amorphous and have characteristic modulations of the composition to the direction of the film thickness. The emission peak was about 520nm and the half width of the peak from the film was wider than that from ZnO powder. It was thought that the characteristic emission is resulted in from the bilayered structure of Zn-Ga-O films which had Zn-rich surface layers and Ga-rich inner layers.

Key words: FED, vacuum system, Zn-Ga-O thin film , luminescence spectrum, bilayered structure

1. Introduction

A Field Emission Display (FED) has been developed as a light emissive display with high resolutions and less electricity consumption.[1] For practical applications of the FED materials of phosphor screen or cathode emitter cones must be still more developed.

Phosphors in the FED need to have a low resistivity, no release of pollution gas, a high efficient emission light, and a stabilization of surface. Conventional phosphors for a high voltage cathode ray tube are not available because of their high resistivity. Acceleration voltage in a vacuum fluorescent display (VFD) is lower than that in FED and VFD phosphors are also not optimized for FED operations. Blue light emission phosphors have not been enough developed in comparison with green or red light phosphors. Then a new type of blue light emissive phosphor is strongly requested for a realization of a practical full color FED. On the other hand, phosphor thin films are expected to reduce impediments about phosphors derived from a high electric resistivity or to increase an efficiency of light emissions.

When we think a thin film type of phosphor instead of conventional phosphors[2], it may be expected that materials with even comparatively high resistivity become candidates or more efficient light emissions are obtained by introducing characteristic layered structures.

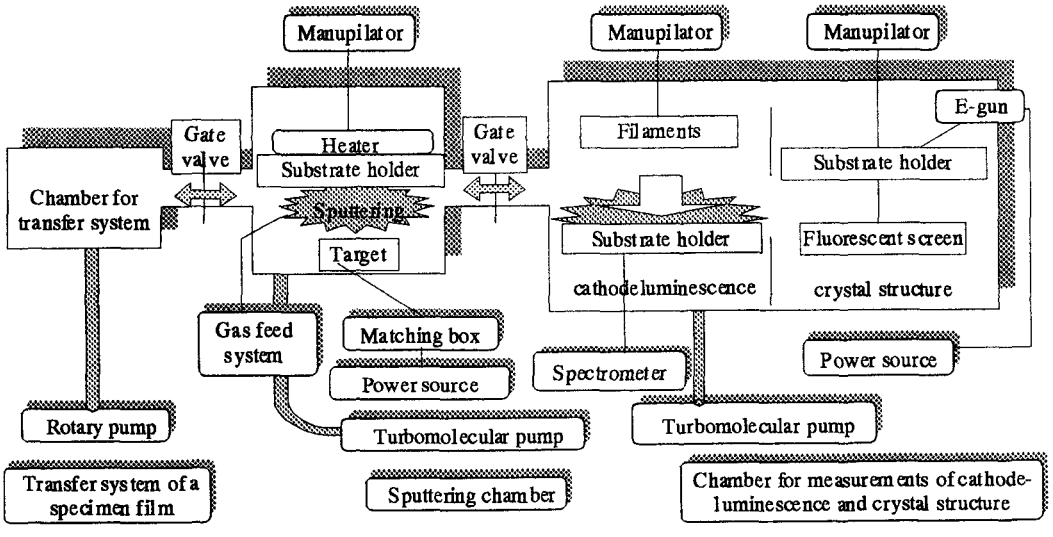

FIG. 1. Schematic of the vacuum system used for a film preparation and measurements.

The purposes of this work are to develop a new type of vacuum system and to study in-situ cathodeluminescence of sputtered thin films without exposing them to the air. Zn-Ga-O thin films were prepared on comparatively low temperature substrates and investigated about structures and/or low voltage electron beam excitation luminescence.

2. Experimental

Since properties of cathodeluminescence strongly depend on phosphor surfaces, it is necessary to investigate latent properties under surface conditions of less contamination. A formed specimen film must be evaluated without exposing in the atmosphere. Then a new vacuum system was developed and its details appeared elsewhere[3].

Figure 1 shows the schematic of the vacuum apparatus constructed in this work. The vacuum system was constructed from three parts: a transfer system of a specimen film, a film preparation chamber with a sputtering process, and a chamber for measurements of cathodeluminescence and crystal structure. It is the feature of this system that the sputtered film can be investigated in-situ just after film depositions.

A $ZnGa_2O_4$ oxide is a strong candidate for blue light emissions in FED[4]. Since sulfide phosphors emit easily sulfide or oxygen gas and are apt to pollute surfaces of emitters for field emission[5], Zn-Ga-O oxides were studied in this work. Thin films of a Zn-Ga-O system were prepared by rf reactive sputtering. $ZnGa_{2-x}O_y$ (x=0 - 2) targets used were sintered disks with a diameter of 40 mm. 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 - 200 W. The distance between the target and substrates was about 3 cm. The typical deposition rate was very small, about 10 nm/hr. A substrates used was a ITO glass. The substrate temperature was varied up to about 500℃.

