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MOCVD Growth of Arsenic Doped Zinc Selenide

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MOCVD growth of As-doped ZnSe using DMZn and DMSe has been investigated. Arsenic-doped ZnSe exhibited a strong bound exciton (BE) line at 2.796 eV and two major deep emission bands at around 2.4 eV and 1.7 eV. This suggests that As forms both shallow and deep levels. The dependence of each emission intensity on the Se-to-Zn mole ratio in the vapor phase suggests that As substitutes the Se-lattice site and that the 1.7 eV deep emission band may be associated with a Se vacancy related complex.

1 Introduction

Zinc selenide is attractive as a blue LED material because of its direct and wide bandgap whose energy corresponds to the blue spectral region. It is also favorable in that it has a lattice constant close to GaAs whose wafer can be used as an epitaxial substrate. The major problem for realizing efficient blue LEDs is the difficulty in achieving low resistivity p-type ZnSe indispensable to a pn junction. From the viewpoint of device application, it is particularly important to attain p-type conduction by epitaxial growth.

With recent developments in metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) technologies, several attempts have been made to dope p-type impurities: nitrogen and phosphorus for MOCVD[1] and sodium and phosphorus for MBE[2], while very little work has been done for arsenic which is also expected to be a shallow acceptor[3].

In this paper, we have investigated the MOCVD growth of As-doped ZnSe and characterized it by low temperature photoluminescence(PL). In order to understand As-doping effects clearly, it is important to obtain undoped ZnSe of high purity. First, undoped layers were examined and cares were taken to reduce residual impurities. Arsenic was doped by arsine and the doping dependence on the As concentration in the vapor phase and on the stoichiometrical condition of the crystal growth was intensively studied.

2 Experimental

The epitaxial layers were grown by MOCVD in an rf-heated vertical reactor. The source materials were dimethylzinc (DMZn) and dimethylselenide (DMSe). This source combination is advantageous over the conventional combination of DMZn and H_2Se because no undesirable premature reaction occurs[4,5]. Arsenic was doped from an arsine (AsH_3) source during growth. Pd-diffused H_2 was used as a carrier gas and cares were taken to minimize contamination from the growth apparatus. The substrate was (100) oriented Cr-doped semi-insulating GaAs.

The epitaxial growth was made at 500°C under atmospheric pressure. The DMZn transport rate was kept at 6.4×10^{-6} mol/min throughout this study. The DMSe to DMZn mole ratio (VI/II) in the vapor phase, which is an important parameter to control the stoichiometry of the grown layers, was varied from 2 to as high as 300. The growth rate under the above condition was 250-450 Å/min. The thickness of the grown layers was about 3 μm.

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

3 Results and Discussion

3.1 Undoped ZnSe

There are very few reports on PL study of undoped ZnSe grown from an alkyl Se source. Figure 1 shows excitonic emission portions of the PL spectra for undoped ZnSe grown under various Se-to-Zn mole ratios (VI/II) in the vapor phase. The dominant emission line was that for free exciton (FE) at 2.802 eV. The major bound exciton (BE) line was situated at 2.796 eV. The energy is the same as that of the Ix line (2.7961 eV) which is dominant emisson in MBE grown ZnSe[6]. The Ix line is tentatively thought to be due to a complex defect involving Se vacancy[7].

The BE line decreased in intensity for samples grown under high VI/II values, i.e. a Se-rich condition, where impurity incorporation at the Se-lattice site and Se vacancy formation are likely to be suppressed. The results may suggest that this BE line is due to an impurity at the Se-lattice site and/or a Se vacancy related defect.

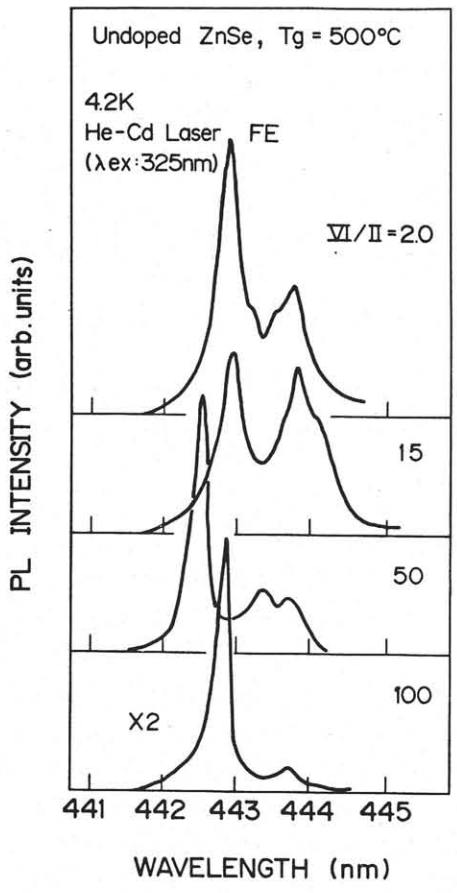

Fig.1 Excitonic emission portions of PL spectra for undoped ZnSe.

