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Blue LED with ZnSe P-N Junction

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The low-resistivity P-layer has been made by the Tl-Zn vapor treatment for the N-type ZnSe crystal. To obtain a good P-N junction, the molten-Zn and Tl-Zn vapor treatments are investigated. The condition of fabricating a P-N junction of ZnSe is as follows: ZnSe substrate was treated with molten-Zn for 142 h at the temperature 1050°C, and then Tl diffusion into ZnSe was performed in Tl-Zn atmosphere at temperature 800°C for 140 h. The fabricated P-N junction diode has a good rectifying property. In the forward bias, the diode exhibits a blue electroluminescence spectrum with a peak at 473 nm (E=2.63 eV) at room temperature. The forward biased impedance and the reverse biased capacitance were measured to clear the junction characteristics.

§1. Introduction

Up to the present, various attempts to produce low-resistivity P-type layer and P-N junction for ZnSe LED have been made.[1~3] Recently, a formation of P-N junction LED in ZnSe has been reported.

Georgobiani et al. have produced low resistivity ZnSe layer with a defect P-type conduction by the heat treatment in Se vapor.[4] Also, Nishizawa et al. have reported that a P-type ZnSe crystal can be grown from Se solution by doping with a group I element under controlled Zn pressure, and then a P-N junction has been made by the formation of the N type layer by Ga diffusion into P-type crystal.[5] In both cases, a blue light was observed with forward biased P-N ZnSe diode at room temperature.

The purpose of the present study is to give evidence that Tl-doped ZnSe shows a low resistivity P-type conduction with shallow acceptor levels[6] and that the fabricated P-N junction diode shows a blue light emitting characteristic at room temperature. It is clear that the impurity diffusion process has an advantage to fabricate the P-layer in N-type ZnSe crystal, because the high quality N-type ZnSe crystal can be easily obtained.

The blue LED with ZnSe P-N junction has a good rectifying property and an inductive characteristic under the forward biased condition, which is evidence of a minority carrier injection. Moreover, the reverse biased capacitance was investigated to clear the junction structure.

§2. Experimental

ZnSe single crystals were grown from source materials of 5-N grade by Piper and Polich's method. The crystal was sliced so that the substrate of about 2×2×1 mm^3 had a (110) face. The slices were mechanically polished and chemically etched in bromine-methanol.

The fabrication of a P-N junction is as follows: At first, ZnSe substrate was treated with molten-Zn for 140-330 h at the temperature of 700-1050°C. Subsequently, Tl diffusion into ZnSe were performed in various Tl-Zn atmospheres at the temperature from 750°C to 800°C for 120-140 h. Good ohmic contacts were obtained by vacuum deposition of Au for Tl diffused P-layer and of In-Hg alloy for N-type ZnSe substrate.

§3. Results and Discussion

1) Measurements for P-type layer

To determine the conduction type, the sample treated by the Tl-Zn vapor was etched in bromine-methanol, and then the conduction type was observed from a hot-probe measurement and/or the Seebeck effect. The experimental result is shown in Fig.1. The sample treated in Tl-Zn vapor (750°C, 15 h) has a P-layer of 1.6 μm. Other treatments of Tl-Se and Tl vapor were carried out for the N-type ZnSe crystal, but these samples exhibit the high-resistivity N-type. Therefore, it is considered that

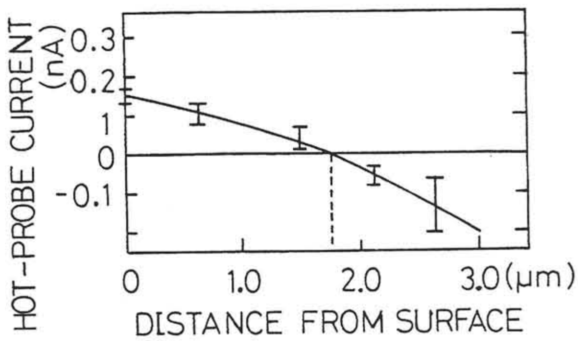

Fig.1 The results of hot-probe measurement.

Tl atoms enter the Se site and the conduction type changes from N-type to P-type.

2) Electrical properties of ZnSe P-N junction

Figure 2 shows the I-V characteristic of a typical diode at room temperature. The diode has a good rectifying property. The impedance with forward bias was measured to clarify whether the minority carriers (holes) were injected from P-layer to N-type substrate. These impedance characteristics are shown in Figs.3(a) and (b). The impedance characteristic of a Schottky barrier diode with Au-N type ZnSe structure was also measured to compare with a P-N junction diode of ZnSe, as shown in Fig.4. The impedance characteristic of ZnSe P-N junction diode changes from capacitive to inductive one with increasing the forward current (I=4 μA to 56 μA), while the Schottky barrier ZnSe diode shows the capacitive property regardless of the increased forward current. Therefore, it can be concluded that the minority carriers are injected from Tl-diffused P-layer to N type substrate.

