Photoluminescence of Nitrogen-Doped Zinc Selenide Epilayers

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Photoluminescence (PL) studies of nitrogen doped ZnSe epilayers grown by molecular beam epitaxy have been performed as a function of excitation wavelength, power density, and temperature. The broad emission from heavily doped ZnSe:N is composed of two distinct bands which we label as $N_I$ and $N_{II}$. The dominant band $N_I$ appears at 2.54 eV, while the $N_{II}$ band position is sensitive to excitation power and occurs between 2.55 and 2.61 eV. The $N_I$ emission energy is insensitive to incident power or temperature over the ranges studied. Further, a 69 meV localized phonon of the $N_I$ band is observed. We propose that the $N_I$ band is related to transitions within a ($V_{Se}^-\ldots Zn-N_{Se}$) close-associate pair. The $N_{II}$ band displays characteristics consistent with the conventional donor acceptor pair model. A third band $N_{III}$ at 2.65 eV is observed under high-power pulsed excitation. Previous studies of heavily doped ZnSe:N had suggested that the broad emission band was described by a modified donor-acceptor pair model. Our PL study does not support this previous model. In addition, our data suggests that singly ionized selenium vacancy complexes form in heavily doped ZnSe:N and play a role in compensation.

Key words: Molecular beam epitaxy (MBE), photoluminescence (PL), ZnSe

INTRODUCTION

In recent years, considerable effort has been focused on improving the efficiency of p-type doping in ZnSe epilayers grown on GaAs substrates. A major goal of this research has been to identify and control the dominant point defects in order to increase the net acceptor concentration in these epilayers, and thus permit efficient current-injection devices to be fabricated. Nitrogen is by far the most promising dopant for p-type ZnSe, but unwanted compensation centers have limited the maximum achievable carrier density to the low 10$^{18}$ cm$^{-3}$ level. It is well known that heavy nitrogen doping is accompanied by a relatively broad deep-level luminescence in the region from 2.5 to 2.6 eV. This broad photoluminescence (PL) band has been attributed$^{1-4}$ to donor-acceptor pair (DAP) recombination involving deep compensating donors and substitutional nitrogen acceptors ($N_{Se}$). The identity of the “deep” donor has not been experimentally determined to date.

Substitutional impurities (e.g., Ga or Cl) create donor energy levels about 26 to 28 meV below the conduction band of ZnSe. In contrast, the ionization energy of the “deep” donor is reported to range from 44 to 57 meV.$^{5-6}$ Two possible candidates for this deep donor have been suggested. One candidate is a selenium vacancy-nitrogen acceptor complex ($V_{Se}^{2-}\ldots Zn-N_{Se}$)$^-$ and another candidate is a $N_{Zn}-N_{Se}$ pair.$^{15}$ Thus far, optically detected magnetic resonance (ODMR) and resonant Raman studies$^{8,10}$ have been performed on ZnSe:N epilayers with excess hole concentrations of about 10$^{17}$ cm$^{-3}$. A signal having a g value of 1.36 was attributed to a deep donor, but no nitrogen hyperfine was resolved. An additional ODMR signal having a g value near 2.0 was associated with $V_{Se}^{2-}\ldots Cu_{Zn}$ donor complexes.$^{11}$ These results do not clearly favor one candidate model over another.

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More information about the identity of the defect center responsible for the compensation of substitutional nitrogen in ZnSe can be obtained from heavily doped samples (nitrogen concentration $>10^{18}$ cm$^{-3}$). ODMR has not been reported from epilayers at this high doping level; however, low temperature photoluminescence has been widely used. The broad PL observed from heavily nitrogen-doped ZnSe is shifted about 0.1 eV lower in energy than the conventional DAP luminescence (at 2.69 eV) which occurs in lightly doped ZnSe:N. A modified DAP model has recently been proposed$^{13}$ to explain this large red shift. The main features of this proposed model are DAP recombination, between the deep donor and nitrogen acceptor, and the presence of perturbed band and impurity states caused by a fluctuation of the concentration of ionized impurities. Thus, those authors suggested that a distribution of spatially separated potential wells was responsible for the ~0.1eV red shift in the PL band. Two key interpretations$^{12}$ of PL data provided the basis for their modified DAP model. These were:

- The broad PL band shifts to higher energy with increasing excitation, and
- The broad band shifts toward lower energies with increasing temperature.

In a separate study, these same authors$^{12}$ reported time-dependent PL measurements and concluded that the results gave further support for their modified DAP model.

