Effects of H_2 Gas in Sputtering Ambient on Pulse Voltage Response of ZnS:Mn Electroluminescent Device

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Synopsis

Electroluminescent (EL) devices were prepared by RF magnetron sputtering method at different partial pressure of H_2 gas in sputtering ambient. The effects of H_2 gas in sputtering ambient on pulse voltage response were investigated for preparing high-quality EL device active layer. Luminance versus applied voltage characteristics, XRD pattern, pulse voltage response and ESR spectrum were examined. When a small amount of H_2 gas was introduced in sputtering ambient, contribution of single Mn^{2+} to pulse voltage response changed. It strongly suggests that small amount of H_2 gas in sputtering ambient affects the concentration of single Mn^{2+}.

KEYWORDS: Electroluminescent device, ZnS:Mn, Sputtering, Pulse voltage response, ESR

Introduction

In recent years, various emissive devices were developed. Cathode-ray tube (CRT) is excellent in luminance and contrast, but its size, weight and power consumption are large and it is not a proper device for small equipment. Therefore light, small and low power consumption device is needed. Thin-film electroluminescent (TFEL) device is one of the devices which is thin and light. TFEL display is resistant to vibration and its viewing angle is wide, because TFEL is completely solid state and emissive. Therefore TFEL devices have been considered as one of the candidate of the flat-panel displays. The TFEL devices have been prepared by sputtering[1)], electron-beam evaporation[2)] and atomic layer epitaxy(ALE)[3)], etc. The sputtering method has a characteristics that a large area device can be prepared at low cost. However, it is important to control gas impurities in sputtering ambient in order to prepare a high quality thin film by sputtering method[4,5)].

In this study, we paid attention to H_2 gas in gas impurities (H_2, H_2O, N_2, O_2) and examined its influence on pulse voltage response of EL device.

Device fabrication and experimental

Fig. 1 shows a schematic structure diagram of EL device 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) . ITO layer serves as a transparent lower electrode. A Mn doped ZnS active layer (about 1600 nm) and an insulating layer (about 250 nm) were successively deposited. Aluminum electrodes were deposited as a top electrode. Both insulating and active layer were deposited by RF magnetron sputtering. The upper aluminum electrodes were deposited by

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vacuum evaporation method.

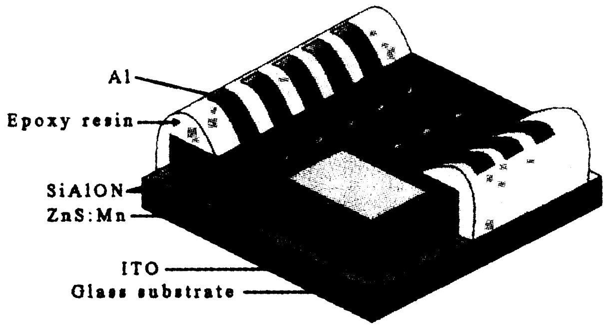

Fig. 1: Schematic diagram of the EL device

In this study, the following four kinds of active layers were prepared. That is, they were active layer (a), (b), (c) and (d) whose partial pressure of H_2 gas in sputtering ambient are (a)1.0×10^{-8}Torr (Not intentionally introduced), (b)1.5×10^{-8}Torr, (c)2.0×10^{-8}Torr and (d)2.5×10^{-8}Torr. Luminance versus applied voltage characteristics of EL device were examined under 5 kHz sinusoidal voltage application condition at room temperature in atmosphere. The crystallinity of the active layer and the state of luminescent center were examined by X-ray diffraction(Shimadzu Works, Model XD-610) and Electron Spin Resonance(BRUKER Works, ESP-300), respectively. Electroluminescent light decay B(t) was measured, applying the pulse voltage (pulse width is about 250 μs, voltage is 150 V ~200 V) to the sample.

