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MOMBE Growth of Nitrogen-Doped p-Type ZnSe

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Growth of ZnSe and nitrogen doping were carried out with metalorganic molecular beam epitaxy (MOMBE), where metalorganic precursors were not precracked. Two types of nitrogen doping, i.e., doping of triallylamine (TAN) and doping with active nitrogen plasma excited by ECR were studied. Doping properties of TAN were critically dependent on the VI/II ratio during the growth. The doped ZnSe films tend to be *n*-type, contrary to our expectation. The samples doped with the nitrogen plasma was dominated by the donor acceptor pair (DAP) emission, and the net acceptor concentration up to $2.3\times10^{17}cm^{-3}$ was measured with the present growth method.

1. Introduction

Recently, continuous-wave operations of blue semiconductor lasers were reported with ZnCdSe/ZnSSe/ZnMgSSe heterostructures grown by molecular-beam epitaxy (MBE) [1]. Further increase of band offsets in the heterostructures by the increase of Mg and S compositions is necessary for the complete carrier confinement to realize reliable operations. However, the control of the S composition is not easy in MBE, because the high vapor pressure of S requires highly stabilized temperature control of Knudsen cells. It is more easily attainable in metalorganic (MO) MBE [2] or gas source (GS) MBE [3] by the flow rate control of S sources. However there remains the problem that high-temperature precracking of MO precursors is usually requested for epitaxial growth and this tends to increase residual impurities in grown layers.

In case of metalorganic vapor phase epitaxy (MOVPE) which is widely used for mass production of commercial III-V devices, the problem of *p*-type conductivity in ZnSe has not been solved completely. It has been observed that hydrogens passivate nitrogen acceptors doped in ZnSe [4]. Although it was reported that hydrogens are decreased by thermal annealing [5], it is a great concern where hydrogen comes from, either MO precursors or hydrogen carrier gas.

In this study, we report nitrogen doping in ZnSe based on the successful MOMBE growth of ZnSe without precracking using precursors which decompose at low temperature [6]. Our MOMBE growth is free from contaminations caused by precracking of precursors. It is also essentially similar to MOVPE except for the absence of the hydrogen carrier gas, and the informations given by *in-situ* monitoring can be forwarded to solve the problem in MOVPE. We tried two types of nitrogen dopant, triallylamine (TAN), $N(C_3H_5)_3$, and active nitrogen gas excited by electron cyclotron resonance (ECR) plasma. *p*-Type conduction was observed by the latter method.

2. Experiment

Substrates used were GaAs(001) substrates, which were chemically cleaned using conventional techniques, and introduced into the MOMBE growth chamber. Precursors for Zn and Se were diisopropyl zinc (DiPZn), $Zn(C_3H_7)_2$, and ditertiarybutyl selenide (DtBSe), $Se(C_4H_9)_2$, which were decomposed above the substrate temperature of 100°C and 150°C respectively by quadrupole mass spectrometry (QMS) [6]. The temperature of the precursor cylinders were kept at 2°C in a thermostat. The flow rate of MO precursors were controlled by needle valves, and they were directly introduced into the growth chamber without precracking. Epilayers were grown at the substrate temperature of 350°C, where the growth

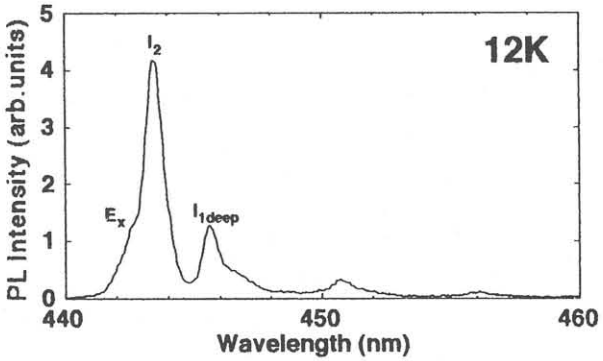

Fig. 1. PL spectrum of nondoped ZnSe. Although E_x and I_{1deep} line can be seen in the spectrum, the dominant peak is I_2 line, and the layer is *n*-type with the net donor concentration of $2.2\times10^{16}cm^{-3}$.

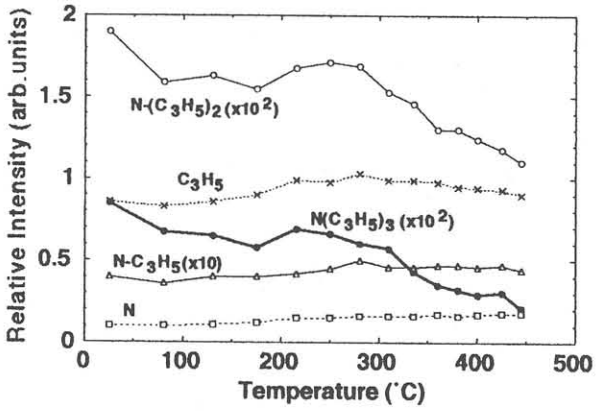

Fig. 2. Temperature dependence of major peaks observed by QMS. TAN and diallylamine, $N(C_3H_5)_2$, decrease above 300°C, suggesting that TAN decomposes above 300°C.