We have recently performed a series of PL measurements on ZnSe:N epilayers grown by molecular beam epitaxy (MBE) at West Virginia University. In the present paper, we describe the results obtained from our studies of the broad-band emission from heavily doped ZnSe:N. Our data strongly suggest that this PL band is more complicated than previously thought. The PL dependence on excitation wavelength, excitation power density, and temperature has been monitored with the goal of identifying the recombination channels involved in the deep-level luminescence. Our data are inconsistent with a "modified DAP" model. In particular, we show that the broad PL is composed of two distinct radiative recombination bands. The lower energy band occurs at about 2.54 eV in the sample studied and is accompanied by a 69 meV localized phonon. We propose a defect model consistent with this phonon energy. Also, we recently performed time-resolved PL measurements which again show the distinct differences between the two recombination bands. Our investigations help to clarify the compensation mechanisms in heavily doped ZnSe:N and will allow future growth studies to focus on reduction of the particular defect responsible for compensation.

**EXPERIMENTAL DETAILS**

A series of ZnSe epilayers were grown at West Virginia University in a custom MBE system. These films were grown at 300°C on semi-insulating (100) GaAs substrates using high purity (7N) elemental Zn and Se from conventional MBE sources. The samples exhibit low stacking fault densities as a result of atomic hydrogen cleaning of the substrate.$^{13}$ Nitrogen doping was accomplished using an atomic nitrogen
flux from a radio frequency (rf) plasma source (Oxford model CARS25). The PL studies presented here focus on a compensated p-type sample heavily doped with nitrogen (free hole concentration, $p \approx 2 \times 10^{18}$ cm$^{-3}$, and $1.5 \times 10^{19}$ cm$^{-3}$) total nitrogen concentration from secondary ion mass spectroscopy). Low-temperature PL from a lightly doped ZnSe:N sample is included for comparison ($p \approx 2-5 \times 10^{18}$ cm$^{-3}$). The heavily doped film also was part of an electron paramagnetic resonance (EPR) study. The concentration of singly ionized selenium vacancies ($V^+_{Se}$) as detected by EPR was estimated to be about $10^{17}$ cm$^{-3}$.

The PL data were obtained under a variety of excitation and temperature conditions. The samples were held in a Janis Super Varitemp Dewar in flowing helium vapor. Initial studies were conducted using continuous-wave (cw) excitation. The 325.0 nm output from a HeCd laser (Liconix model 4240) was focused onto the sample surface for above-band-gap cw excitation. Below-band-gap cw excitation (457.9 nm) was provided by an argon ion laser (Coherent Innova 400). Excitation powers were measured using a silicon photodiode (Coherent model 212) with calibrated wavelength response. Incident power densities were varied from 0.4 mW/cm$^2$ to 8 W/cm$^2$ using standard neutral density filters. The PL signals produced by cw excitation were detected with an Instrumenta SA HR-640 spectrometer, a photomultiplier tube with GaAs(Cs) cathode, and a lock-in amplifier.

Time-resolved PL studies were conducted using the frequency-tripled output (355 nm) from a Q-switched Nd:YAG laser and will be briefly described in this paper. The PL signals produced by pulsed excitation were measured using the HR-640 spectrometer, GaAs PMT, and a digital oscilloscope (Tektronix TDS 684A). The system time decay response, determined by direct measurement of the laser pulse, was 3.5 ns.

All PL spectra shown in this paper have been corrected for the wavelength response of the detection system determined by a calibrated white light source. The reflective losses caused by optical filters, lenses, and dewar windows have been accounted for in determining the incident power densities.

RESULTS AND DISCUSSION

Figure 1 shows the PL spectra obtained at 4.8K under 2 W/cm$^2$ of above-band-gap excitation (325 nm) from a lightly doped ZnSe epilayer (a) and a heavily doped ZnSe epilayer (b). The liquid-helium-temperature bandgap of ZnSe is 2.82 eV. A sharp nitrogen-related acceptor-bound exciton ($A^0, X$) is seen at 2.7889 eV in Fig. 1a. Below this near-edge emission region, a series of sharp bands are observed. The conduction band-to-nitrogen acceptor ($e, A^0$) transition is seen at 2.71 eV and is consistent with a $N_{Se}$ ionization energy of 110 meV. Donor-acceptor pair recombination occurs at 2.694 eV. Several orders of phonon replicas are observed for the ($e, A^0$) and DAP bands. The shallow donor participating in this DAP recombination is most likely Ga or Cl. The “Y” line at 2.60 eV has been associated with extended structural defects, such as dislocation loops.

