Compensating processes in nitrogen δ-doped ZnSe layers studied by photoluminescence and photoluminescence excitation spectroscopy

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Abstract

The compensating acceptors and donors in nitrogen δ-doped ZnSe epilayers grown by molecular beam epitaxy using a nitrogen rf-plasma source are studied by means of photoluminescence and photoluminescence excitation spectroscopy. A deep acceptor and a deep donor with ionization energies of ~170 meV and ~88 meV are reported for the nitrogen δ-doped layers. These two deep centres are assigned to N-clusters, i.e., N e−Zn−N e− for the deep acceptor and N e−N z− for the deep donor.

1. Introduction

Over the past few years nitrogen has been found to be the best dopant in the production of p-type ZnSe [1,2], but it can be highly compensated. One of the N-associated deep donors in ZnSe:N with N a−N D = 1 × 10^17 cm^{-3} was reported with an ionisation energy of 44 meV. This was estimated from the emission energy at about 2.681 eV of the transition between a deep donor and a shallow N-acceptor (10 meV) (D^{4}AP), and the Coulomb energy (10 meV) for the deep-donor-acceptor pairs was assumed to be equal to that for the shallow-donor-acceptor pairs [3]. The ionisation energy for the deep donor in a highly compensated ZnSe:N was estimated as 55 ± 5 meV from the emission energy of transition between a free hole and a deep donor (D^{4}F) at high temperatures [4]. Most recently, the D^{4}AP and D^{4}F emissions have been related to an identical deep donor with an ionization energy of 57 meV through the detailed study of the selective excitation spectroscopy [5]. This paper reports the compensating acceptors and donors in highly N-doped ZnSe epilayers fabricated using a δ doping technique studied by photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE). A deep acceptor and a deep donor with ionization energies of ~170 and ~88 meV, respectively, are found in the N δ-doped layers.

2. Experimental procedure

The nitrogen δ-doped ZnSe samples were grown by MBE using a nitrogen rf plasma source for p-type doping. The samples used for the present PL and PLE studies consist of uniformly N-doped epilayers containing a single N δ-doped layer. Initially, a 0.4
Fig. 1. The PL spectra: (a) near the bandgap at 4 K obtained from the N δ-doped ZnSe sample (HWA522), and (b) from the uniformly doped buffer layers after removal of δ-doped layer. An intense new emission line at 2.7854 eV (I_p) appears from the δ-doped layer.

μm thick uniformly N-doped ZnSe buffer layer with around \( N_A - N_D = 2 \times 10^{17} \text{ cm}^{-3} \) was grown on a p-type GaAs(100) substrate at a growth temperature of 330°C and then the growth was interrupted for the N δ-doping. The N δ-doping was carried out by directing both N and Zn beams onto the ZnSe surface at different temperatures ranging from 200 to 300°C for 60 s, where the Zn flux was used to maintain a Zn-terminated surface during the N δ-doping in order to enhance the N sticking coefficient. Immediately after N δ-doping, the N- and Zn-cell shutters were closed, and the Se-cell shutter was opened to direct the Se beam onto the ZnSe in order to suppress the formation of Se-vacancies due to high N-doping. Finally, a uniformly N-doped cap-layer with thickness of 0.1 μm was deposited. The plasma power for N doping was kept at 200 W and the N flow rate was set to give a pressure of \( 8 \times 10^{-7} \text{ mbar} \) in the growth chamber.

The PL spectra were measured using the 351 nm line from an argon ion laser (10 mW) as an excitation source while the sample temperature ranged from 4 to 300 K. The PLE measurements were performed using a cw-argon ion laser (351 nm) pumped tunable dye laser which covered the spectral range of 440–470 nm. \( (N_A - N_D) \) was determined by electrochemical capacitance–voltage profiling. The \( (N_A - N_D) \) in the uniformly N-doped ZnSe layers was set at about \( 2 \times 10^{17} \text{ cm}^{-3} \). An increase in \( (N_A - N_D) \) in the δ-doped layer was clearly observed for each sample, indicating a high N concentration due to the δ-doping. The C–V profile gives a \( N_A - N_D \) value averaged over several layers around the δ-doped layer because of Debye spreading of the free holes and also surface roughness of the sample due to the electrochemical etching process. Thus, the maximum net acceptor density related to δ-doping observed in sample HWA522 was estimated as \( 2.4 \times 10^{11} \text{ cm}^{-2} \) by integrating the increase in \( (N_A - N_D) \) around the δ-doped layer.

