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Effects of crystallinity on the luminescence of ZnS:Tb,P powder and film

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Abstract

To investigate the possibility of applying donor (D)–acceptor (A) pair emission in ZnS crystals to electroluminescence (EL) devices, the luminescence properties of ZnS:Tb,P are examined. In the cathodoluminescence spectra of ZnS:Tb,P powder, f–f emission of Tb^{3+} ions and D–A pair emission related to Tb donors and P acceptors are observed. It is found that D–A pair emission decreases more easily than f–f emission with degradation in crystallinity. In the cathodo- and electroluminescence of ZnS:Tb,P film, however, only f–f emissions, not D–A pair emissions, are observed. This is because of the lack of good crystallinity in the film. Based on these findings, it is proposed that not only less distortion but also a critical size are required for the observation of D–A pair emission in ZnS films.

Keywords: Electroluminescence; Cathodoluminescence; D–A pair emission; Crystallinity

1. Introduction

Thin-film electroluminescence (EL) devices for full-colour flat-panel display have been studied extensively for the past 15 years. The most promising green emitting material is ZnS:Tb,F [1] film prepared by r.f. sputtering. Various kinds of preparation methods [2,3], atomic structures of the complex centre of Tb^{3+} and F^- ions [4] and excitation mechanisms of Tb^{3+} ions have been discussed [5,6]. EL devices using ZnS:Tb,P film have been proposed to clarify the effect of the charge compensation on Tb^{3+} ion doping [7]. An investigation into the possibility of using ZnS doped with donors and acceptors, the most efficient blue-emitting phosphor for cathodoluminescence (CL), has revealed that D–A pair emission can be observed in the electroluminescence when high-quality ZnS film is prepared by metallorganic chemical vapour deposition (MOCVD) with precise doping control [8]. This report investigates the relationship between the crystallinity and emissions of f–f and D–A pairs in ZnS crystals to determine the possibility of applying D–A pair emission to EL devices. The effect of the crystallinity of ZnS on the luminescence was examined by measuring CL and EL of ZnS:Tb,P powders and films, both of which have the possibility of showing both D–A pair and f–f emissions related to Tb^{3+} ions.

2. Experimental

In preparing ZnS:Tb,P powder samples, undoped 99.999% purity ZnS was mixed with 99.99% purity Tb_4O_7 and $(NH_4)_2HPO_4$ of reagent grade, and then fired in a quartz crucible in a temperature range of 900–1050 °C for 2 h in an H_2S and Ar gas flow.

Films of ZnS:Tb,P were obtained by magnetron sputtering in an atmosphere of Ar gas, using cold-pressed ZnS:Tb,P powder of 1 mol.% as the sputtering target. The growth conditions were varied for substrate temperature (T_s) in the range 100–300 °C, Ar pressure 1.3–6.0 Pa, and input power 80–140 W, thus yielding the optimized conditions at 300 °C, 1.3 Pa and 120 W.

Undoped ZnS film was prepared by MOCVD on indium tin oxide (ITO) glass under reduced pressure. Diethyl zinc (DEZn) and hydrogen sulphide diluted to 2% with helium gas were used as source reactants for Zn and S, respectively. The ratio of the molar flow rate of S to that of Zn was fixed at 10, keeping the DEZn flow rate at 2.0×10^{-4} mol min^{-1}. The substrate

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temperature (T_s) was varied from room temperature to 450 °C.

Cathodoluminescence spectra were obtained with a Nikon P-250 monochromator. The concentrations of the Tb and P ions in ZnS were analysed by ICPS (inductively coupled plasma spectroscopy). The crystallinity was evaluated from the full width at half-maximum (FWHM) of the X-ray diffraction main peak.

The structure of EL devices is Al/SiO_2/Ta_2O_5/emitting layer/Ta_2O_5/SiO_2/ITO/glass. A stacked insulating layer of Ta_2O_5 (380 nm thick)/SiO_2 (120 nm) was prepared by r.f. sputtering, and an Al electrode was formed by thermal evaporation. As the emitting layer, ZnS:Tb,P film (500 nm) deposited by sputtering on undoped ZnS (100 nm) prepared by MOCVD was examined in addition to a single ZnS:Tb,P film.