Figure 2 shows the schematic of the specimen holder for the measurement of cathodeluminescence. After transferring the specimen film VFD filaments were moved toward the film surface by a manipulator. Thermal electrons emitted from the filaments were accelerated by anode up to 350V. A cathode luminescence generated was guided to a spectrometer (Hamamatsu Photonics K. K., C5966-11) through a hemisphere lens of 2 mm diameter and an optical fiber.

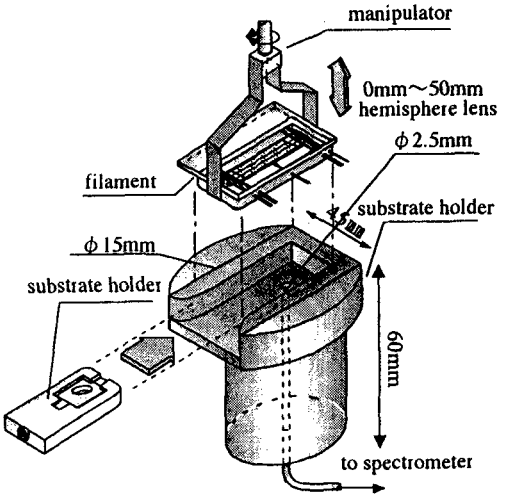

FIG.2. Schematic of the specimen holder developed for in-situ measurements of cathodeluminescence.

The film surface structure was studied in-situ by reflected high energy electron diffraction (RHEED) and/or the crystal structure was analyzed by reflected X-ray diffraction (XRD). The depth profile of the film composition was investigated by X-ray photoelectron spectroscopy (XPS). The morphology of the film was observed by an atomic force microscope (AFM) and a secondary electron microscope (SEM).

3. Results and Discussion

Only Halo pattern was observed in the film by RHEED. Any diffraction peaks were not observed in XRD patterns, excepting peaks of ITO. The films prepared had an amorphous or microcrystalline structure.

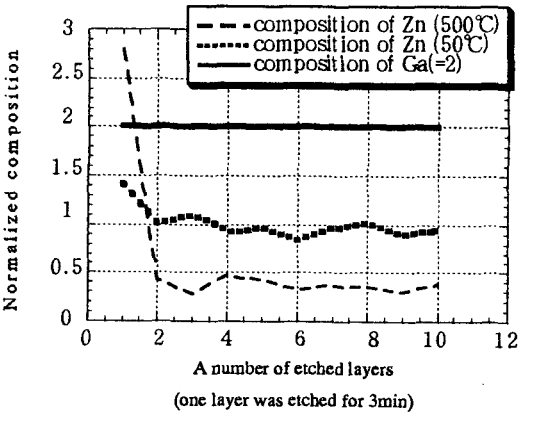

FIG. 3. Depth profile of the Zn composition x in Zn_xGa_2O films deposited on a 500 ℃ and 50 ℃ substrate.

Figure 3 shows the typical depth profile of the composition in the films obtained from the $ZnGa_2O_4$ target. In the film deposited on a 500℃ substrate surface layers were Zn-rich and inner layers were Ga-rich, while the film on a 50℃ substrate was almost stoichiometry. A comparatively high vapor pressure of Zn resulted in the deficiency of Zn. The thickness of the Zn-rich layers was about one tenth of that of the film.

Surface morphology of the film deposited on a 500℃ substrate is shown in Fig. 4. The film had a smooth surfaces and fine particles with a diameter of about 60 nm.

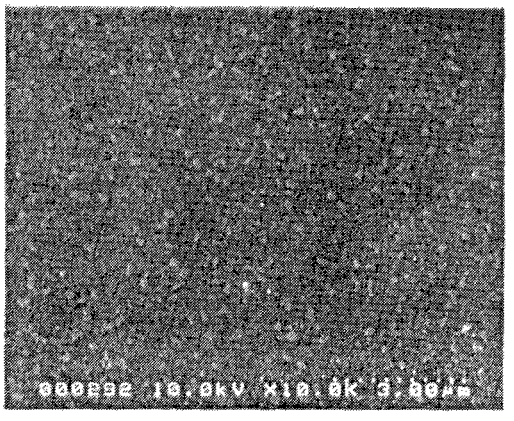

FIG. 4. SEM photograph of the film surface deposited on a 500℃ substrate.

Any emission was not observed in Zn-Ga-O films on low temperature substrates and/or in ZnO films sputtered from the ZnO target. A greenish blue light emission was, however, observed only in the film which was deposited on a 500℃ substrate from a $ZnGa_2O_4$ target.

