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/cm², respectively. The net acceptor concentration was estimated as 2×10¹⁷ cm⁻³ for the ZnSe:N layer with nitrogen concentration of 5×10¹⁷ 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 9×10¹⁷ cm⁻³ and demonstrated p-n junction LEDs,¹) doping of nitrogen from NH₃ has shown the as-grown hole concentrations only as low as 10¹⁴-10¹⁵ cm⁻³.²,³) However, recent report by Tasker et al.⁴) showing the net acceptor concentrations up to 3×10¹⁶ 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-BNH₂) 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/cm², 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-BNH₂.

(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/cm². 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 (Ex) and the ZnSe layers showed high-resistance. When the flow rate of t-BNH₂ 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.
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-BNH₂ 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-BNH₂ was 90 μmol/min. Higher light intensity, 80 mW/cm², yielded strong Iₓ 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/cm², 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 p³-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 mm thickness of Au (Au) electrodes, respectively. The slope of 1/(capacitance)²-voltage (1/C²-V) characteristics of the Schottky diodes suggested the net acceptor concentration of 2×10¹⁷ cm⁻³ for the ZnSe layer grown at [t-BNH₂]=90 μmol/min, while the secondary ion mass spectroscopy (SIMS) for this sample had shown nitrogen concentration of 5×10¹⁷ 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 (444 nm, 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 quanti-
Nitrogen doping of ZnSe in photo-assisted MOVPE successfully revealed the net acceptor concentration as high as $2 \times 10^{17}$ cm$^{-3}$ for the sample where the nitrogen concentration revealed by SIMS was $5 \times 10^{17}$ 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.

5. CONCLUSIONS

Nitrogen doping of ZnSe in photo-assisted MOVPE successfully revealed the net acceptor concentration as high as $2 \times 10^{17}$ cm$^{-3}$ for the sample where the nitrogen concentration revealed by SIMS was $5 \times 10^{17}$ 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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