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Photo-induced MOCVD of Group V Element Doped ZnSe

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Nitrogen or phosphorus doped ZnSe, grown by photo-induced MOCVD using organic compounds as source materials and NH_3 or PH_3 as dopoing materials have been investigated. Formation of a shallow acceptor level was confirmed in nitrogen-doped ZnSe. High doping efficiency has been achieved in photo-induced MOCVD as compared with conventional thermal MOCVD. It has been confirmed that doping efficiency was enhanced by lowering the growth temperature and by doping material photolysis.

1. Introduction

Zinc selenide(ZnSe) is an attractive material for blue light emitting devices because of its direct gap of 2.7 eV at room temperature. However, a highly efficient blue light emitting diode has not been reported as yet, because of the difficulty in obtaining p-type crystals. Group 1 elements(Li,Na) replacing Zn and Group V elements(N,P,As) replacing Se are both expected to be shallow acceptors in ZnSe.

With recent development in MOCVD and MBE technologies, several attempts have been made to dope p-type impurities : nitrogen(N) and phosphorus(P) for MOCVD and MBE.[1]-[3] Stutius[1] has reported that N is incorporated as shallow acceptors in hydride MOCVD using dimethylzinc(DMZ) and hydrogen selenide(H_2Se). But in MOCVD using only organic compounds, formation of shallow acceptors by N or P has not been reported as yet. The photo-induced epitaxial growth technique has possibilities of p-type ZnSe due to doping reaction enhancement.

In this paper, the authors have investigated N or P-doped ZnSe, grown by photo-induced MOCVD using organic compounds as source materials, and NH_3 or PH_3 as doping materials and characterized it by low temperature photoluminescence(PL).

2. Experimental

The source materials were dimethylzinc (DMZ) and dimethylselenide(DMSe). This source combination is advantageous over the conventional combination of DMZ and H_2Se, because no undesirable premature reaction occurs.[4,5] Mixtures of 1000ppm NH_3 in hydrogen and of 1000ppm PH_3 in hydrogen were used as doping materials. The light source was ArF excimer laser (λ=193nm). Absorption cross sections of NH_3 and PH_3 were $0.04A^2$ and $0.06A^2$,respectively.[6] These doping materials have been expected to be photo-excited by ArF laser energy. The substrate was (100) oriented Cr-doped semi-insulating GaAs. During the growth, the substrate was irradiated by an ArF laser beam. The irradiation laser energy was about $30mJ/cm^2$ at the outlet of the excimer laser system. The repetition rate was 80pps. The growth of ZnSe was carried on under low

pressure(50Torr). The DMZ and DMSe transport rates were kept at 6.9×10^{-5}mol/min and 8.4×10^{-5}mol/min, respectively, throughout this study. The epitaxial layers of ZnSe were grown under varying transport rates of the doping materials and growth temperatures. The thickness of the grown layers was about 1um.

The grown ZnSe layers were characterized by 4.2K PL measurement. Photoluminescence was excited by a 10mW He-Cd laser (λ=325nm).

3. Results and Discussions

3-1. Phosphorus(P)-doped ZnSe

Figure 1 shows a PL spectrum in the whole visible region for P-doped ZnSe grown under various PH_3 to DMSe mole ratios ([PH_3]/[DMSe]) in the vapor phase. The growth temperature was 400°C. The excitonic emission band (E_x) and the deep emission band increased in intensity as the PH_3 transport rate was raised. The P-doped ZnSe grown under a high PH_3 transport rate exhibited an only deep emission band. A shallow donor-acceptor pair (DAP) emission could not be observed in all of the P-doped ZnSe.

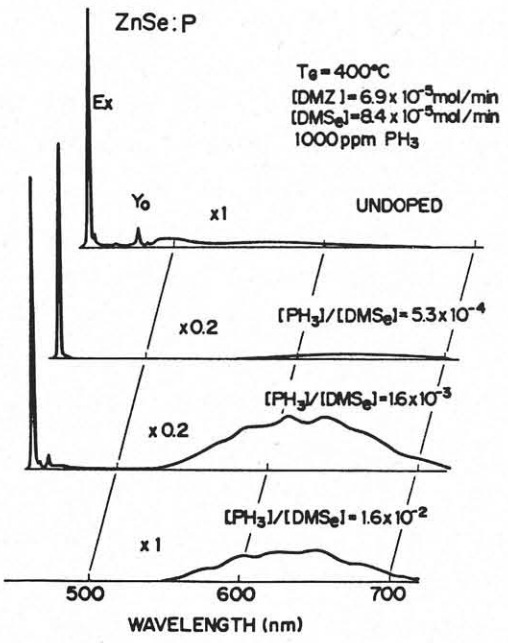

Fig.1 Whole visible region of PL spectrum for P-doped ZnSe

Figure 2 shows a PL spectrum in the excitonic emission region for P-doped ZnSe. The undoped ZnSe exhibited a free-exciton emission (FE) line at 2.801eV, donor bound-exciton emission lines at 2.797eV (I_2) and 2.795eV (I_x)[7] and an ionized donor bound-exciton emission line (I_3) at 2.794eV. The FE line disappeared and the I_x line increased in intensity as the PH_3 transport rate was raised. The I_x line is tentatively thought to be due to a complex defect involving Se vacancy.[8] These results imply that formations of the donor level and deep level are induced by PH_3 doping.