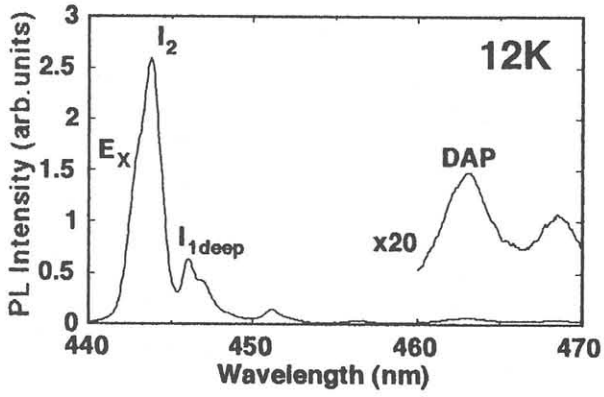

Fig. 3. PL spectrum of ZnSe doped with TAN. The dominant peak is I_2 line, and the layer is *n*-type with the net donor concentration of $1.6\times10^{15}cm^{-3}$. E_x and DAP emission is also weakly observed.

rate was maximum [6]. The pressure of the precursors during growth were 7.5×10^{-4}~1.0×10^{-3}Torr for DiPZn, and 3.0 ~4.2×10^{-3} Torr for DtBSe.

We tried two types of nitrogen dopants for *p*-type doping of ZnSe. One is TAN, with which growth of *p*-type ZnSe was reported by MOVPE recently [7]. Prior to doping, the decomposition process of TAN was studied by QMS. The pressure of TAN during growth was 3.0×10^{-4}~1.0×10^{-3}Torr. The other is active nitrogen gas excited by ECR plasma. The flow rate of the nitrogen gas was 1.0~4.0sccm and the pressure was 3×10^{-4}~1.5×10^{-3}Torr. The microwave power incident in the resonator was 40~80W.

Photoluminescence (PL) spectra of the grown samples were observed at 12K excited by He-Cd laser (325nm). The electrical properties of the samples were measured with the C-V method. The measurement was carried out by surface contact on evaporated gold films at the frequency of 1kHz.

3. Results and discussion

Firstly, properties of nondoped ZnSe films will be discussed. Figure 1 shows a typical PL spectrum of nondoped ZnSe measured at 12K. This specific sample was grown with the pressure of 2.1×10^{-3}Torr for DiPZn and 4.2×10^{-3}Torr for DtBSe (VI/II=2) and the layer thickness is 1μm. The spectrum was dominated by the I_2 line, which originates from neutral donor bound excitons. This will be due to residual impurities in precursors. The net donor concentration was measured to be $2.2\times10^{16}cm^{-3}$ with the C-V method.

The decomposition process of TAN was studied by QMS. The main peak intensities in the spectra observed by QMS are plotted in Fig. 2 as a function of the substrate temperature. The intensities of TAN and diallylamine, $N(C_3H_5)_2$, decreased above 300°C. This suggests that TAN decomposes above 300°C. We tried doping of ZnSe using TAN at the substrate temperature of 350°C. The pressures of TAN and DtBSe were fixed at 3.0×10^{-3}, 4.2×10^{-3}Torr, respectively. When the DiPZn pressure was 1.1×10^{-3}Torr (VI/II=4), the I_2 line in the PL spectra increased further with the TAN doping compared to the nondoped case shown in Fig. 1. The net donor concentration in this case was estimated to be $2\times10^{17}cm^{-3}$. Figure 3 shows the PL spectrum of the layer doped with TAN when the DiPZn pressure was 2.1×10^{-3}Torr (VI/II=2). Weak DAP emission was observed in this case, but the spectrum was still dominated by the I_2 line. The net donor concentration was reduced to $1.6\times10^{15}cm^{-3}$. The reason why the donor concentration increases with the TAN doping is not well understood at present. It may be due to residual impurities in TAN precursors, but the doping properties are drastically changed with the VI/II ratio. Similar VI/II ratio dependence

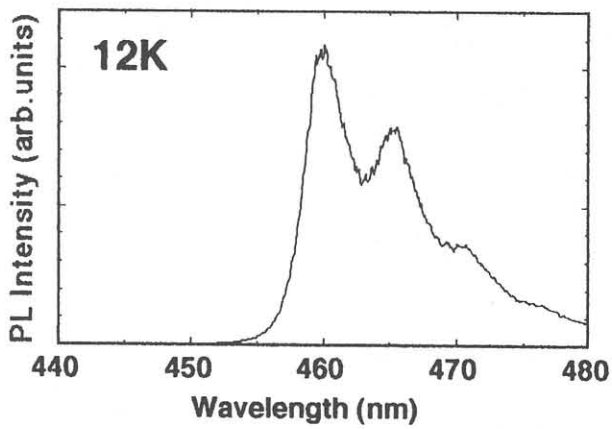

Fig. 4. PL spectrum of nitrogen-doped sample. D^sAP and its LO phonon replicas are observed. D^dAP and its LO phonon replicas are also overlapped to the D^sAP spectrum.