The frequency dependence on the junction capacitance under the reverse bias condition was measured to investigate the relation between the deep traps and the electroluminescence properties as a function of the heat treatment temperature. The junction capacitance is given as follows;[7]

$$C = C_{hf} + (C_{lf} - C_{hf})/(1 + \omega^2 \tau^2). \qquad (1)$$

Here, C_{hf} is the junction capacity at the high frequency, C_{lf} is the capacity at the low frequency, and τ is the relaxation time. As the relaxation time decreases, it is observed, from eq.(1), that the capacitance curves shift to the higher frequency.

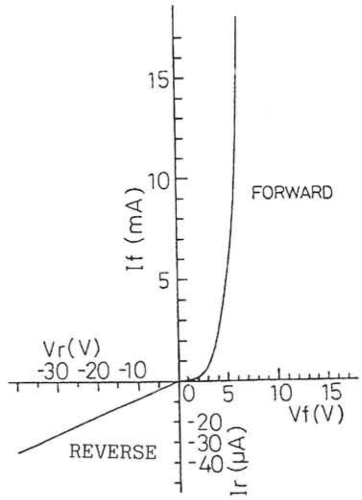

Fig.2 I-V characteristic of ZnSe diode.

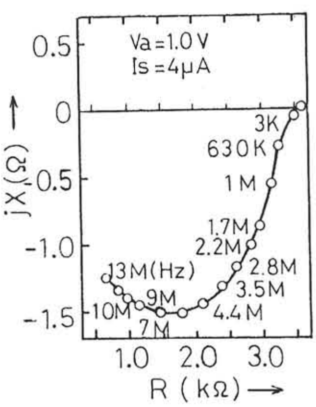

Fig.3(a)

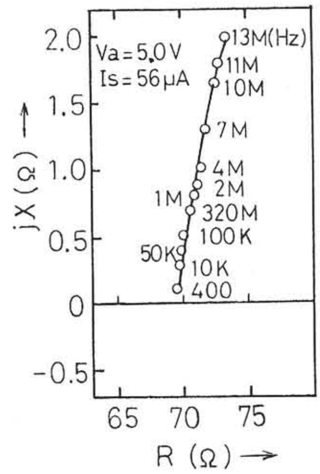

Fig.3(b)

Fig.3 Impedance characteristics of ZnSe diode under the forward bias conditions.

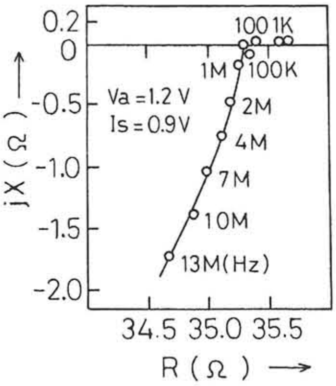

Fig.4 Impedance characteristics of ZnSe Schottky diode under the forward bias condition.

The experimental results were obtained for the molten-Zn treated ZnSe P-N junctions with T=700°C -1070°C for 120 h (the heat treatment of Tl-Zn vapor is T=780°C for 142 h). As shown in Fig.5, the junction capacitance treated at T=1030°C shows the shallow level. Its result agrees well with the light emitting property of ZnSe junction diode. Also, the temperature dependence on Tl-Zn vapor treatment is investigated. As shown in Fig.6, the vapor treatment of T=800°C shows the good

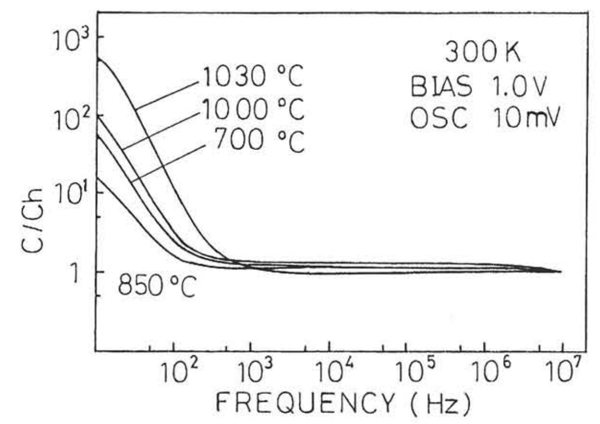

Fig.5 Temperature dependence of molten-Zn treatments for 120 h on the ZnSe junction capacity.