Electroluminescence properties were measured under a 5 kHz sinusoidal wave or 1 kHz pulse excitation at room temperature. Conduction charges were measured with a Sawyer-Tower circuit.

3. Results and discussion

3.1. *Crystallinity and cathodoluminescence properties of ZnS:Tb,P powder*

Powder samples of ZnS:Tb,P are well crystallized and their average particle sizes measured by their SEM images are around 7 μm.

In the cathodoluminescence spectra of ZnS:Tb,P powder, both line and band spectra were observed. Their relative intensity is sensitive to a change in the preparation atmosphere, as shown in Fig. 1. When the powder was prepared at 1050 °C in an H_2S gas flow for 1 h and subsequently in an Ar gas flow for 1 h, keeping the concentrations of both Tb and P at 1 mol.%, its CL spectra show the f–f emission of Tb^{3+} ions and the broadband emission peaked at 520 nm. When the gas flow conditions are changed to 0.75 h in Ar and then 1.25 h in H_2S gas, a new broadband emission with a peak at 460 nm appears. For firing conditions of 1 h in Ar and 1 h in H_2S, the concentration of P was changed with the Tb concentration being at 1 mol.%. The resulting cathodoluminescence spectra of ZnS:Tb,P powder are shown in Fig. 2. With a decreasing concentration of P ions, the intensity of the emission peak at 520 nm decreases. When there are no P ions, it shows only the broadband emission peak at 460 nm, coinciding with the peak reported for ZnS:Tb prepared by atomic layer epitaxy [9]. This shows that the emission peak at 460 nm is observed when Zn vacancies are introduced due to an excess supply of S or when there is no intentional acceptor doping for donor impurities. The centre of this peak can be ascribed to the SA centre.

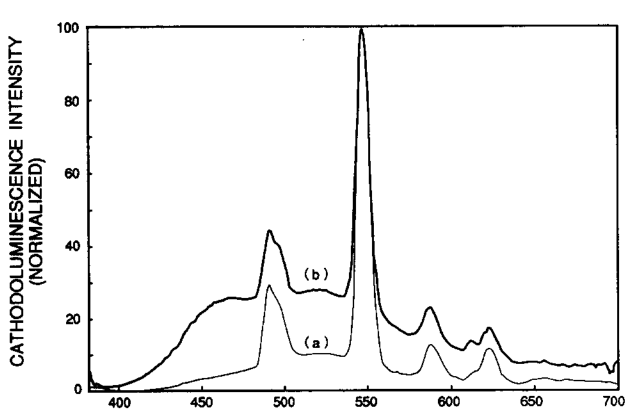

Fig. 1. Cathodoluminescence spectra of ZnS:Tb,P powder prepared at 1050 °C with different preparation atmosphere (a) in Ar 1 h and in H_2S 1 h; (b) in Ar 3/4 h and in H_2S 5/4 h.

Cathodoluminescence spectra were measured also by changing the concentration of Tb^{3+} ions in the range 0.1–1 mol.%, while keeping the concentration ratio of Tb^{3+} and P^{3-} ions at approximately 1 (Fig. 3). Each

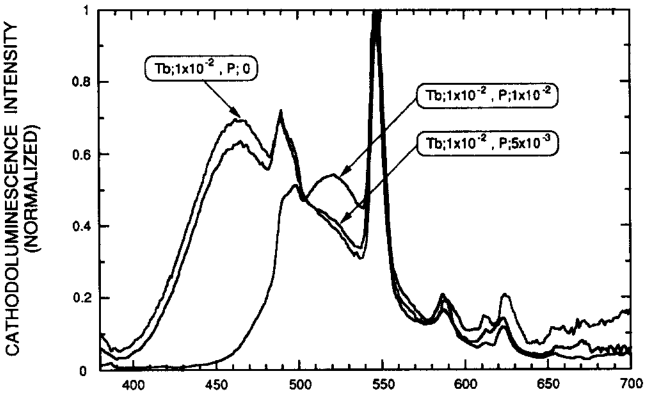

Fig. 2. Cathodoluminescence spectra of ZnS:Tb,P powder prepared at 1050 °C in Ar 1 h and H_2S 1 h with the different P concentrations.

