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Optical emission spectroscopy of rf–magnetron sputtering plasma for fabrication of ZnS:Mn active layer in thin–film EL devices

by

Satoshi UMEKAWA*, Atushi NITTA**, Kenji TANAKA***,
Minoru KUSABIRAKI****, Yoshiharu MAEKAWA**** and Masao AOZASA*****
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Synopsis

ZnS:Mn active layers in electroluminescent devices were fabricated by rf–magnetron sputtering, and the luminous characteristics of the devices were examined. The optical emission spectra of the sputtering plasma for active layers were examined, and the dependence of the qualities of active layers and the luminous characteristics of the devices on the plasma was investigated.

Keywords : electroluminescence, EL, ZnS:Mn, sputtering, optical emission spectroscopy, OES

1. Introduction

Ac thin–film electroluminescent (ACTFEL) devices have been considered as one of the promising flat–panel displays because of their advantages such as completely solid state and emissive display with wide viewing angle. The TFEL devices have been fabricated by sputtering, electron–beam (EB) deposition, metalorganic chemical vapor deposition (MOCVD) and atomic layer epitaxy (ALE). The sputtering is a convenient fabrication method which enables easy concentration control of doping material and large area device fabrication at low cost. However, the sputtering processes are not yet well understood and they have been investigated by many workers.

In this study, we fabricated TFEL devices of the structure that an active layer is sandwiched between two insulating layers by rf–magnetron sputtering. The optical emission spectra of the sputtering plasma were examined when the active layer was deposited and the effect of the plasma state on the qualities of active layer and the luminous characteristics of the devices were investigated.[1]

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* Student, Master Course of Dept. of Electrical Engineering
** Student, Doctor Course of Dept. of Electrical Engineering
*** Research Associate, Department of Electrical Engineering
**** Lecturer, Department of Electrical Engineering
***** Professor, Department of Electrical Engineering

2. Device fabrication and experimentals

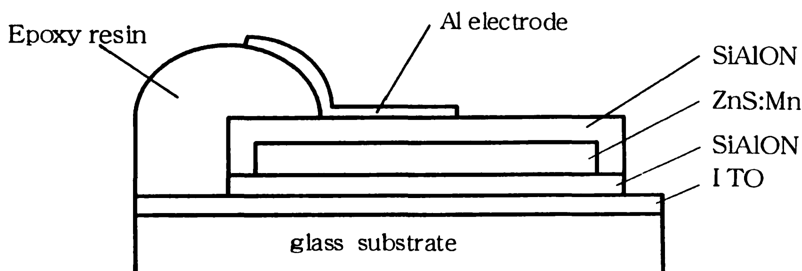

Fig. 1. Structure of the EL device

Fig.1 shows a schematic diagram of EL device structure used for investigating the luminous characteristics. The substrate was an indium–tin–oxide (ITO) coated glass. An insulating layer of about 200 nm was first deposited on the substrate and an active layer of about 700 nm and a insulating layer of about 200 nm were successively deposited. An aluminum electrode was deposited as the top electrode.

Both insulating and active layer were deposited by rf–magnetron sputtering, and Table 1 shows the deposition condition. The aluminum electrode was deposited by vacuum evaporation.

Table 1. Deposition conditions

(a)Insulating layer

Target	Si_3N_4 powder + Al_2O_3 powder
Substrate temperature [°C]	260
RF power [W]	200
Gas pressure [mTorr]	5.0
Sputtering gas flow rate[ccm]	Ar:4 N_2:1
Thickness [nm]	250

(b)Active layer

	A	B	C
Target	ZnS powder + MnS powder (1wt%)		
Substrate temperature [°C]	200		
RF power [W]	50		
Gas pressure [mTorr]	2.0		
Sputtering gas flow rate[ccm]	Ar:5 He:5	Ar:5 He:5	Ar:8 He:5
Thickness [nm]	700		

In this study, the following three kinds of active layers were prepared. They are active layer A with insufficient degassing and gas flow rate of 5 ccm at deposition, active layer B with sufficient degassing and gas flow rate of 5 ccm and active layer C with sufficient degassing and gas flow rate of 8 ccm.

Fig. 2 shows an experimental system consisting of a rf−magnetron sputtering (Tokki, Model SPK−301) and optical emission spectroscopy. While each active layer was deposited, emission light from sputtering plasma was introduced through an optical fiber cable to a monochrometer (Shimadzu Works, Model SPG−100S). The monochromatic light was detected by a photomultiplier and the light intensity data was aquisited and processed by a personal computer.

