

Influence of Heat Treating for ZnS:Mn Sputtering Targets on Inorganic Electroluminescent Device Active Layer Films

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Synopsis

Electroluminescent device active layer thin films were fabricated by radio frequency magnetron sputtering from targets that were heat-treated mixture of ZnS and MnS powder. Heat treating eliminates impurities and makes it solid solution (Mn incorporates ZnS). We prepared three kinds of target that vary firing temperature: 550°C, 700°C and 900°C.

Properties of targets and films are investigated by X-ray diffraction (XRD) to evaluate crystallinity and by photoluminescence (PL) to estimate state of luminescent center. Results from XRD showed that crystal properties of powder were improved with increasing temperature during heat treating but, films one were almost same for different conditions. PL spectra showed that increasing Mn²⁺ concentration with increasing firing temperature. Luminescence property was improved by using target which has a higher concentration of single Mn²⁺.

KEYWORDS: heat treating, sputtering, electroluminescence, ZnS:Mn, photoluminescence

1. Introduction

Inorganic thin film electroluminescent (TFEL) device is expected as a good candidate for flat panel display because of the advantages such as long lifetime, self-luminous property and slimness. Applied voltage to the device generates electroluminescence. Electrical excitation type EL occurs when luminescent center that is excited by accelerated electron returns to the ground state.

In this report, we prepared ZnS:Mn active layer thin film. ZnS:Mn is well known inorganic phosphor for TFEL device. Mn²⁺ in this phosphor behaves as a luminescent center. Luminescence spectrum of Mn²⁺ is broad with maximum luminescent intensity at about 585 nm (the color is orange-yellow). Luminescence of localized type luminescent center for instance Mn²⁺ was occurred by direct collision excitation process. Mn²⁺ is excited from ⁶S(⁶A₁) that is ground to higher state than ⁴G(⁴T₁) by hot electron that accelerated by electric field and it returns to the ground state by radiation of a photon. ZnS:Mn active layers fabricated by electron beam evaporation, ALE(atomic layer epitaxy) and MOCVD(metal organic chemical vapor deposition) have high luminous efficiency, although such a ZnS:Mn film is not easily prepared using the sputtering method. However we selected this method since it has some advantages that enables large area device fabrication at low cost ,moreover, that is high controllability of luminescent center concentration in film with changing the composition of the target. We focus attention on preparation condition of targets, especially firing temperature of targets. Heat treating eliminates contamination and incorporates Mn into ZnS crystal. The states of Mn²⁺ ions may be changed depending on heat treating parameters. In this report, influence of firing temperature on properties of sputtering targets and active layer films that made from them were investigated by photoluminescence and XRD.

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2. Experimental

Sputtering targets with Mn concentration 0.5 wt% were made from ZnS powder (Furuuchi Chemical Corporation, purity 99.999%) mixed with MnS powder (KOJUNDO CHEMICAL LABORATORY CO.,LTD, purity 99%) . The powder was heat-treated by the following procedures: (i) at 100°C under vacuum to remove H₂O; (ii) at three kinds of temperature (550°C, 700°C and 900°C) in Ar atmosphere without exposing to air. Finally, the powder became targets that were classified according to the firing temperature. Moreover, we call targets P550, P700 and P900 corresponding to firing temperature, respectively. We set temperature to higher than 550°C on the basis of our earlier experimental result such that heat-treating at higher temperature than 450°C would remove hydrocarbon contamination and other impurities. Furthermore, crystal structure of ZnS is usually cubic system and structural phase transition to hexagonal system occurs at about 1000°C. Heat-treating temperature should be lower than the transition temperature because Mn that substitutes Zn site in cubic system ¹⁾ works as luminescence center.

ZnS:Mn films were deposited on glass substrates (GEOMATEC Co.,Ltd, Corning #1737) by radio frequency magnetron sputtering in Ar plasma. Glass substrates had been cleaned sufficiently when films were deposited.