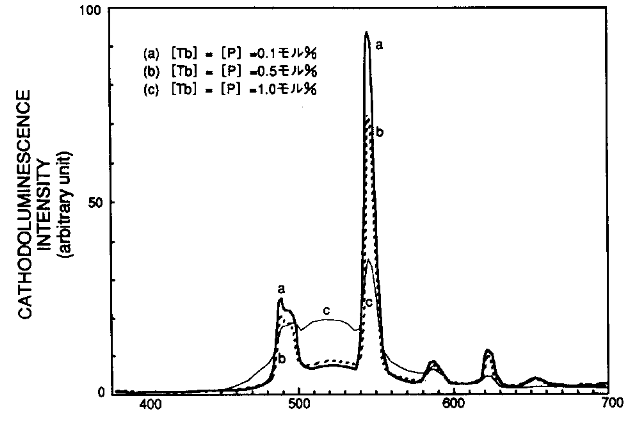

Fig. 3. Cathodoluminescence spectra of ZnS:Tb,P with different concentrations of activators.

spectrum consists of a broadband emission peaked at 520 nm and f–f emissions of Tb^{3+} ions. The intensity of the f–f emissions decreases with an increasing concentration of Tb^{3+} ions. The broadband is ascribed to the D–A pair emission because its time-resolved spectra show a peak shift to a lower energy with increasing delay time (Fig. 4). The emission can be assigned to Tb donor and P acceptor centres, because the emission intensity increases with an increasing concentration of Tb^{3+} and P^{3-} ions.

To investigate the effect of crystallinity on the intensity of D–A pair and f–f emissions, cathodoluminescence intensity was measured for ZnS:Tb,P powder, the crystallinity of which was degraded by grinding. In spite of the grinding, the average particle size of ZnS:Tb,P powder does not show any change and keeps its value at around 7 μm. The FWHM of the X-ray diffraction main peak (111), and the intensity of the D–A pair and f–f emissions are shown in Fig. 5 against the grinding time. Corresponding to the degradation in crystallinity, the intensity of D–A pair emission decreases drastically, becoming less than a half at 30 min grinding. In contrast, the intensity of the f–f emission decreases a little with 10 min grinding, and increases after 10 min. It shows a maximum at 30 min, where its value is more than 10% that of D–A pair emission. This increase in intensity in the 10–30 min grinding region may be explained by assuming the following: (i) by grinding, quenching centres are introduced between the donors and acceptors that have been contributing to the D–A pair emissions, (ii) the electrons captured by the Tb donors recombine with the holes, for example, in the valence band, because the appropriate acceptor centres do not exist in their neighbours, (iii) with this recombination energy, Tb^{3+} ions are raised to their excited states, and thus show f–f emissions. That is to say, D–A pair emissions are changed into f–f emissions with the introduction of quenching centres in the crystal. This phenomenon is very similar to that of SA centre emission in ZnS, where both SA emission and emission caused by the transition in the SA centre are observed [10]. With grinding for more than 45 min, the intensity of f–f emissions decreases again, but more slowly than that of D–A pair emission, and at 90 min grinding, they become equal. At 120 min grinding, where the FWHM is 0.22, D–A pair emission becomes very weak and f–f emission becomes dominant, though the average particle size still remains at around 7 μm.

