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Blue/Blue-Green Electroluminescence from ZnSe-Based Wide-Gap II-VI Semiconductor Homo- and Double Hetero-Junction Diodes Grown by Photo-Assisted Metalorganic Vapor-Phase Epitaxy

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Acceptor doping of ZnSe was carried out with nitrogen as dopant in photo-assisted metalorganic vapor-phase epitaxy. Higher doping was achieved by the substrate temperature and the irradiation intensity as low as 350 °C and 45 mW/cm^2, respectively. The net acceptor concentration was estimated as 2×10^{17} cm^{-3} for the ZnSe:N layer with nitrogen concentration of 5×10^{17} cm^{-3} revealed by secondary ion mass spectroscopy. Blue/blue-green electroluminescence from homo- and double hetero-junction diodes supported p-type behavior of the ZnSe:N layers.

1. INTRODUCTION

Recent development of blue/blue-green lasers (LDs) and light emitting diodes (LEDs) with ZnSe-based wide-gap II-VI semiconductors is deeply indebted to successful p-type doping with nitrogen in molecular beam epitaxy (MBE). On the other hand, in metalorganic vapor-phase epitaxy (MOVPE), although codoping of lithium and nitrogen has resulted in the hole concentration up to 9×10^{17} cm^{-3} and demonstrated p-n junction LEDs, [1] doping of nitrogen from NH_3 has shown the as-grown hole concentrations only as low as 10^{14}-10^{15} cm^{-3}.[2,3] However, recent report by Tasker *et al.*[4] showing the net acceptor concentrations up to 3×10^{16} cm^{-3} after rapid thermal annealing encourages the potential of nitrogen as p-type dopant in MOVPE. In this paper, an effort is given for nitrogen doping from tertiary-butylamine (t-BNH_2) as a source precursor in photo-assisted MOVPE.[5,6] Optical and electrical properties, together with blue/blue-green electroluminescence (EL) from homo- and double hetero-junction diodes, will suggest high potential of this technique for acceptor doping.

2. EPITAXIAL GROWTH

The epitaxial growth was carried out at the substrate temperature of 350 °C, the reactor pressure of 200 Torr, and the irradiation intensity from a xenon lamp of 45 mW/cm^2, unless otherwise noted. The source precursors for ZnSe growth were diethylzinc (DEZn) and dimethylselenium (DMSe), whose flow rates were typically 9.4 and 72 μmol/min, respectively. The doping source for nitrogen was t-BNH_2. (100)-oriented GaAs wafers were used as substrates.

3. PROPERTIES OF ZnSe:N

Figure 1 shows the photoluminescence (PL) spectra measured at 4.2 K under excitation by a He-Cd laser with the intensity of 200 mW/cm^2. Here, thickness of ZnSe layers was about 1 μm. No appreciable deep emissions were observed at the wavelength region longer than that shown in Fig. 1, i.e., from 500 to 700 nm.

For non-doped ZnSe, the PL spectrum was dominated by free-excitonic emission (E_x) and the ZnSe layers showed high-resistance. When the flow rate of t-BNH_2 was 90 μmol/min, the PL was characterized by two series of donor-acceptor pair (DAP) emissions

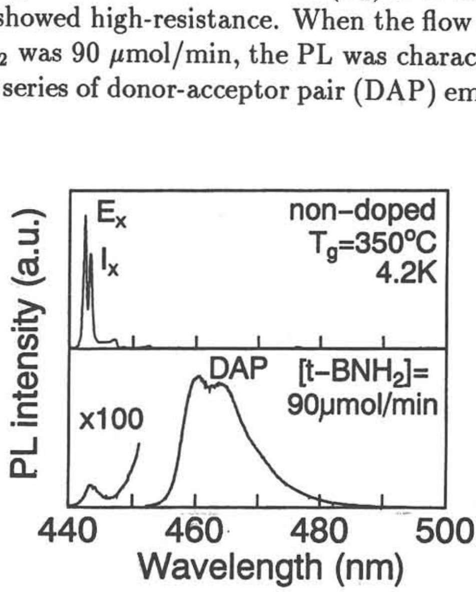

Fig. 1 4.2 K PL spectra from non-doped and nitrogen-doped ZnSe layers grown at 350 °C.