In our sputtering equipment, the distance between target and substrate is 50 mm and dimension of electrode is 78.5 cm² and magnetic flux density by permanent magnet is 10⁻² T. Substrates are placed on the anode and they can be heated by heater. Three kinds of active layer were prepared at the same deposition conditions shown in Table 1. We call prepared films as F550, F700 and F900 according to each target: P550, P700, and P900.

Table 1 Deposition conditions

Base pressure	6.0 × 10 ⁻⁷ Torr
Gas pressure	2.0 × 10 ⁻² Torr
Sputtering gas	Ar
RF power	50W
Deposition time	50 min
Substrate temperature	200 °C
Annealing temperature	200 °C
Annealing time	40 min

In general, the structure of ZnS:Mn EL device is Glass substrate/ITO/Insulating layer/ZnS:Mn (active layer) /Insulating layer/ Al electrode. However in this study, depositions of insulating layer and electrode (ITO and Al) were not performed, because we were interested just in the investigation of the state of luminescent center and crystallinity.

The crystallinity of targets and films were evaluated by X-ray diffraction (Shimadzu Corporation, Model XD-610).

Photoluminescence spectra were measured to get information about concentration of luminescent center. A 20 mW He-Cd laser (wavelength 325 nm) was used as an excitation source. The emission from sample was measured with a combination of monochromator (JASCO Corporation, Model CT-25C) and photomultiplier (Hamamatsu Photonics K.K., Model R1387). We measured PL spectra of samples P550, P700, P900, F550, F700 and F900. When measuring PL spectra of target powders, sample was made as follows: extremely small amount of the powder was placed on the quartz substrate.

3. Results and Discussion

3.1 Crystallinity of targets and thin films

Figure 1 and 2 illustrate XRD patterns of sputtering targets and films respectively. In those figures, $C(\)$ denotes plane indices of zinc blende structure (cubic system). Figure 3, 4 and 5 show temperature dependence of crystallite sizes for each plane indices. The crystallite diameters were calculated on the basis of Scherrer's equation using Table 2 that indicates half bandwidth of peaks that were determined by Fig.1. In the calculations, the following constants were used: the Scherrer's constant is $K = 1.05$ and wavelength of X-ray(Cu-K α line) is 1.54056 Å.

There are intensive diffraction lines at $2\theta = 28.5^\circ$, 47.5° and 56.5° in sputtering targets.(Fig.1) These correspond to diffraction at C(111), C(220) and C(311) respectively. Consequently, it indicates that ZnS in sputtering targets is cubic system. Increasing of temperature during heat treating leads to increase of peak intensity.

It seems that the decreasing of full width of half maxima (FWHM) which is shown in Table 2 is caused by the increase of lattice constant that meets Bragg's condition of diffraction by growth of crystallite under high temperature. Figure 3, 4 and 5 show obtained crystallite diameters, which indicate growth of grain by heat treating. In the case of P550, large amount of Mn would be located at crystal surface, because of smallness of the crystallite diameter and expansion of crystal grain boundary. Hence, Mn^{2+} is captured by crystal grain boundary during solid solution and it can come to cluster easily. In P900, high temperature during heat-treating would enhance diffusion of Mn and increase the number of single Mn^{2+} .

Since P900 has the minimum FWHM, we regarded P900 as the sample which has the best crystallinity in our targets. Improvement of crystallinity leads to improvement of crystal field's symmetrical property. This prevents the generation of the gap into which impurities may be incorporated. Additionally, the improvement makes Mn^{2+} ions to be isolated in ZnS crystallite.

Figure 2 shows the intensive diffraction peak at around 28.5° and the small peak at around 56.5° . But, it is difficult to confirm one at around 47.5° that is detected in XRD patterns of sputtering targets.

Above-mentioned experimental results (Fig.2) mean that C(111) of zinc blends structure aligned parallel to substrate by priority. Table 3 shows FWHM of peaks at around 28.5° . It seems that crystallinity get worse because FWHM of peaks increases in all films as compared with those in targets. Each peak's intensity and each peak's FWHM at around 28.5° show little difference in Fig.2, and there is distinguished distinction in Fig.1. Atoms and molecules are ejected from targets and deposited on substrate, so crystallinity of powder may not affect film's one directly. Crystallinity will be affected by deposition conditions rather than by firing temperature for targets.