Fig. 2 shows the measurement system. Pulse voltage with both polarity(4 ms intervals) was applied to the device. Under these pulses, electroluminescent light of EL device is converted to an electric signal by photomultiplier, and the signal is taken in a personal computer through A/D board. B(t) is supposed to be the sum of two components $B_1(t)$ and $B_2(t)$ with decay time constant τ_1 and τ_2 respectively as

$$B(t) = B_1(t) + B_2(t) = B_1' \exp(-t/\tau_1) + B_2' \exp(-t/\tau_2), \tag{1}$$

where B_1', B_2', τ_1 and τ_2 are constant. The ratio of the two components Q_1 and Q_2 are defined by the following equations,

$$Q_1 = \frac{\int_0^\infty B_1(t)dt}{\int_0^\infty B(t)dt}, \quad Q_2 = \frac{\int_0^\infty B_2(t)dt}{\int_0^\infty B(t)dt}. \tag{2}$$

B_1', B_2', τ_1 and τ_2 were calculated by least squares method. To solve least squares problems, we used a FORTRAN program which was created by ASNOP (Application System for Nonlinear Optimization Problems). ASNOP is an application system which creates a FORTRAN program, and this FORTRAN program is used for solving optimization problems. Because FORTRAN program is created by ASNOP automatically, an user doesn't need writing long FORTRAN program and has only to prepare a file in ASNOP's format. In this file, type of the problem, method, constraint functions, measurement data, and etc. are written. According to this file, ASNOP assembles necessary parts into a FORTRAN program. These parts are built in ASNOP system in advance. The FORTRAN program is compiled and linked and an execution file is created. By executing this program, the values of B_1', B_2', τ_1 and τ_2 are obtained. To solve a nonlinear least squares problem, the problem type was NLS(Nonlinear Least Squares problems) and the method was NLSSQP(Sequential Quadratic Programming method for Nonlinear Least Squares Problems). To compile FORTRAN program, g77(FORTRAN77 compiler of GNU) was used.

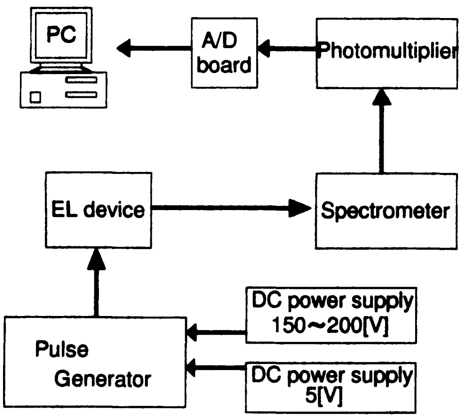

Fig. 2: Measurement system of pulse voltage response

Experimental results and discussion

Fig. 3 shows the luminance versus applied voltage characteristics of EL devices with active layers (a) through (d). Maximum luminance of each device were (a)3447 cd/m^2, (b)4600 cd/m^2, (c)5333 cd/m^2 and (d)3119 cd/m^2.

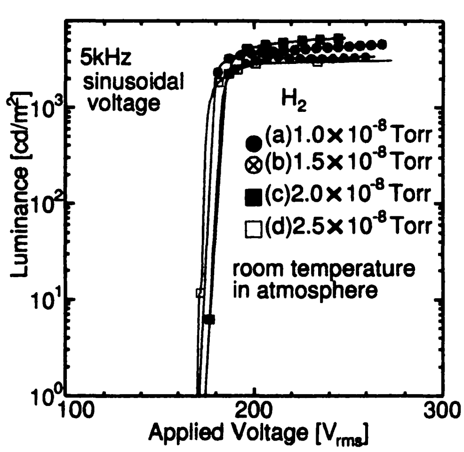

Fig. 3 Luminance versus applied voltage characteristics

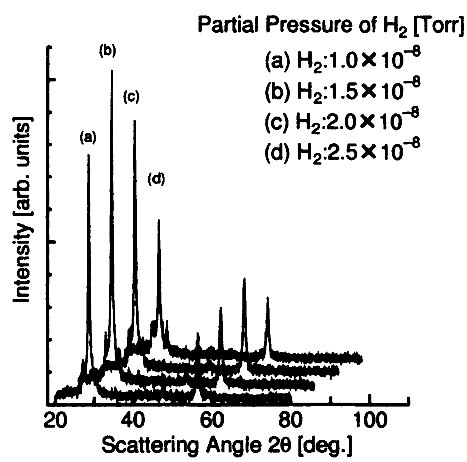

Fig. 4 XRD patterns of the active layers

Fig. 4 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 becomes the strongest in the condition of (b) (H_2:1.5 $\times$ 10^{-8} Torr).

Fig. 5 shows pulse voltage response of the device with active layer (a). Table 1 shows τ_1, τ_2, Q_1 and Q_2. Decay time constants are almost constant, $\tau_1 = 0.22$ ms and $\tau_2 = 1.2$ ms, respectively. These values are close to the decay time constants of pair Mn^{2+} and single Mn^{2+} that were already reported, respectively[6].