3. Results and discussions

Fig. 1(a) shows the PL spectra near the bandgap at 4 K obtained from the N δ-doped ZnSe sample (HWA522). A strong emission due to an exciton bound at a neutral shallow N-acceptor at 2.7917 eV (I_1) and a weak emission from the free excitons at 2.803 eV (E_x) were observed. Additionally, an intense new emission line at 2.7854 eV (denoted as I_p) appears in this spectrum of the sample which includes both the uniformly and δ-doped layers. Fig. 1(b) shows the emissions from the uniformly doped buffer layer after removal of the δ-doped layer in the sample by electrochemical etching, and it can be seen that the I_p line becomes very weak in the spectrum of the buffer layer. Thus, the I_p emission comes mainly from the high N δ-doped layer. It is noted that the I_p line is different from the I_d line which is observed at 2.781 eV in the PL spectrum at 4 K and has been attributed to an exciton bound at a

Fig. 2. The PL spectra at 80 K obtained from (a) the N δ-doped ZnSe sample (HWA522) where a new D^3AP emission at 2.627 eV appears, and (b) from the uniformly doped buffer layers after removal of δ-doped layer.
double acceptor (Zn-vacancy) with an ionization energy of about 220 meV [6]. The phonon replicas of the I₁ and I₃⁺ lines appear at 2.760 and 2.7538 eV respectively, separated by the LO phonon energy (31.6 meV), suggesting that the I₃⁺ line is due to a neutral deep-acceptor-bound exciton. According to Haynes’s rule [7], the ionization energy of the deep acceptor (A₃) is estimated to be about 170 meV.

The temperature dependence of the PL has been investigated in detail in the temperature range from 4 to 300 K [8]. The PL spectrum at 4 K shows dominant D₃AP emission at 2.683 eV and D₃AP at 2.698 eV with strong phonon replicas. At 50 K, the shallow donors (D₁) are partially ionised and the emission due to transitions from free electrons to neutral shallow acceptors (FA) appears. As the temperature increases, both the D₁ (≈ 30 meV) and D₃ (≈ 57 meV) levels are ionised. At 70 K, the D₃AP emission disappears and a strong emission with LO-phonon replicas appears at 2.601 eV (denoted as FA). At 80 K, the D₃AP emission disappears and a new peak appears at 2.627 eV (denoted as D₄AP), as shown in Fig. 2a. At 100 K, the D₄AP emission disappears and the FA emission dominates the spectrum. The temperature dependence of the PL spectra of the uniformly doped ZnSe buffer layer has also been investigated. In this case the D₄AP emission was not observed but the FA emission appeared strongly, as shown in Fig. 2b. This result indicates that the D₄AP emission is related to the N δ-doped layer, i.e., due to high N doping. A detailed excitation intensity dependence has been investigated in order to assign these peaks and the results are shown in Fig. 3. As the excitation intensity is increased by a factor of 5, the energy of the D₄AP peak shifts from 2.627 to 2.640 eV, while the FA and FA peak positions do not change. Since, as the temperature increases, the D₄AP emission disappears followed by the D₄AP emission and the D₄AP emission then appears, the D₄AP peak is attributed to the transition between a new deep donor (D₄) and a N-acceptor. The ionization energy of D₄ is measured approximately as 89 meV from the D₄AP emission energy, where a Coulomb energy of 10 meV is used, estimated from the D₄AP emission energy. The ionization energy for the deep acceptor due to Zn vacancy which is responsible for the FA emission is measured to be 218 meV.

The PLE spectra of the sample at various temperatures were obtained by monitoring either the LO phonon replicas of the D₄AP emission or the FA emission [8]. The 4 K spectrum reveals the following: The absorption peaks of the free excitons in the excited state (n = 2) at 2.816 eV and ground states at 2.8045 eV for the light hole and 2.800 eV for the heavy hole, the peak associated with a neutral-N-acceptor-bound exciton at 2.791 eV and the peak related to an A₃-bound exciton at 2.785 eV. At 70–80 K, a additional peak appeared at 2.724 eV, which corresponds to the D₄F emission since the donors are ionised at 70 K. The ionization energy for D₄ is estimated as 88 meV, and so the PLE results are consistent with the PL results.
The origins of the deep acceptor (A\textsuperscript{p}) and deep donor (D\textsuperscript{p}) centres found in the present study are discussed. It should be noted that I\textsuperscript{p} and D\textsuperscript{p}F emissions have been observed most recently from uniformly doped ZnSe with high N concentrations (typically [N] > 5 \times 10^{17} \text{ cm}^{-3}) [9]. These emissions are enhanced in the N δ-doped layers and are shown definitively in this study. Yao et al. [10] has shown by ion beam analysis that even in heavily doped ZnSe:N with [N] = 1.5 \times 10^{20} \text{ cm}^{-3} an interstitial N atom should not be responsible for the carrier compensation. Since these two deep centres have been observed only from highly N-doped ZnSe, it is proposed that the origins for the centres are related to the N-clusters [10], i.e., N\textsubscript{Se}−Zn−N\textsubscript{Se} for the A\textsuperscript{p} and N\textsubscript{Se}−N\textsubscript{zn} for the D\textsuperscript{p}. The energy level diagram proposed for N-doped ZnSe is shown in Fig. 4.

4. Conclusion

We have studied the N-associated deep acceptors and donors in nitrogen δ-doped ZnSe layers grown by MBE by means of photoluminescence and photoluminescence excitation spectroscopy. A deep acceptor and a deep donor with ionization energies of ~170 and ~88 meV respectively are found in the N δ-doped layers. The origins for these two deep centres are proposed to be N-clusters, i.e., N\textsubscript{Se}−Zn−N\textsubscript{Se} for the deep acceptor and N\textsubscript{Se}−N\textsubscript{zn} for the deep donor.

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References