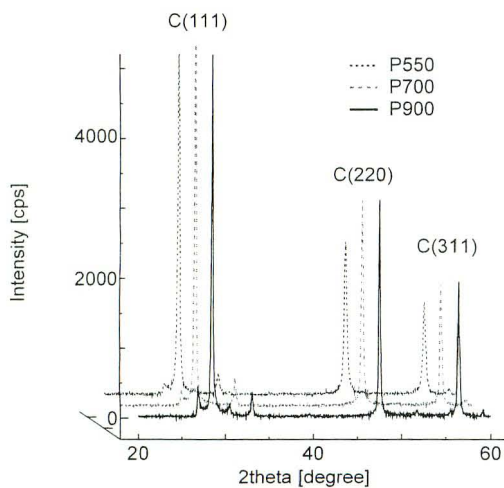


Table 2 FWHM of each peak at powders

	28.5[deg]	47.5[deg]	56.5[deg]
P550	0.290	0.346	0.354
P700	0.268	0.277	0.260
P900	0.196	0.214	0.233

Fig.1 XRD patterns of sputtering targets heat-treated at different temperatures

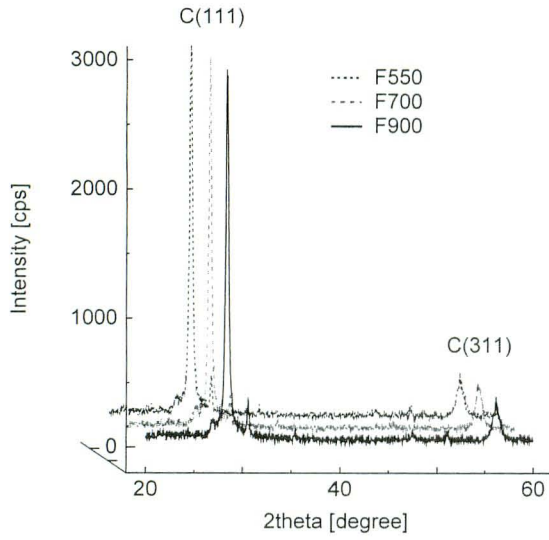


Table 3 FWHM of C(111) peak at films

F550	0.391 [deg]
F700	0.385 [deg]
F900	0.384 [deg]

Fig.2 XRD patterns of deposited films using different targets

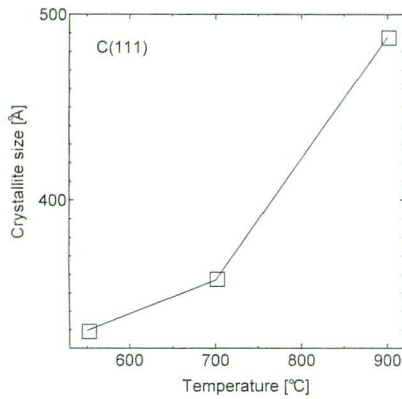


Fig.3
Temperature dependence
of crystallite sizes of C(111)

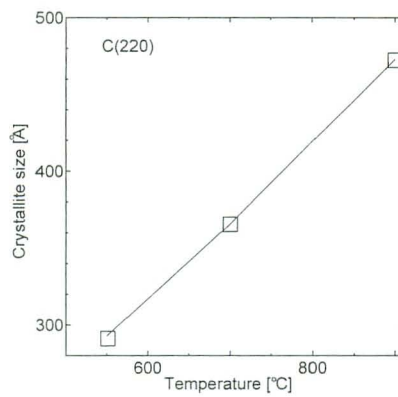


Fig.4
Temperature dependence
of crystallite sizes of C(220)