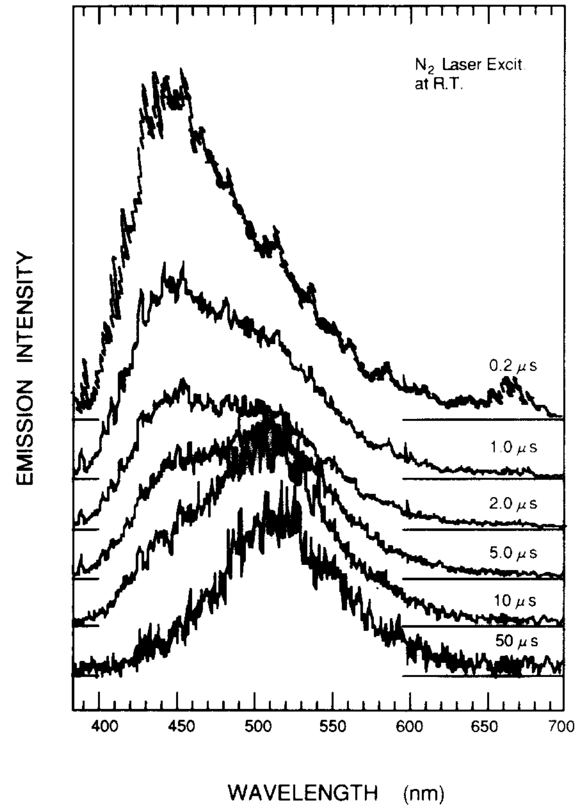

Fig. 4. Time-resolved luminescence spectra of ZnS Tb,P powder.

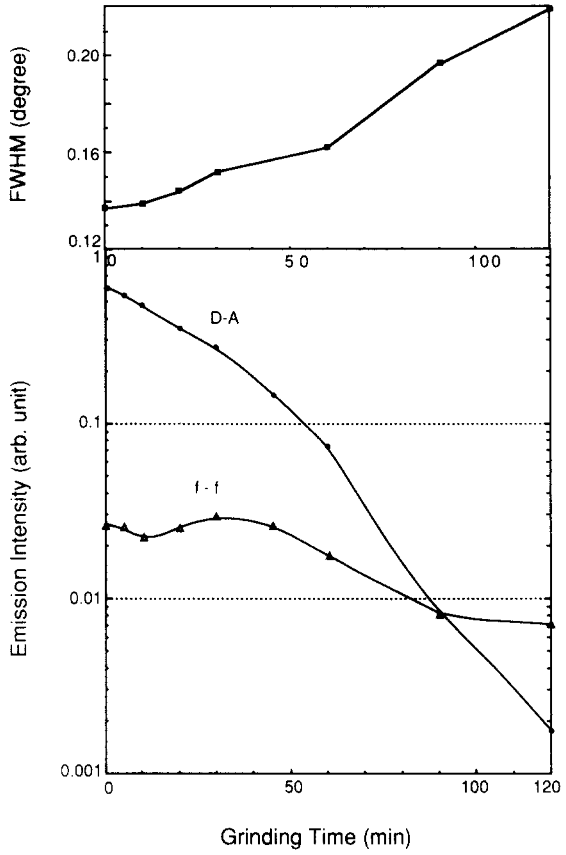

Fig. 5. The full width at half-maximum (FWHM) of the X-ray diffraction peak (111) and the intensity of the D–A pair and f–f emissions against the grinding time.

Summarizing the above results, Tb^{3+} ions act as the centre responsible for both f–f and D–A pair emissions in ZnS:Tb,P. When the concentration of Tb^{3+} ions is low, the Tb^{3+} ions act mainly as localized centres. With increases in the concentration of donors and acceptors,

Table 1
Properties of ZnS:Tb,P films on different substrates

Substrate	Glass	ITO/glass	Y_2O_3/Al_2O_3 (by EB) on ITO/glass	Ta_2O_5/SiO_2 (by sputtering) on ITO/glass	ZnS (by MOCVD) on ITO/glass
CL intensity (arb. unit)	3.8	4.7	5.0	5.6	6.8
FWHM of (111)	0.28	0.25	0.24	0.235	0.21

they function as donor centres. The change in the emission ratio between f–f and D–A pair emissions in the CL spectra with slight changes in the firing atmosphere can be explained as transitions between these two states of the Tb^{3+} ion centres resulting from slight changes in crystallinity. When the crystallinity of ZnS:Tb,P deteriorates, the degradation of D–A pair emission proceeds much faster than f–f emission.