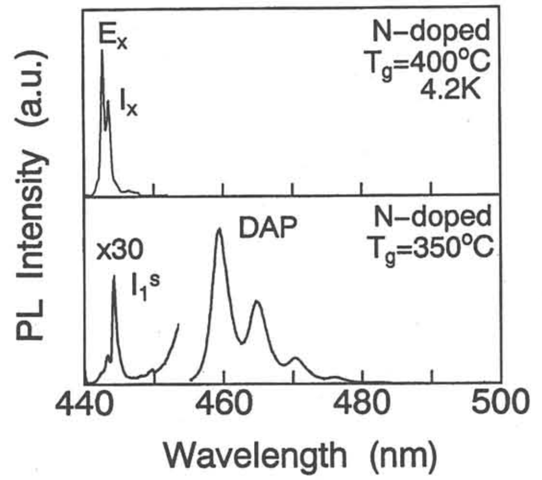

Fig. 2 Comparison of 4.2 K PL spectra from ZnSe:N layers grown at different substrate temperature. Flow rate of t-BNH_2 was 30 μmol/min.

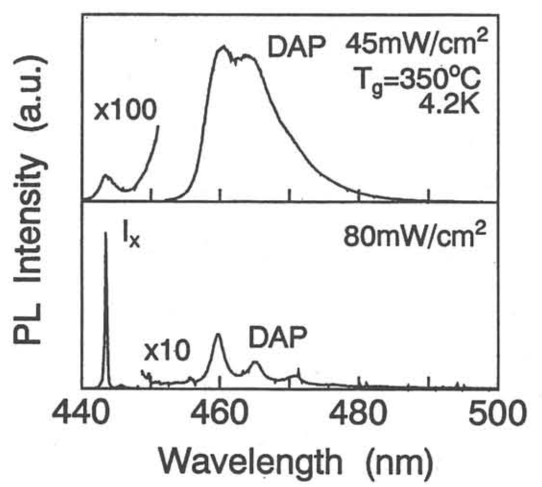

Fig. 3 Comparison of 4.2 K PL spectra from ZnSe:N layers grown at different irradiation intensity. Flow rate of t-BNH_2 was 90 μmol/min.

with zero phonon lines (ZPLs) at 460 nm and 463 nm. The DAP peak at 463 nm indicates formation of electrically active acceptors.[7,8]

With the flow rate of t-BNH_2 at 30 μmol/min, comparison of PL spectra for different substrate temperature is shown in Fig. 2. Higher substrate temperature, 400 °C, did not result in any DAP emission.

Figure 3 shows the PL spectra for different irradiation light intensity, where the flow rate of t-BNH_2 was 90 μmol/min. Higher light intensity, 80 mW/cm^2, yielded strong I_x line rather than DAP emission. Together with Fig. 2, it is concluded that at the present growth conditions, the low growth temperature, *e.g.*, 350 °C and the low irradiation intensity, *e.g.*, 45 mW/cm^2, are desirable for effective nitrogen doping.

Impurity concentration in ZnSe:N layers were characterized by capacitance-voltage characteristics of Schottky contacts. For this purpose, ZnSe:N layers were grown on p$^+$-GaAs substrates, and then ohmic contacts to the substrates and Schottky contacts to the ZnSe:N layers were fabricated by evaporating/alloying of indium (In) and by evaporating 1 mmϕ gold (Au) electrodes, respectively. The slope of 1/(capacitance)^2-voltage ($1/C^2$-V) characteristics of the Schottky diodes suggested the net acceptor concentration of 2×10^{17} cm^{-3} for the ZnSe layer grown at [t-BNH_2]=90 μmol/min, while the secondary ion mass spectroscopy (SIMS) for this sample had shown nitrogen concentration of 5×10^{17} cm^{-3}.

4. ELECTROLUMINESCENCE

Homo- and double hetero-junction LEDs, as shown in Fig. 4, were fabricated in order to show p-type behavior of the ZnSe:N layers. For the ZnSe homo-junction diode shown in Fig. 4(a), the 77 K EL spectrum together with 77 K PL spectra of ZnSe:N and ZnSe:Ga layers are shown in Fig. 5.

It is seen in Fig. 5 that the blue EL peak wavelength (460 nm) is nearly equal to the PL peak wavelength from the ZnSe:N layer (probably free-to-acceptor emission) rather than that from the ZnSe:Ga layer (444nm, free-to-donor emission), suggesting that electrons are injected from the ZnSe:Ga layer to the ZnSe:N layer, and recombine with holes in the ZnSe:N layer, i.e., the ZnSe:N layer behaves as p-type.