Figure 5 shows the spectrum of cathodeluminescence from the film in comparison with that of $ZnGa_2O_4$ and ZnO powder. The luminescence of the film was similar to that of ZnO powders rather than that of $ZnGa_2O_4$ powder. Then the half width of the emission peak of the film was wider than that of ZnO powder.

Several groups reported green/blue light emissions of well crystallized $ZnGa_2O_4$ films[6)7)] or ZnO:Ga films[8)]. Here greenish blue luminescence was first observed in the amorphous Zn-Ga-O films which had a compositional heterostructure. So it is noticed that the film prepared in a comparatively low temperature process reveals the feasibility of greenish blue light emission.

The oxygen vacancy in ZnO:Zn is responsible for green emissions.[9)] P. Han et al.[10)] discussed green light emissions from Mn-doped $ZnGa_2O_4$, where the reduction of host material is also necessary for green emission. The greenish light emission observed here is thought to be brought from ZnO-based host materials in very thin surface layers.

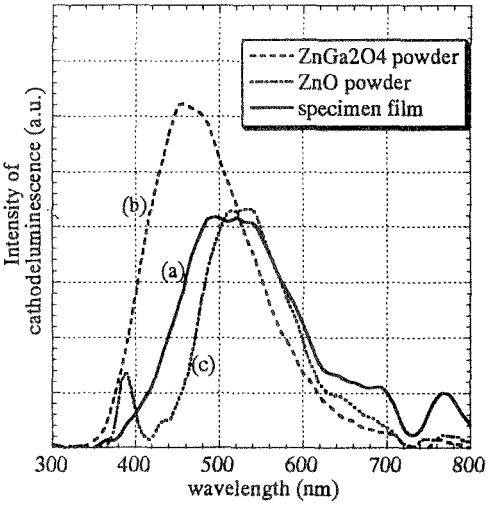

FIG. 5. (a)Cathodeluminescent spectrum of a Zn-Ga-O film deposited on a 500 ℃ substrate, (b) $ZnGa_2O_4$ powder and (c)ZnO powder on an ITO glass.

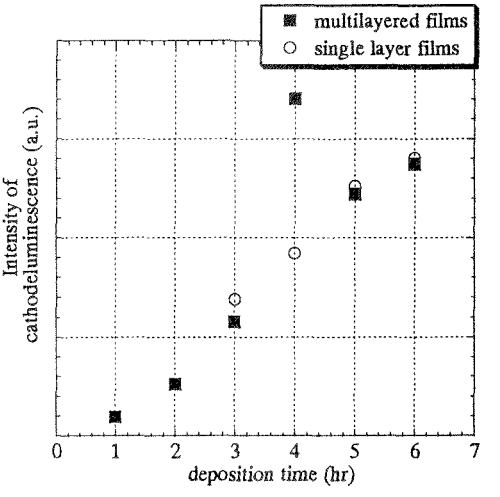

FIG. 6. Normalized peak intensity of cathodeluminescence vs. the film deposition time.

The layer with thickness of about 10 nm was alternately deposited for 1hr and successively in-situ measurements of cathodeluminescence were proceeded.

Figure 6 shows the peak intensity of cathodeluminescence depending on the number of the layer for the multilayered films, comparing with the results of single layer films continuously deposited. The

strength of light emission intensity tended to increase as increasing the number of the layer. In the case of the multilayered films the maximum emission was obtained in the 4 layered film. The emission intensity tended to be saturated with above 5 layers. The multilayered structure accompanying with compositional modulations may be related to the enhancement of cathodeluminescence though the detail is not clear. As shown in Fig. 6 an enhancement mechanism of light emission should be considered in the film with the characteristic heterostructure. The surface layers had comparatively narrow band gaps of ZnO-based materials. On the contrary the inner Ga rich layers had the more wider band gaps. Then the heterostructure near the surface may behave as a puseudo-potential well for electron-hole pairs excited by electrons. So the obtained results may reveal that the pseudo-potential well increase the probability of recombinations of carriers by luminescent centers and the efficiency of light emission.

In the results of the multilayered films, the depth of active luminescent layers was comparatively smaller than that expected in well crystallized phosphors because of small mean free paths of carriers. It is expected, however, the stronger light emission even in an amorphous film, if the heterostructure is optimized for accelerated electrons.

4. Conclusion

The amorphous films on a 500℃ substrate showed greenish blue light emission by low voltage accelerated electrons. It was thought that the cathodeluminescence is resulted in from the heterostructure of Zn-Ga-O films which had Zn-rich surface layers and Ga-rich inner layers. Also an enhancement mechanism of cathode luminescence can be expected in the compositional heterostructure. Conclusively the vacuum system constructed in this work was a useful tool to study properties of phosphor thin films.

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