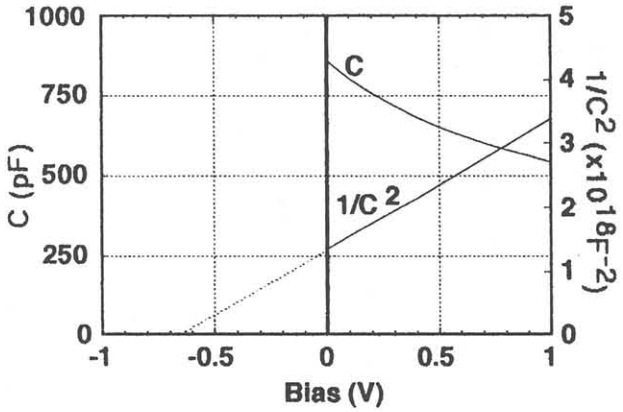

Fig. 5. C-V and $1/C^2$-V characteristics of *p*-type ZnSe doped with ECR plasma. The sample corresponds to that of Fig. 4. $1/C^2$-V property shows linear dependence on the bias, and built-in voltage is about 0.65 V. The net acceptor concentration of N_A-N_D=2.3x10^{17}cm^{-3} was obtained.

was also observed in MOVPE [8, 9], and spectra dominated by the DAP emission were observed with the lower VI/II ratio. Therefore, there remains a possibility that the decomposition process of TAN and the resultant impurity incorporation in the grown films are dependent on the VI/II ratio.

The other nitrogen doping technique was studied with ECR plasma source. The pressures during growth were 1.1x10^{-3} Torr for DiPZn and 4.2x10^{-3}Torr for DtBSe (VI/II=4). The N_2 flow rate was 2.0sccm and the microwave power for exciting ECR plasma was 40W. With the nitrogen plasma irradiation, the DAP emission with the zero-phonon line around 460nm appeared, which is associated with the shallow donors (D^sAP). Figure 4 shows the PL spectrum of the grown film. Although the PL spectrum was dominated by the shallow D^sAP emission and its phonon replicas, the deep D^dAP emission and its phonon replicas overlap the spectrum and the dip of the shallow D^sAP emission lines are buried in Fig. 4. Figure 5 shows the C-V and $1/C^2$-V properties measured on this sample. The built-in voltage was about 0.65V, and the net acceptor concentration (N_A-N_D) was estimated to be 2.3x10^{17}cm^{-3}. In samples with lower nitrogen doping, only the shallow D^sAP emissions were observed in PL spectra and the net acceptor concentrations measured on these samples were 10^{15}~10^{16}cm^{-3}. These results demonstrate the first successful *p*-type doping in MOMBE with precursors introduced without precracking. The comparison of the present results with conventional MOVPE suggests that the hydrogen passivation originating from the MO precursors is not crucial to the control of *p*-type conductivity in ZnSe.

4. Conclusion

p-Type doping in ZnSe was carried out with precracking-free growth by MOMBE. Two types of nitrogen doping techniques were studied. One is the doping with the nitrogen precursors, TAN. It was found that TAN decomposes above 300°C with the QMS study. However, samples doped by TAN showed PL spectra dominated by the I_2 line, which suggested to be *n*-type. The net donor concentration was measured to be in the range of 10^{15}~10^{17}cm^{-3}. It is noted that the doping characteristics of TAN were sensitively dependent on the VI/II ratio, where the tendency of higher DAP intensities were observed for the lower VI/II ratio. *p*-Type conductivity was not observed with the TAN doping in MOMBE at present. The other is the nitrogen doping with ECR plasma. The spectra of the samples doped with nitrogen plasma were dominated by the DAP emission, and the net acceptor concentration up to 2.3x10^{17}cm^{-3} was measured. The PL spectra of the samples showed the tendency that the intensity of the deep D^dAP emissions increased over the shallow D^sAP emission with the higher net acceptor concentrations. This successful *p*-type doping in ZnSe with precracking-free MOMBE suggests that the hydrogen passivation of acceptors originating from MO precursors is not crucial for the further development of blue semiconductor lasers with MOMBE and MOVPE.

Acknowledgements

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