Effects of H₂ Gas in Sputtering Ambience on ZnS:Mn Electroluminescent Device Active Layer

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Synopsis

Control of impurity gases in sputtering ambience is important to prepare a good active layer. In this study, we paid attention to H₂ gas of the impurity gases, and examined its effects on electroluminescent (EL) device active layer. Luminance versus applied voltage characteristics, emission spectrum and ESR spectrum were examined. Results show that if H₂ introduced in a small quantity in sputtering ambience, effective luminescent center is incorporated, and maximum luminance is improved.

KEYWORDS: Electroluminescent, sputter, ESR, XRD, spectrum, ZnS:Mn

Introduction

A thin-film electroluminescent (ACTFEL) device has advantages that it is completely solid state and emissive display with wide field of view. The TFEL devices have been prepared by sputtering¹, electron-beam (EB) evaporation², multi-source deposition (MSD)³, metal organic chemical vapor deposition (MOCVD)⁴, and atomic layer epitaxy (ALE)⁵. The sputtering is a remarkable technique which enables large area device fabrication at low cost.

In this study, we fabricated TFEL devices of the structure that an active layer is sandwiched between two insulating layers by RF magnetron sputtering method. In sputtering, impurity gases in sputtering ambience give large influence on fabricated thin film quality. Therefore we paid attention to H₂ gas in the main impurity gases, and examined its influence on active layer.

Device fabrication and experimental

Fig. 1 shows a schematic diagram of our RF magnetron sputtering equipment (Tokki, Model SPK-301) with quadrupole mass spectroscopy (Leda-Mass.VACSCAN). We used quadrupole mass spectroscopy (QMS) for gas analysis. The analytical data were acquired to personal computer through RS232C. A partial pressure of H₂ gas in sputtering ambience was read by QMS.

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Fig. 1: RF magnetron sputtering

Fig. 2 shows a schematic diagram of EL device structure used for investigation of the luminous characteristics. An insulating layer of about 250 nm was first deposited on an indium-tin-oxide(ITO)coated substrate glass(Corning #7059) where ITO serves as a transparent lower electrode. And an Mn doped ZnS active layer (about 1600 nm) and an insulating layer (about 250 nm) were successively deposited. An aluminum electrode was deposited as a top electrode. Both insulating and active layer were deposited by RF magnetron sputtering and Table.1 shows the preparation condition. The upper aluminum electrode was deposited by vacuum evaporation method.

Fig. 2: Structure of the EL device

In this study, the following four kinds of active layers were prepared. That is, they were active layer (a), (b), (c) and (d) which were prepared at the partial pressure of H₂ gas in sputtering ambience of 1.0 × 10⁻⁸Torr (Not introduced), 3.0 × 10⁻⁸Torr, 4.0 × 10⁻⁸Torr, 5.0 × 10⁻⁸Torr and 6.0 × 10⁻⁸Torr, respectively.

Luminance versus applied voltage characteristics of EL device was examined under 5 kHz sinusoidal voltage application condition at room temperature in ambience. The crystallinity and the condition of luminescent center was evaluated by X-ray diffraction (Shimadzu Works, Model XD-610) and Electron Spin Resonance (BRUKER Works, ESP-300), respectively.

Experimental results and discussion

Fig.3(a) shows luminance versus applied voltage characteristics of EL device with active layers (a) through (d). Maximum luminance of each device were 3447cd/m², 4600cd/m², 5333cd/m², 3119cd/m², respectively.
<table>
<thead>
<tr>
<th>Table 1. Deposition conditions</th>
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<tr>
<td><strong>Active layer</strong></td>
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<tr>
<td>Target: ZnS:Mn (Mn: 0.5wt.%)</td>
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<tr>
<td>Base pressure</td>
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<tr>
<td>Gas pressure</td>
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<tr>
<td>Sputtering gas flow rate</td>
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<tr>
<td>Sputtering time</td>
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<tr>
<td>Substrate temperature</td>
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<tr>
<td>RF power</td>
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<td>Thickness</td>
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<table>
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<tr>
<th>Insulating layer</th>
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<tbody>
<tr>
<td>Target: Si$_3$N$_4$ + Al$_2$O$_3$ (3 : 2)</td>
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<tr>
<td>Base pressure</td>
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<tr>
<td>Gas pressure</td>
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<td>Sputtering gas flow rate</td>
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(a) Luminance versus applied voltage characteristics
(b) XRD patterns of the active layer

Fig. 3: Luminance and XRD patterns

Fig.3(b) shows the X-ray diffraction patterns of active layer (a) through (d). An intensive diffraction line at a scattering angle of around 28.5 degrees arising from (111) plane of zinc-blende structure is observed and a line which peaks at around 56 degrees due to (311) plane of zinc-blende structure is also observed. The peak intensity arising from (111) plane of zinc-blende structure decreased as partial pressure of H$_2$ increased.

To examine influences of H$_2$ gas on the luminosity of the EL device, we measured EL spectra of the devices. And we separate the spectra assuming gaussian function. Fig.4 shows each spectrum and separated spectrum. The intensity of each spectrum is proportional to a maximum
luminance of its device. The intensity of separated spectra peak at around 610nm were increased as partial pressure of H₂ increased.

![EL spectrum and separated spectrum](image)

**Fig. 4: EL spectrum and separated spectrum**

Fig. 5 shows ESR spectrum of each active layer. They have six sharp peaks originating from isolated and dispersed Mn²⁺ centers, and one broad peak originating from clustered Mn²⁺.

![ESR spectrum of active layers](image)

**Fig. 5: ESR spectrum of active layers**

Fig. 6(a) shows relations between the value of double integral value of the ESR spectra and the partial pressure of H₂ gas. In this figure, the integral value for the case of (a) is taken as a standard as 1.
(a) Intensity of isolated Mn$^{2+}$ peaks versus partial pressure of H$_2$ characteristics

(b) Intensity of isolated Mn$^{2+}$ peaks and line width of ESR Mn$^{2+}$ versus partial pressure of H$_2$ characteristics

Fig. 6: ESR spectrum characteristics

Fig. 6(b) shows relations between the peak intensity of the single element and line width of the single element. The intensity and line width are the average of six peaks. The intensity becomes the strongest and line width the smallest in the case of the condition of (c) (H$_2$:2.0 $\times$ 10$^{-8}$Torr). It shows that the concentration of isolated and dispersed Mn$^{2+}$ is the biggest for the condition of (c).

Fig. 7: Intensity of single Mn and EL Emission Intensity of separated peaks

Fig. 7 shows relations between the EL emission peak intensity of two separated spectra and the intensity of the single Mn peak. The intensity of the EL emission peak at around the 580nm and intensity of single Mn takes a peak at the same pressure of 2.0 $\times$ 10$^{-8}$Torr. And it shows that there is a good correlation between them.
Conclusion

The conclusions can be summarized as follows:

1. Luminance increases when H₂ gas was introduced in a small quantity at lower than $2.0 \times 10^{-8}$ Torr, but luminance decreases when partial pressure was higher.

2. Effective luminescent center is incorporated when H₂ gas was introduced in a small quantity.

3. There is a good correlation between intensity of the separated spectrum peak at around 580 nm and intensity of the single Mn peak.

From the above, if H₂ introduced in a small quantity in sputtering ambience, effective luminescent center is incorporated, and maximum luminance is improved. And more the EL emission spectrum also shows condition of luminescent center.

References

5) TORNQVIST, et al. Transactions on Electron Devices pp.468-471 No5 May