3.2. Crystallinity of ZnS:Tb,P film and its luminescence properties

3.2.1. The effect of the substrate on the crystallinity of ZnS:Tb,P film

Under the optimized sputtering conditions, ZnS:Tb,P films were grown on different substrates, i.e. glass, ITO glass, electron beam-deposited Y_2O_3 (300 nm)/Al_2O_3 (100 nm) films on ITO glass, sputtered Ta_2O_5 (380 nm)/SiO_2 (120 nm) films on ITO glass, and undoped ZnS (100 nm) film prepared by MOCVD on ITO glass. The FWHM of the main X-ray diffraction peak (111) and the CL intensity of the films are shown in Table 1. The FWHM of the X-ray diffraction peak depends on the substrates. The ZnS:Tb,P film grown on undoped ZnS film has the smallest value. For this sample, the average particle size is found to be less than 100 nm by the TEM image of the cross-section of the film. RHEED pattern images which show the crystallinity near the top surface of the film are shown in Fig. 6 for sputtered ZnS:Tb,P films grown directly on ITO glass and on undoped ZnS film prepared by MOCVD. When grown on the undoped ZnS film, the film shows well-defined diffraction patterns, indicating improved crystallinity.

Next, to determine the effect of this improved crystallinity near the substrate interface, the electroluminescence properties of two EL devices were examined. It is generally known that in the active layer of thin-film EL devices, the crystallinity on the bottom (substrate side) is worse than that on the top, resulting in smaller luminance [11]. For the EL devices, sputtered ZnS:Tb,P films without (sample A) and with (sample B) undoped ZnS film by MOCVD were used as active layers. The EL devices are driven by pulse excitation at a pulse width of 1 ms. The results are shown in Fig. 7. In the case of sample A, when electrons come from the substrate side, its luminance is about 30% lower than when they come from the upper Al electrode. However, in the case of sample B, the relative luminance of both sides is almost the same, and the overall luminance is higher than that on the top of sample A. This shows that in sample B, the crystallinity of the sputtered ZnS:Tb,P film is improved from the beginning of crystal growth, thus yielding undoped ZnS film with good crystallinity. Luminance changes relative to the conduction current, as measured with a Sawyer-Tower circuit, are shown in Fig. 8. The luminance to conduction charge is larger for sample B than sample A. This is another indication of improved crystallinity.

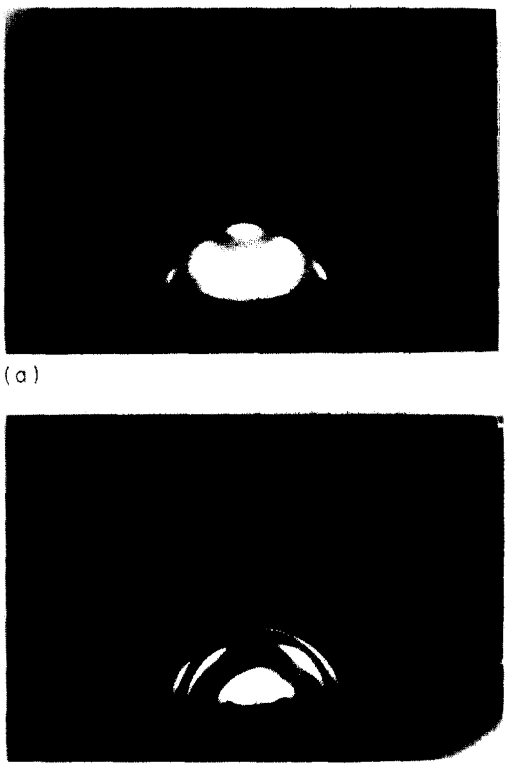

Fig. 6. RHEED patterns of ZnS:Tb,P film (a) on ITO glass and (b) on undoped ZnS prepared by MOCVD on ITO glass.