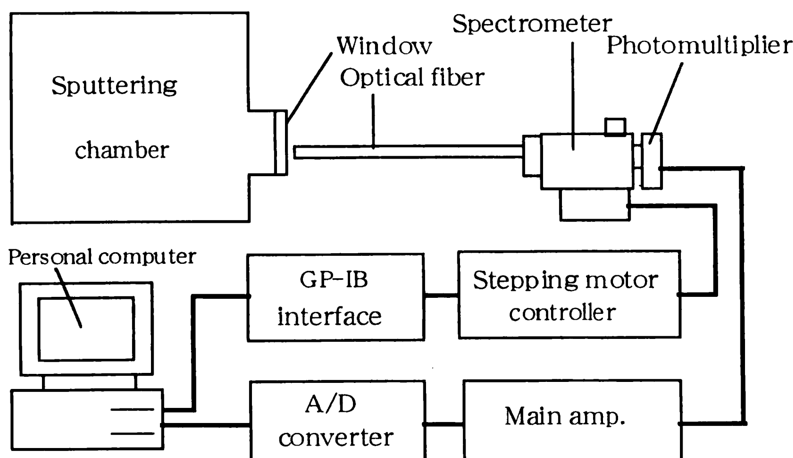

Fig. 2. Measurement system of optical emission spectra

The luminance versus applied voltage characteristics of EL device was usually examined at room temperature in atmosphere. The crystallinity and the stoichiometry of active layers were evaluated by X−ray diffraction (Shimadzu Works, Model XD−610) and X−ray photoelectron spectroscopy (Shimadzu Works, Model ESCA−750) respectively.

3. Experimental results and discussions

3.1 Optical emission spectra

Fig. 3 shows the optical emission spectra of the plasma in the case of active layer A, B and C. Emission from Ar and He which are sputtering gases, and emission from Zn which is the ingredient of the target were detected. Emission from S and Mn, which are the other ingredients of the target, was not detected. The maximum peak intensity of the spectra from Ar at 750.3 nm was normalized as unity, and the spectra of active layer A, B and C are compared.

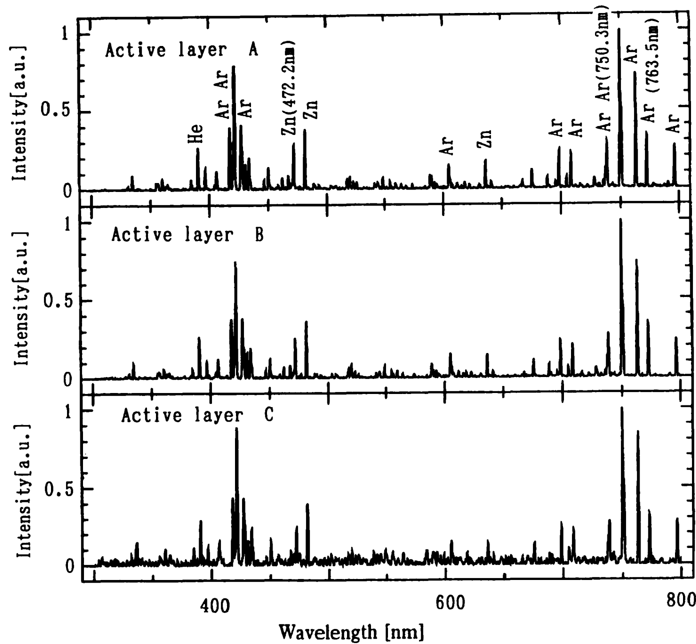

Fig. 3. Plasma emission spectra

Table 2. Peak intensity of plasma emission spectra

	active layer A	active layer B	active layer C
Zn(472.2nm)	0.282	0.260	0.234
Ar(763.5nm)	0.721	0.738	0.856

Ar emission peak at 750.3 nm is due to 4s'−4p' transition[2]. The relative intensity of Zn emission at 477.2 nm decreases in the order of A, B, and C, and the relative intensity of Ar emission at 763.5 nm increases in the order of A, B, and C. The results are summarized in Table 2. It suggests that the degassing of active layer and the gas flow rate at deposition affects on the plasma state.

3.2 Luminous characteristics

Fig. 4 shows luminance versus applied voltage characteristics of the devices with active layer B and C. The luminance of the device with active layer A was very low and extremely unstable and available data could not be obtained. The device with an active layer C has lower threshold voltage and larger maximum luminance than that with an active layer B. Therefore the active layer quality is in the order of C, B and A.