The 77 K EL spectra for the ZnCdSe/ZnSe quan-

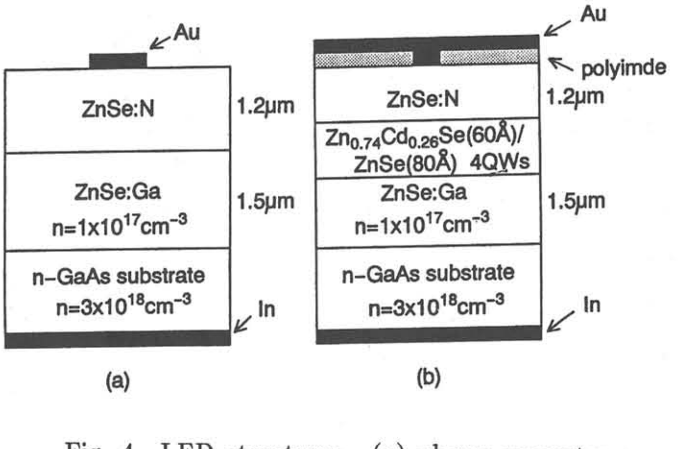

Fig. 4 LED structures. (a) planer geometry homo-junction diode with the Au electrode of 1 mmϕ, and (b) creaved geometry double hetero-junction diodes with the stripe-shaped Au electrode of 1mm$\times$20μm.

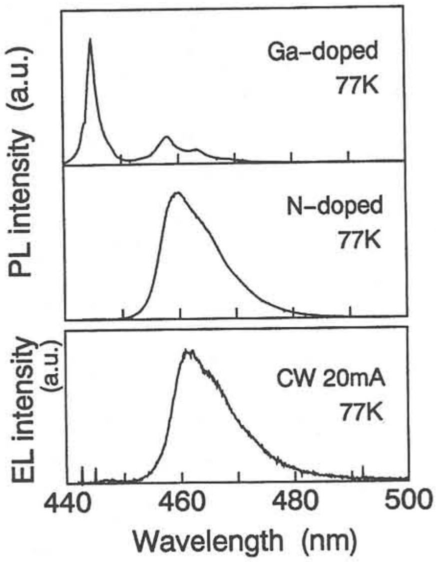

Fig. 5 77 K EL spectrum from a homo-junction diode shown in Fig. 4(a) together with 77 K PL spectra from ZnSe:N and ZnSe:Ga layers.

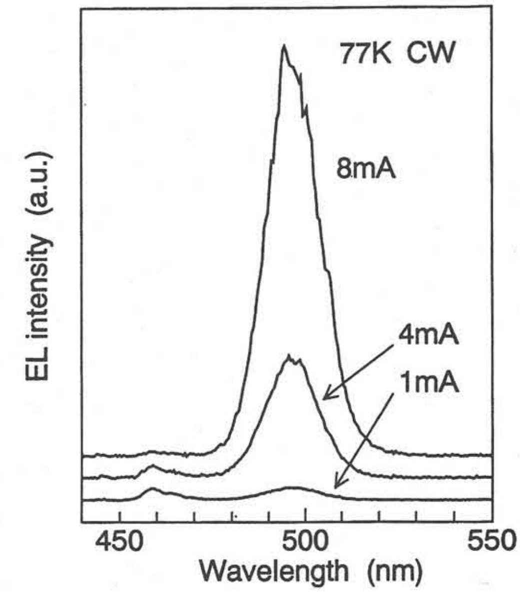

Fig. 6 77 K EL spectra from a double hetero-junction diode shown in Fig. 4(b).

tum well (QW) double hetero-junction diode given in Fig. 4(b) are shown in Fig. 6. The blue-green emission at 496 nm, which seems to be from the QW region, remarkably increases with current, and the strong blue-green emission was observed by naked eyes under the normal room lighting condition at the applied dc voltage of about 10 V and the current of 2–4 mA (100–200 A/cm^2).

5. CONCLUSIONS

Nitrogen doping of ZnSe in photo-assisted MOVPE successfully revealed the net acceptor concentration as high as 2×10^{17} cm^{-3} for the sample where the nitrogen concentration revealed by SIMS was 5×10^{17} cm^{-3}. The lower substrate temperature and weaker irradiation intensity were found to be important for the effective acceptor doping. These results, showing promising potentials of photo-assisted MOVPE for acceptor doping, seem to be brought by increased sticking coefficient of nitrogen at low temperature growth, highly nonequilibrium conditions during the growth, and enhanced decomposition of t-BNH_2 by photo-irradiation.

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