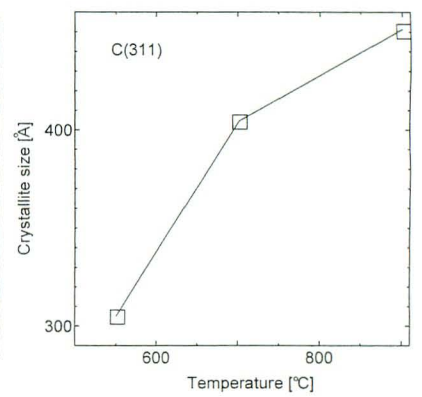


Fig.5
Temperature dependence
of crystallite sizes of C(311)

3.2 PL spectra of targets and films

Figure 6 and 7 show the PL spectra of sputtering targets and active layer films respectively. The luminescent center (Mn^{2+}) has emission peak at around 585 nm due to ligand-field transition (${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$). Although the peak of P550 can not be seen in this scale, we can detect it with turning up sensitivity of measurement system. Photons of photoluminescence source impact luminescent centers and excite them. Accordingly, PL intensity has a relationship with amount of laser-illuminated luminescent centers, namely with concentration of luminescent center³). In the case of powder, the luminance increase with increasing the temperature. Therefore, it means that in concentration of single Mn^{2+} , P900 is the highest, the next is P700 and P500 is the lowest. Additionally, electron spin resonance spectra, not shown in this paper, also show that P900 will have the highest concentration of single Mn^{2+} .

The spectra of active layer films also show the peak at 585 nm (Fig.7). F900 indicates the most intensive peak, and F700 shows second highest peak. So, F900 would have the highest concentration of luminescent center in films. The peak shift cannot be observed in any spectra.

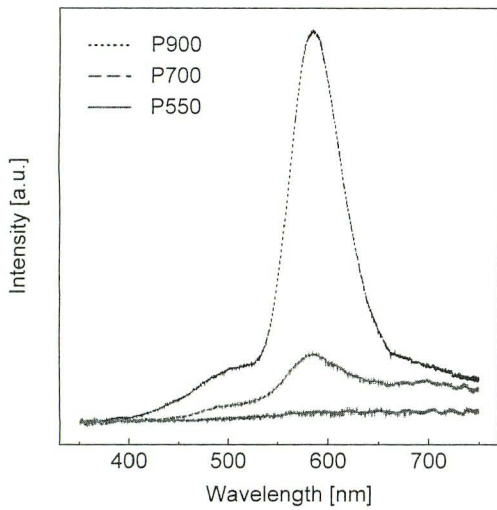


Fig.6 Upper, middle and lower curve show PL spectrum of P900, P700 and P550 respectively.

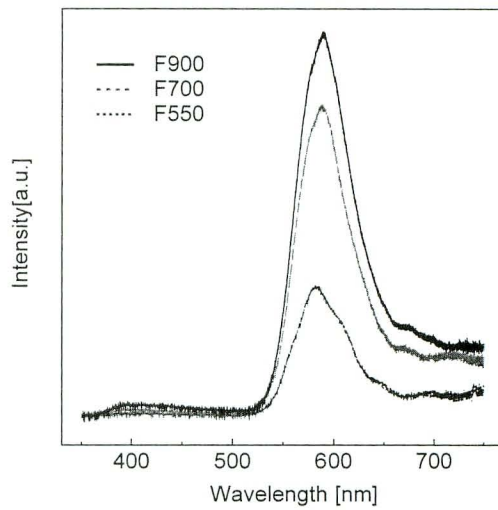


Fig.7 Upper, middle and lower curve show PL spectrum of F900, F700 and F550 respectively

4. Conclusion

XRD patterns of sputtering targets showed that crystallinity were improved by increasing of temperature during heat treating(Fig.1). On the other hand, there were little differences in crystallinity of each deposited films (Fig.2).

For both powder targets and deposited films, each maximum intensity of PL spectra at around 585 nm was increased with heat-treating temperature.

Luminescent centers in targets were increased by influence of firing temperature

Consequently, sputtering using ZnS:Mn powder target that contains high concentration of single Mn^{2+} , which was effective as luminescent center, improved luminescent characteristics of active layer.

5. References

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