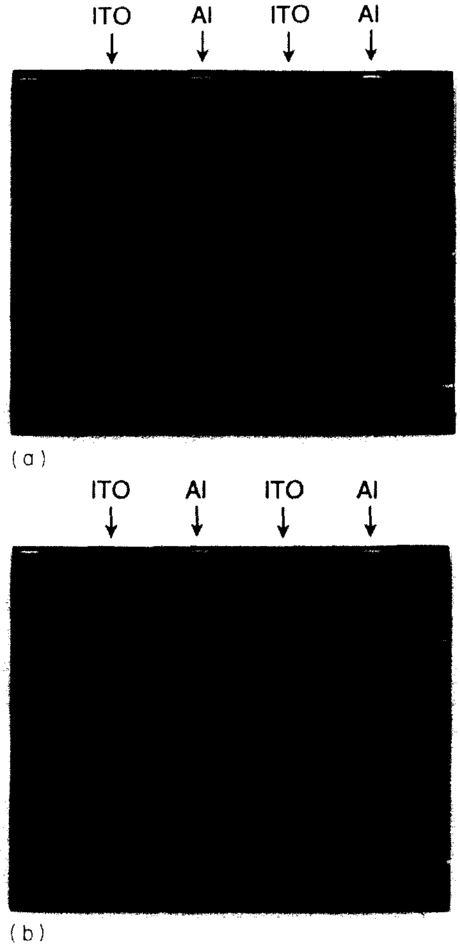

Fig. 7. Luminance of ZnS:Tb,P EL device under 1 kHz pulse drive. (a) ZnS:Tb,P on ITO glass, (b) ZnS:Tb,P on undoped ZnS by MOCVD on ITO glass. Al is the electrode of the upper side and ITO is that of the substrate side.

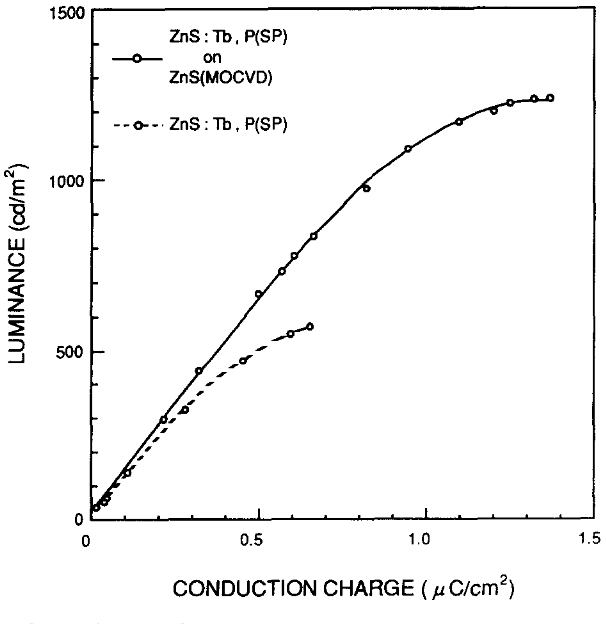

Fig. 8. Luminance of ZnS:Tb,P EL device against the conduction charge.

3.2.2. *Luminescence properties of ZnS:Tb,P films*

The above EL devices show EL luminescence spectra consisting of only f–f emissions of Tb^{3+} ions and no D–A pair emission. As an example, EL spectra of the sample B are shown in Fig. 9. Also in the cathodoluminescence spectra, ZnS:Tb,P films show no broadband emission such as D–A pair or SA emission. The concentrations of Tb^{3+} ions and P^{3-} ions in the film analysed by inductively coupled plasma spectroscopy (ICPS) indicate that there is little difference in the concentrations between the films and powders. This fact shows that it is more difficult to obtain D–A pair emissions than f–f emissions in the film.

The reason for this difference is thought to be that the crystallinity of the film is worse than that of the powder, and the degradation of D–A pair emission proceeds faster than that of f–f emissions.

As shown in Table 1, all the FWHM of the X-ray diffraction main peaks of the ZnS:Tb,P sputtered films except that of the film grown on undoped ZnS film prepared by MOCVD are larger than 0.23° and their crystallinities are worse than ZnS:Tb,P powder ground for 120 min which shows little D–A pair emissions, it is reasonable that no D–A pair emission can be observed in these films.