The FE line dominant spectra indicate that undoped ZnSe has very small amount of shallow residual impurities and that high purity ZnSe layers can be grown by MOCVD using alkyl Se. The results are comparable to the best results obtained by conventional MOCVD using H_2Se[8] and by MBE[9] in spite of the higher growth temperature of the present method. The undoped ZnSe was of high resistivity, which may be due to close compensation.

3.2 As-Doped ZnSe

Figure 2 shows excitonic emission portions of the PL spectra for undoped and As-doped ZnSe with relatively low As concentration grown under VI/II=50. The As-doped ZnSe exhibited a strong BE line (2.796 eV) compared with the undoped layer, whereas the FE line intensity decreased.

If we assume this BE line to be related to a shallow As acceptor, the acceptor activation energy is roughly estimated to be about 60 meV from a simple empirical rule[10] using the dissociation energy of free excitons from the neutral acceptors (i.e. the energy difference between FE and BE). The value is smaller than the previously reported value of 110 meV derived from the donor-acceptor pair (DAP) emission energy for LPE grown ZnSe[3]. In the present study, the DAP emission due to shallow donors and acceptors was not observed. It is probably due to the difference in growth technique. More work is necessary to confirm that As forms a shallow acceptor.

The energy of the BE line enhanced by As-doping coincides with that of the BE line observed in undoped layers grown under small VI/II values. This may suggest that the BE line in undoped layers is ascribed to As which is a probable impurity in the not-deliberately-doped ZnSe layers grown on GaAs substrates.

Figure 3 shows the PL spectra for undoped and As-doped ZnSe with different As concentration in the vapor phase grown under VI/II=50. The undoped ZnSe layer showed the strong FE line, the Y-line[11] and weak deep emission in the longer wavelength region. It confirms that the undoped

ZnSe is of high purity. The As-doped ZnSe exhibited two major deep emission bands at around 2.4 eV (520 nm) and 1.7 ev (710 nm), according to As concentration in the vapor phase. Similar deep emission bands were observed in As-doped ZnSe grown by a Bridgemann technique[12], though their peak energies are not exactly the same as those of the present work.

As the As concentration in the vapor phase increased, the lower energy band intensity became stronger and the BE line and the higher energy band decreased in intensity. This suggests that As forms deep levels and that they increase in number at higher As concentration.

The Se-to-Zn mole ratio (VI/II) in the vapor phase plays a significant role in controlling a major vacancy lattice site, Zn- or Se-site, and resultant impurity incorporation. The dependence of PL intensity for the various emissions on the VI/II value and As transport rate is shown in Fig.4. The open and solid circles represent FE and BE intensity, respectively. And the open triangle and the open square respectively represent 2.4 eV (520 nm) and 1.7 eV (710 nm) band intensity.

The BE line exhibits almost the same dependence on the As transport rate as the 2.4 eV (520 nm) band. This BE line behavior agrees with the assumption that the BE line is associated with As.

With increasing VI/II values, each curve shifts toward a higher As transport rate region. This means that As incorporation is suppressed under a Se rich condition. The results suggest that As substitutes the Se-lattice site.

The 1.7 eV (710 nm) band shows different behavior from that of the BE line and the 2.4 eV (520 nm) band. It appears at a higher As transport rate where the BE line and the 2.4 eV band decreases in intensty. The maximum intensity of the 1.7 eV band decreases with increasing the VI/II value, where Se vacancy

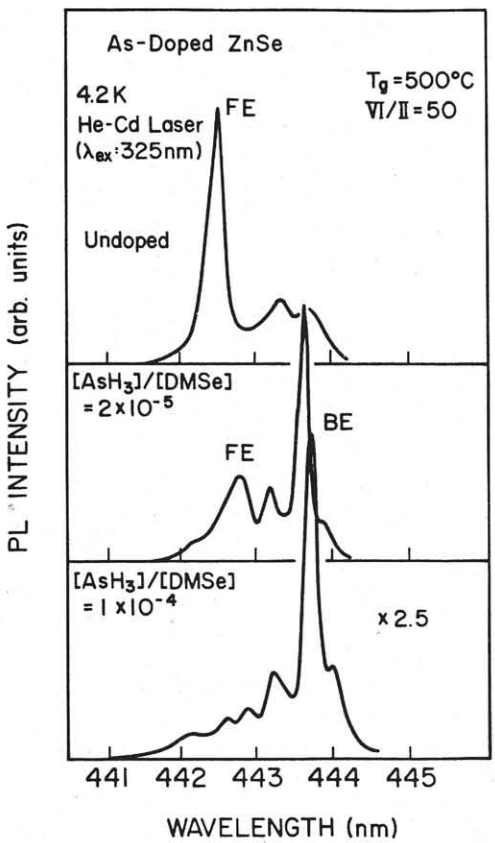

Fig.2 Excitonic emission portions of PL spectra for undoped and As-doped ZnSe grown under VI/II=50.