3-2, Nitrogen(N)-doped ZnSe

Figure 3 shows a PL spectrum in the whole visible region for N-doped ZnSe grown under various NH_3 to DMSe mole ratios ([NH_3]/[DMSe]) in the vapor phase. The growth temperature was 400°C. The shallow DAP emission, which could not be observed in P-doped ZnSe, was observed in N-doped ZnSe. The shallow DAP emission increased in intensity as the NH_3 transport rate was raised. But in N-doped ZnSe grown under a

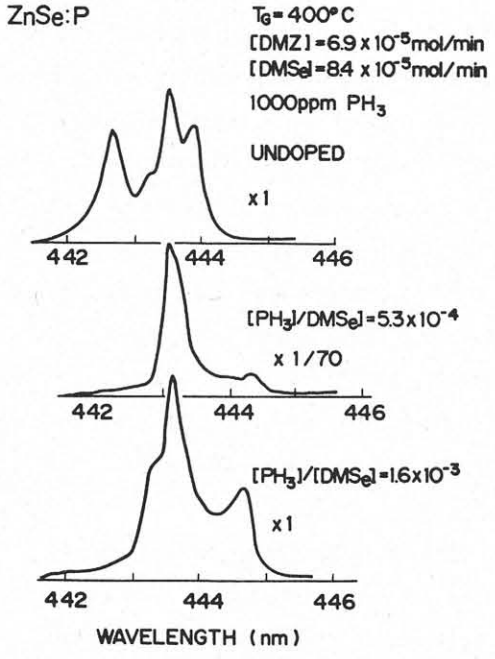

Fig.2 Excitonic emission region of PL spectrum for P-doped ZnSe

high NH_3 transport rate, The E_x line disappeared and only broad DAP emission was observed. This implies that crystallinity deformation was induced by high NH_3 doping.

Figure 4 shows a PL spectrum in the excitonic emission region for N-doped ZnSe. The N-doped ZnSe exhibited a strong bound-exciton emission line at 2.790eV, which could not be observed for both undoped and P-doped ZnSe. This emission line was assigned to be acceptor bound-exciton emission line (I_1) formation by nitrogen, because its intensity increased as the NH_3 transport rate was raised. No deep emission band was observed in N-doped ZnSe. Assuming that the donor ionization energy and the coulomb interaction term were equal to 25meV and 15meV, respectively, the acceptor ionization energy is estimated to be 115meV which was almost in agreement with the value for a N acceptor determined by Dean, et al.[9]

3-3, Laser irradiation effect on doping efficiency

In order to study the doping mechanism and the laser irradiation effect in photo-induced MOCVD, the dependence of doping efficiency on the growth temperature and the laser irradiation effect on doping efficiency were investigated. Figure 5 shows a PL spectrum in the whole visible region for N-doped ZnSe grown under various growth temperatures. N-doped ZnSe grown at 350°C exhibited broad DAP emission, and it is almost in agreement with that of N-doped ZnSe grown under a high NH_3 transport rate at 400°C as shown in Fig.3. The shallow DAP emission was weak in N-doped ZnSe grown at 450 °C. These results imply that doping efficiency increased as growth temperature decreased. This dependence of doping efficiency on growth temperature is considered to be the result from N or NH_x(x=1∿3) sticking coefficients due to growth temperature decrease.

Next, in order to study the laser irradiation effect on doping efficiency, the PL spectrum of N-doped ZnSe grown with and without laser irradiation were compared. Figure 6 shows the excitonic emission region for N-doped ZnSe grown with and without