Table 1. Decay time constants and ratio of the components

H_2[Torr]	τ_1 [ms]	τ_2 [ms]	Q_1	Q_2
1.0×10^{-8}	0.2797	1.2962	0.10224	0.89776
1.5×10^{-8}	0.25616	1.11534	0.07585	0.92415
2.0×10^{-8}	0.2171	1.1934	0.05786	0.94214
2.5×10^{-8}	0.2316	1.1152	0.29916	0.70085

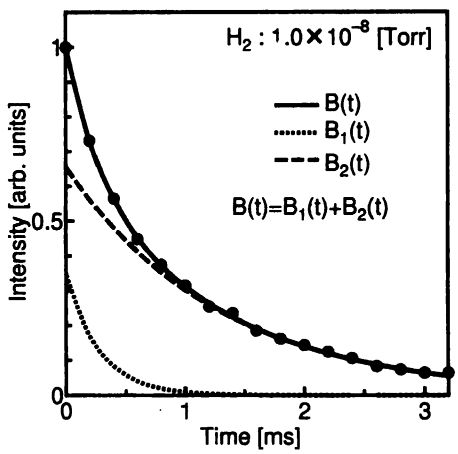

Fig. 5 Pulse voltage response of active layer (a)

Fig. 6 shows maximum luminance and Q_2 against partial pressure of H_2. Q_2 is the largest in the case of (c). And maximum luminance takes its maximum also in the case of (c) corresponding to that of Q_2. It suggests that H_2 gas in sputtering ambient strongly affects the density of single Mn^{2+}.

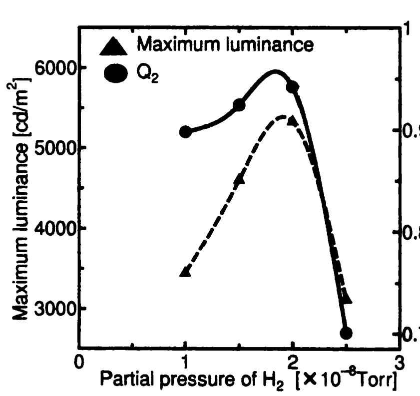

Fig. 6 Maximum luminance and Q_2 against partial pressure of H_2

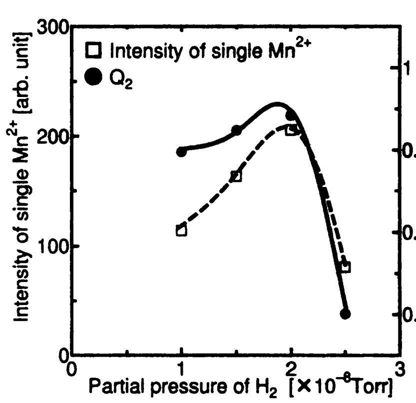

Fig. 7 Peak intensity of single Mn^{2+} and Q_2 against partial pressure of H_2

Fig. 7 shows peak intensity of single Mn^{2+} and Q_2 against partial pressure of H_2. The peak intensity of single Mn^{2+} was obtained by analyzing ESR signal. Results on ESR observation were reported in the previous work[7]. Both the peak intensity of single Mn^{2+} and Q_2 were the largest in the case of (c). The quantity of H_2 gas in sputtering ambient affects the concentration of Mn^{2+}, and thus on the luminance characteristics of the device.

Conclusion

The conclusions can be summarized as follows:

1. Partial pressure of small amount of H_2 gas in sputtering ambient strongly affects the crystallinity of the active layer.

2. Partial pressure of H_2 gas in sputtering ambient also affects the concentration of single Mn^{2+} which determine the luminance characteristics of the device.

References

1) M. Aozasa, et al., *Japanese Journal of Applied Physics*, **29**, 1997 (1990)

2) T. Matsuoka, et al., *Japanese Journal of Applied Physics*, **27**, 1430 (1988)

3) Runar O. Tornqvist, et al., *IEEE Transactions on Electron Devices*, **ED-30**, 468 (1983)

4) A. Nitta, et al., *Record of The 1998 Kansai-Section Joint Convention of Institutes of Electrical Engineering, Japan*, G 183

5) A. Nitta, et al., *Proceedings of The 1999 Electronics society Conference of IEICE*, C-6-3

6) E. Walentynowicz, et al., *Journal of Luminescence*, **17**, 109 (1978)

7) T. Fujita, et al., *Memoirs of the Faculty of Engineering, Osaka City University*, **40**, 19 (1999)