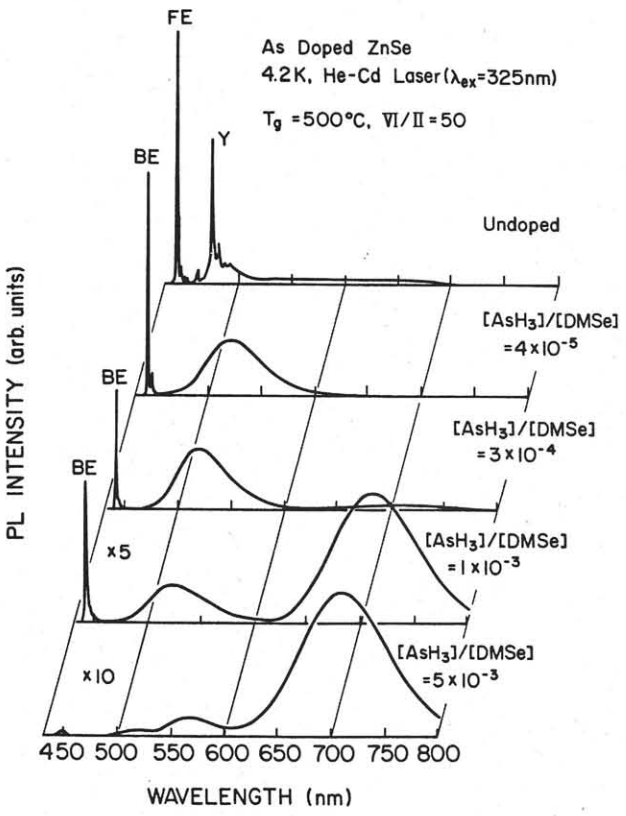

Fig.3 PL Spectra for undoped and As-doped ZnSe with different As concentration in the vapor phase grown under VI/II=50.

formation is likely to be suppressed. The intensity for VI/II=300 is about one order of the magnitude smaller than that for VI/II=2. This implies that the 1.7 eV deep emission band may be due to a Se vacancy related complex.

The epitaxial layers obtained so far were of high resistivity. It is probably due to compensation by Se vacancy related donors. If the BE line, enhanced by As doping, actually represents shallow As acceptor formation and the Se vacancy related donors can be effectively suppressed, it can be expected to achieve p type conduction by As doping.

4 Conclusion

MOCVD growth of As-doped ZnSe using DMZn and DMSe has been investigated. Undoped layers exhibited free exciton line dominant PL spectra, which indicates that ZnSe grown from DMZn and DMSe is of high purity and comparable to the best results obtained by conventional MOCVD and MBE.

Arsenic-doped ZnSe exhibited a strong BE line at 2.796 eV and two major deep emission bands at around 2.4 eV (520 nm) and 1.7 eV (710 nm). This suggests that As forms both shallow and deep levels. If we assume that the BE line is due to a shallow acceptor, its activation energy is roughly estimated to be 60 meV. More work is necessary to confirm that As forms a shallow acceptor.

With increasing As concentration in the vapor phase, the relative intensity of the 1.7 eV deep emission band became stronger, while those of the BE line and the 2.4 eV band decreased. The dependence of each emission intensity on the Se-to-Zn mole ratio in the vapor phase suggests that As substitutes the Se-lattice site and that the 1.7 eV deep emission band may be associated with a Se vacancy related complex.

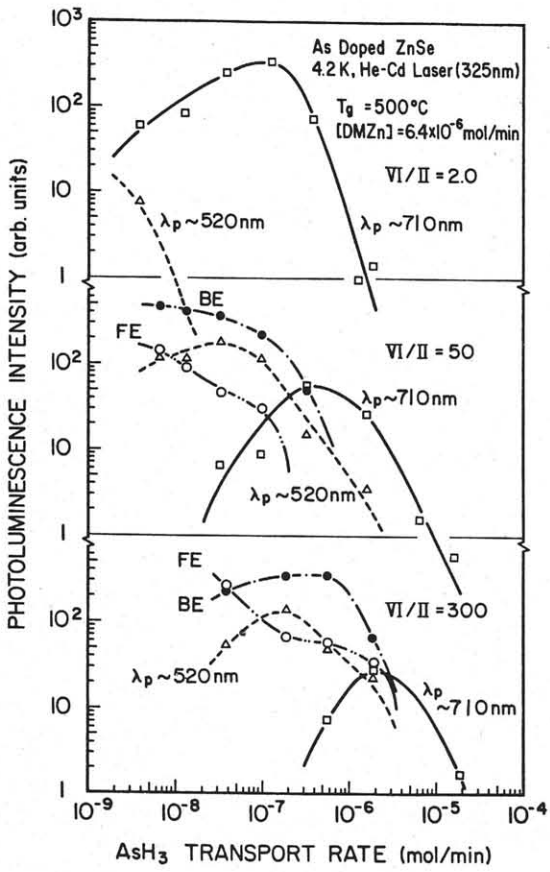

Fig.4 Dependence of PL intensity for various emissions on VI/II value and As transport rate.

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