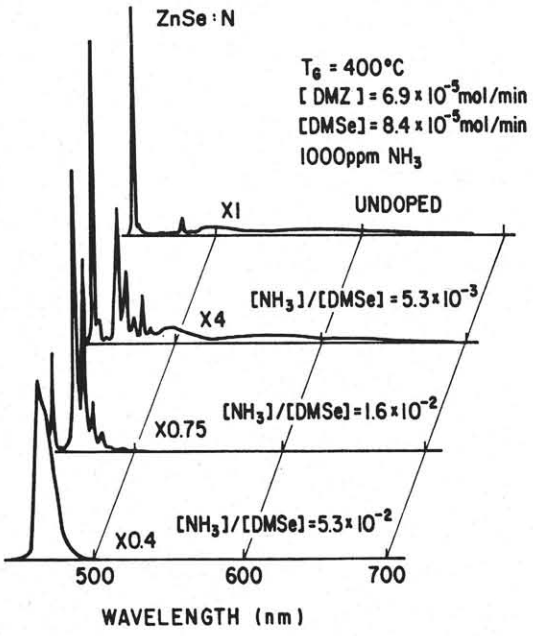

Fig.3 Whole visible region of PL spectrum for N-doped ZnSe

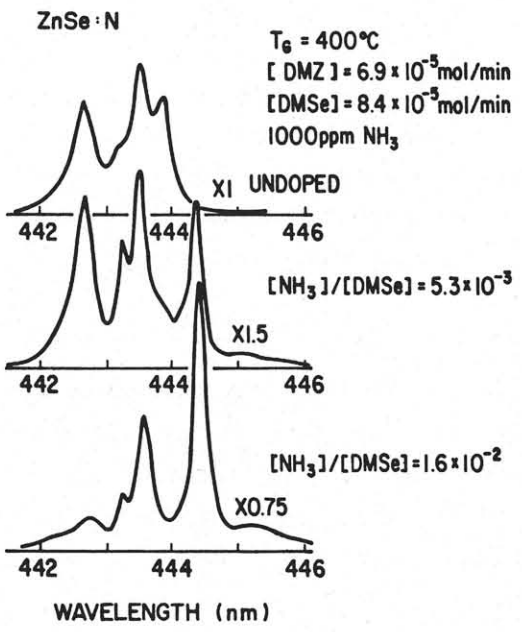

Fig.4 Excitonic emission region of PL spectrum for N-doped ZnSe

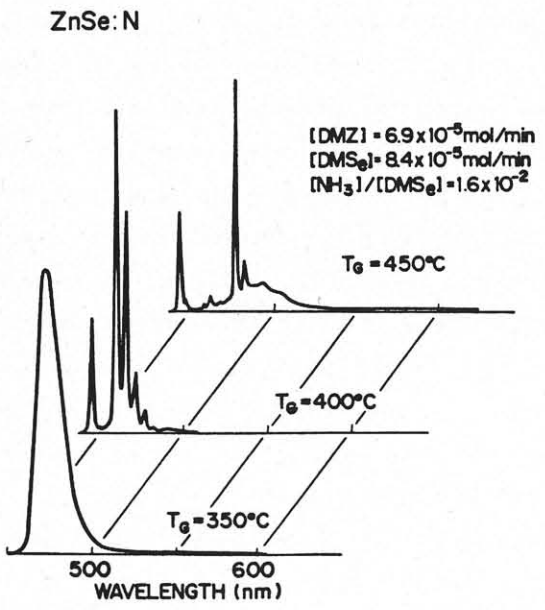

Fig.5 Whole visible region of PL spectrum for N-doped ZnSe grown under growth temperatures

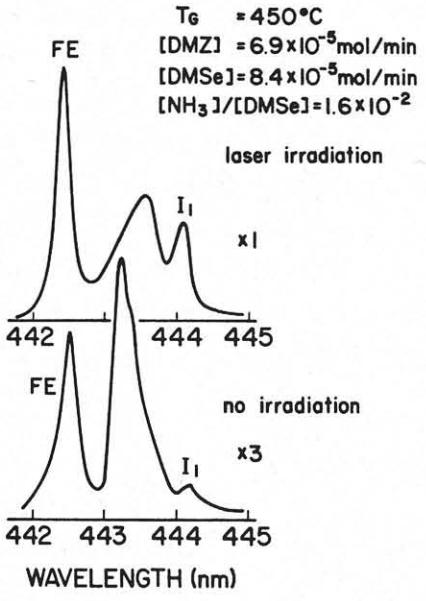

Fig.6 Excitonic emission region of PL spectrum for N-doped ZnSe with and without laser irradiation

laser irradiation. The intensity of the I_1 emission line for N-doped ZnSe with laser irradiation was very strong as compared with that of N-doped ZnSe without laser irradiation. This implies that NH_3 photolysis was enhanced by laser irradiation. It was found that doping efficiency was enhanced by lowering the growth temperature and by doping material photolysis in photo-induced MOCVD.

4. Summary

N or P-doped ZnSe, grown by photo-induced MOCVD using organic compounds as source materials and NH_3 or PH_3 as doping materials, was investigated. In P-doped ZnSe, the formation of a shallow acceptor could not be enhanced, but the formation of deep levels were enhanced by PH_3 doping. In N-doped ZnSe, the formation of a shallow acceptor could be enhanced by NH_3 doping. High doping efficiency was achived in photo-induced MOCVD using organic compounds, as compared with conventional thermal MOCVD. It has been confirmed that doping efficiency was enhanced by lowering the growth temperature and by doping materials photolysis in photo-induced MOCVD. Photo-induced MOCVD seems to be a promising technology for doping a shallow acceptor into ZnSe.

References

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