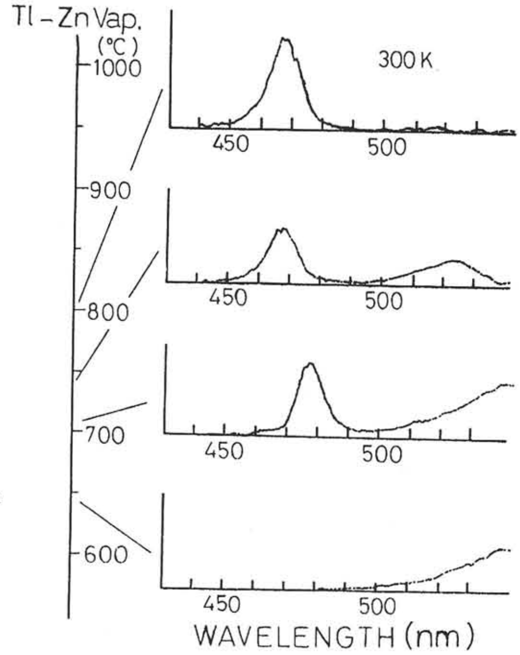

Fig.7 Temperature dependence of Tl-Zn vapor treatments on the luminescence spectrum of ZnSe diode.

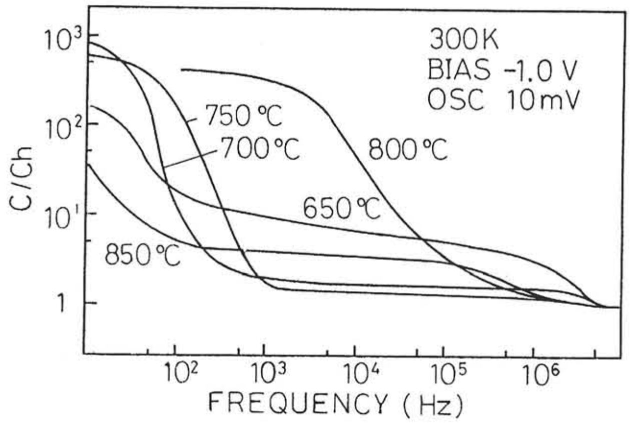

Fig.6 Temperature dependence of Tl-Zn vapor treatments for 142 h on the ZnSe junction capacity.

characteristic, which corresponds to the shallow level.

Figure 7 shows the relation between the temperatures of Tl-Zn vapor treatments and the spectrum of LED at room temperature. For the thermal treatment of T=640°C, the blue light emission was not observed. As increasing the treatment temperatures from 640°C to 820°C, it is observed that the intensity of blue light emission increases and the intensity of green light emission ($\lambda = 500 \sim 600$ nm) decreases. These experimental results of electroluminescence spectrum coincide well with the relation between the temperature of Tl-Zn vapor treatment and the junction capacitance, as shown in Fig.6.

3) Electroluminescent properties of ZnSe P-N junction diode

Under the forward biased condition, the diode exhibits a blue electroluminescent spectrum with a peak at 473 nm (E=2.63 eV) at room temperature, as shown in Fig.8. This blue luminescence can be characterized by a transition from conduction band to an acceptor level. The emission power of the 473 nm line increases rapidly with increasing current at low current levels ($I < 2.2$ A/cm^2), as shown in Fig.9, and then power decreases with increasing the forward current. However, the full width at half maxima at a 473 nm peak has a constant value of $\Delta\lambda = 10$ nm.

To investigate the luminescence spectrum exactly, the electroluminescence was measured at low temperatures. The spectra at T=77 K$\sim$110 K are shown in Fig.10. The peaks of spectrum at P_0, P_1, P_2, P_3 and S are clearly observed. It is considered that P_0 is the luminescence of DA pair, and P_1, P_2 and P_3 are the phonon replica because the energy gap of each peaks correspond to E=32 meV and its value coincides with the LO-phonon energy of ZnSe. Also, the peak value of S is attributed to FB luminescence.

Figure 11 shows the temperature dependence of the molten-Zn and Tl-Zn vapor treatments on the luminescence spectrum of ZnSe LED.