However, in the sputtered ZnS:Tb,P film grown on the undoped ZnS film prepared by MOCVD, the FWHM is 0.21° and smaller than that of the ZnS:Tb,P powder ground for 120 min. What is the reason for why the D–A pair emissions cannot be observed in the film in spite of the smaller FWHM than powder? The crystallinity expressed by the FWHM of the XRD main peak involves two factors. First, it indicates the amount of lattice distortion, such as point defects, dislocations and stacking faults, in other words, deviation from perfect crystallinity. Secondly, it indicates the effect of the particle size when the samples are composed of small particles, less than 100 nm. In the case of ZnS:Tb,P powder samples, their FWHM depend only on the

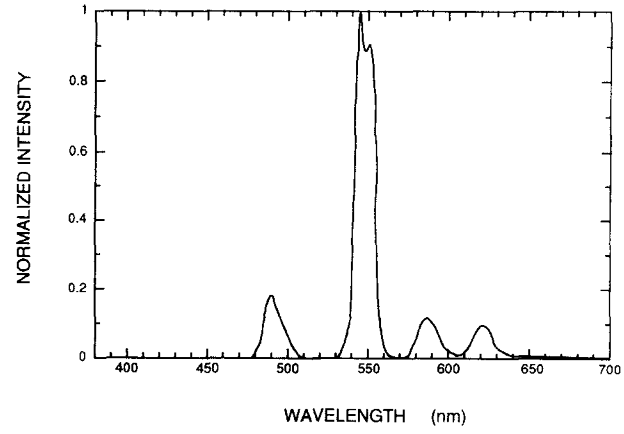

Fig. 9. Electroluminescence spectrum of the sputtered ZnS:Tb,P film on undoped ZnS prepared by MOCVD.

amount of the lattice distortion because their particle sizes are much larger than 100 nm. On the other hand, as the average crystalline size of the sputtered ZnS film on undoped ZnS film by MOCVD is less than 100 nm, its FWHM includes the effects of these two factors. This shows that for the observation of D–A pair emission, crystalline size works as the restriction factor in addition to the amount of lattice distortion. In other words, it needs some critical size for the observation of D–A pair emissions. As for the reason why D–A pair emission needs larger particle size than f–f emission, it can be understood that D–A pair emission needs larger space because of the recombination of two centres compared to f–f emissions in the localized Tb^{3+} ions.

At present, it is difficult to know the critical size for the observation of D–A pair emission because of the lack of high-quality ZnS:Tb,P film. It can be suggested, however, by the data of ZnS:Ag,Cl films prepared by MOCVD [10] that 60 nm is large enough as the critical size. In that case, the largest value of the FWHM of the film which show the D–A pair emissions is 0.17°. This value corresponds to the crystalline size of 60 nm when the line broadening is caused only by the crystalline size, assuming that there is no distortion.

As the result, it can be said that for the observation of D–A pair emission in ZnS film, not only less distortion but also the critical size are required as necessary conditions.

4. Conclusions

The effects of crystallinity on the luminescence of ZnS:Tb,P powder and film were examined to investigate the possibility of applying D–A pair emission in ZnS to EL device. In the cathodoluminescence spectra of ZnS:Tb,P powder, f–f emission of Tb^{3+} ions and D–A pair emission related to Tb donors and P acceptors were observed. It was found that D–A pair emission decreases more easily than f–f emission with degradation in crystallinity. In the growth of sputtered ZnS:Tb,P film, the effects of the substrate on the crystallinity were examined. ZnS:Tb,P film shows the best crystallinity when it was grown on undoped ZnS film prepared by MOCVD. In the cathodo- and electroluminescence spectra of ZnS:Tb,P film, however, only f–f emission, and no D–A pair emission was observed. This is due to the relatively poor crystallinity in the film compared with that in powder. Based on these findings, it is proposed that not only less distortion but also the critical size are required for observation of D–A pair emission in ZnS film.

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