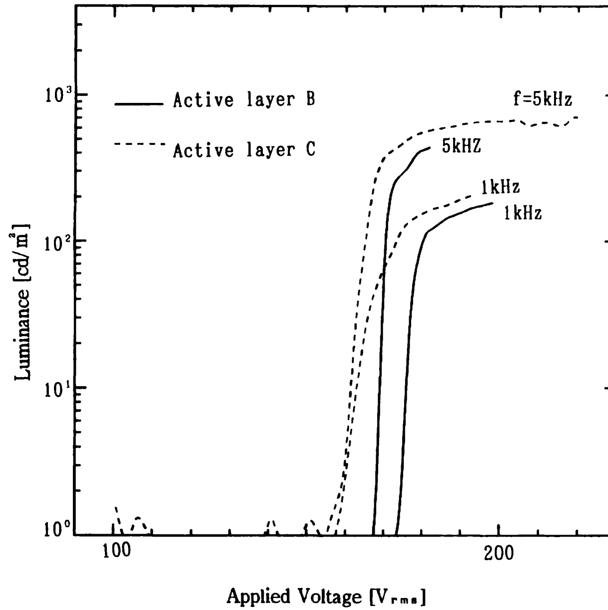

Fig. 4. Luminance versus applied voltage characteristics

3.3 Crystallinity

Fig. 5 shows the X−ray diffraction patterns of active layer A, B and C. The intensive diffraction line at around 28.5 degrees arising from (111) plane of zinc−blende structure has been observed and the peak at around 56 degrees is due to (311) plane of zinc−blende structure. The crystal orientations of these films are almost the same. The peak near 30 degrees is due to ITO. Table 3 shows the peak intensity and the full width at half maxima (FWHM). Each peak intensity and each peak FWHM shows little difference, which means that the crystallinity of the three kinds of films is almost the same.

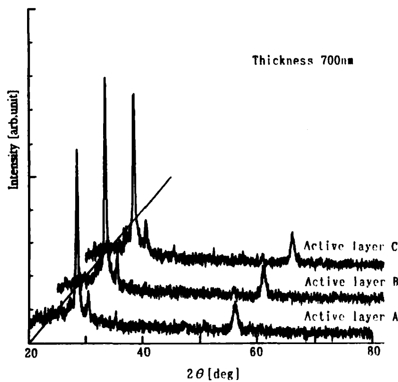

Fig. 5. XRD patterns of the active layer

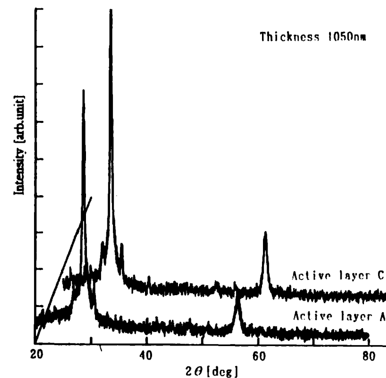

Fig. 6. XRD patterns of the active layer

Fig. 6 shows the X-ray diffraction patterns of active layers A and C with about 1050 nm thickness. Table 4 shows the peak intensity and FWHM. Active layer C has higher peak intensity at 56 and 28.5 degrees and smaller FWHM than active layer A. Therefore, active

Table 3. XRD Peak intensity and full width at half maxima (FWHM) of active layers with 700 nm thickness

	active layer A	active layer B	active layer C
ZnS(111) intensity [cps]	903	1068	828
ZnS(111) FWHM [deg]	0.342	0.342	0.376
ZnS(311) intensity [cps]	144	146	151
ZnS(311) FWHM [deg]	0.785	0.820	0.752

Table 4. XRD Peak intensity and full width at half maxima (FWHM) of active layers with 1050 nm thickness

	active layer A	active layer C
ZnS(111) intensity [cps]	1315	1675
ZnS(111) FWHM [deg]	0.273	0.205
ZnS(311) intensity [cps]	333	410
ZnS(311) FWHM [deg]	0.478	0.478

layer C has better crystallinity than active layer A. The comparison between Table 3 and Table 4 shows that active layers with the thinner thickness of about 700 nm thickness had higher portion of dead layer, which is uncrystallized part of the layer, which results in little difference in XRD peak intensity.

3.4 Stoichiometry

Table 5 shows the result of stoichiometry analysis by XPS. It was obtained after three minutes etching by Ar ion at 500 V of acceleration voltage and 20 mA of discharge current.

We assumed that the stoichiometry of Zn to S in ZnS powder is 1 to 1. The stoichiometry of Zn to S in active layer C is the closest to 1 to 1 in the three kinds of active layers.

Table 5. Stoichiometry of active layers

	Zn	S
ZnS powder	1.00	1.00
active layer A	1.23	1.00
active layer B	1.15	1.00
active layer C	1.01	1.00

4. Conclusion

The conclusions can be summarized as follows:

1. Sufficient degassing of active layer and higher Ar gas flow rate at sputtering of active layers results in better films.
2. Degassing of active layers and Ar gas flow rate at sputtering change the plasma state.
3. In the optical emission spectra in sputtering plasma, when Ar (750.3 nm) peak intensity is normalized as unity, emission from Zn (472.2 nm) and Ar (763.5 nm) can be good guidelines for the deposition of the active layer of the ZnS:Mn electroluminescent devices.

References

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