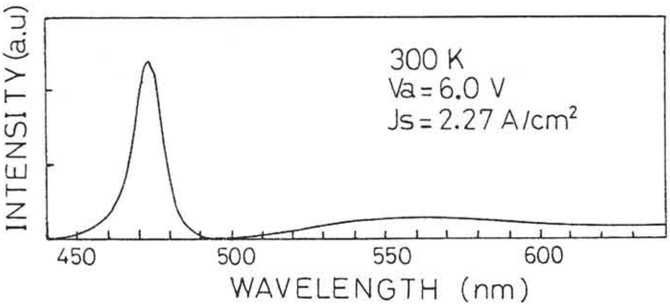

Fig.8 Electroluminescence spectrum of ZnSe diode. (molten-Zn treatment: 1050°C, 142 h; Tl-Zn vapor treatment: 800°C, 142 h)

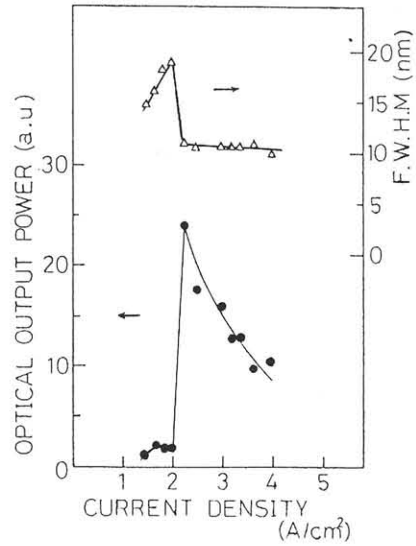

Fig.9 Optical output power and full width of half maxima at 473 nm.

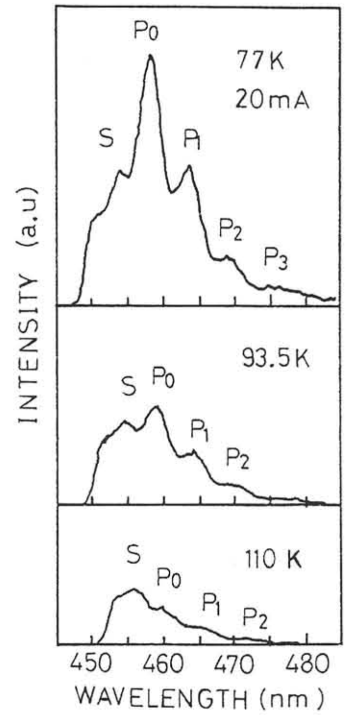

Fig.10 Luminescence spectrum of ZnSe diode at T=77, 93.5 and 110 K.

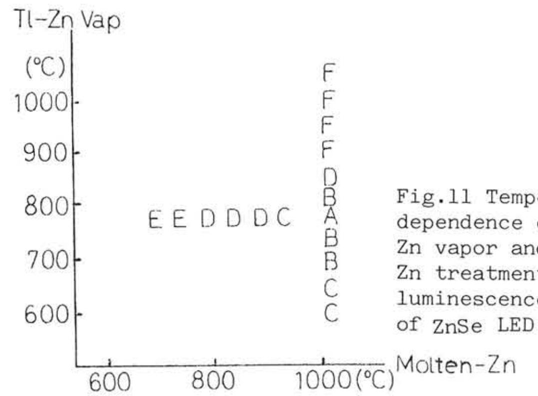

Fig.11 Temperature dependence of Tl-Zn vapor and molten-Zn treatments on the luminescence spectrum of ZnSe LED.

A:Blue light emission at T=300 K,
B:White light emission at T=300 K,
C:Blue light emission at T=77 K,
D:Blue and green light emission at T=77 K,
E:Green light emission at T=77 K,
F:Without light emission.

In order to obtain the blue LED, the desirable condition is that the temperature of molten-Zn treatment is 1050°C and the Tl-Zn vapor treatment is 800°C. The heat treatment of molten-Zn vapor is necessary to reduce the resistivity of N-type ZnSe. As shown in Fig.11, when the temperature of molten-Zn vapor treatment decreases from T=1050°C to 950°C, the emission of LED changes to the type C (blue light emission at T=77 K). While, the temperature dependence on Tl-Zn vapor treatment is not so influenced. If the temperature of heat treatment decreases from T=800°C to 700°C, the emission of LED changes to the type B (white light emission at T=300 K). Therefore, it is considered that the heat treatment of molten-Zn, namely the fabrication of low resistivity ZnSe with N-type conduction, is important to obtain the good blue LED.

§4. Conclusion

The blue emitting diode can be fabricated by the Tl-diffused P-layer in the N-type ZnSe grown by the Piper and Polich's method. The emitting light of 473 nm under the forward bias condition was observed at room temperature.

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