The PL shown in Fig. 1b is considerably different and is characteristic of heavily doped ZnSe:N. This latter emission consists of an intense broad band located about 0.1 eV lower than the conventional DAP emission. Because the spectrum depicted in Fig. 1b is much more intense, portions of the spectrum in Fig. 1a have been enhanced by the factors indicated in order to facilitate comparison.

Early in our studies, we observed that the line shape of the broad band in heavily doped ZnSe:N (shown in Fig. 1b) depended strongly on excitation wavelength. This effect is illustrated in Fig. 2a obtained using above-band-gap 325 nm excitation and Fig. 2b using below-band-gap 457.9 nm excitation. The high energy component is absent in trace b which indicates that the structure seen in trace a arises from two separate electronic transitions. We label these two distinct bands $N_1$ and $N_2$. The lower energy band $N_1$ is the dominant recombination and its position can be better determined by using the below-band-gap
excitation. Previous investigators\(^{12}\) had suggested that the contribution we label as \(N_I\) was simply a longitudinal optical phonon replica of \(N_{II}\).

Figures 3 and 4 show the power dependence of the \(N_I\) and \(N_{II}\) emission bands when excited with 325 and 458 nm light, respectively. A cursory examination of the data in Fig. 3 might suggest a shift of the composite PL emission to higher energies as the incident power density is increased, and this apparent effect was a supporting factor in the recently proposed\(^{13}\) modified DAP model. However, this apparent shift is much better explained as an increasing relative intensity of the higher energy \(N_{II}\) band. The lower energy \(N_I\) band, which is best seen in Fig. 4, does not appear to shift in energy for changes in power density of more than three orders of magnitude. The peak position of \(N_{II}\) does appear to shift slightly (see Fig. 3) to higher energy with increasing power density, a behavior which would be consistent with conventional DAP recombination.

To determine the actual peak positions and amplitudes for the \(N_I\) and \(N_{II}\) PL bands, we performed a least-squares, sum-of-Gaussians curve-fitting analysis on the data depicted in Fig. 3 and Fig. 4. A representative example of this process is shown in Fig. 5 for the spectrum corresponding to a power density of 2 W/cm\(^2\) and 458 nm excitation (trace c in
Fig. 4). In addition to $N_i$ and $N_{iii}$, we found that a third band is needed to simulate the spectrum. The data are represented by dots and the solid curve is the sum of the three component bands. As discussed later in this paper, the third band is a localized phonon of $N_i$, which we have labeled $N_i-\Gamma_{ph}$. Based on the curve fitting of all the data in Fig. 3 and Fig. 4, we conclude that the $N_i$ peak does not shift (within experimental error of our analysis) as a function of incident excitation power and that the $N_{iii}$ peak does shift from about 2.55 eV (at low power) to nearly 2.61 eV (at the highest cw powers used in our study). Clearly, the dominant PL emission ($N_i$ band) from heavily nitrogen-doped ZnSe does not exhibit conventional DAP behavior. The higher energy $N_{iii}$ band may still be associated with DAP emission.

Figure 6 shows the intensities ($I_{pp}$) obtained from the curve-fitting analysis of the $N_i$ (closed circles) and $N_{iii}$ (open circles) bands as a function of incident power density ($I_p$) for both 325 and 458 nm excitations. The “best-fit” line to a standard power-law equation is shown by the dashed lines. $N_i$ and $N_{iii}$ exhibit different rates of increase in intensity with increasing power. In particular, $N_i$ increases almost linearly (average power-law exponent $\nu = 1.06$) with excitation power, while $N_{iii}$ increases more rapidly (average $\nu = 1.25$).

Figure 7 shows the $N_{iii}$ peak position as a function of luminescence emission intensity obtained from the curve-fitting analysis of the 325 nm data (see Fig. 3). The peak position shifts logarithmically with the emission intensity, $L$. This shift can be described by the standard expression, $L = L_0 \exp(h\nu/E_0)$, where the coefficient $E_0$ describes the level of compensation. The $N_{iii}$ peak shift is described by $E_0 = 5.2$ meV. If the $N_{iii}$ band is DAP recombination, the $E_0$ value suggests some compensation. Uncompensated samples would be described by a smaller $E_0$ value and the peak shift would be negligible.

We have recorded the temperature dependence of the $N_i$ and $N_{iii}$ bands under both 325 and 458 nm excitation. Selected data obtained using 2 W/cm$^2$ of 458 nm light, which provides a clearer study of the $N_i$ band, are shown in Fig. 8. The $N_{iii}$ peak quenches rapidly with increasing sample temperature. The $N_i$ peak position does not appear to change significantly over this range in temperature. At the higher temperatures, two phonon sidebands (spaced equally in energy) of the $N_i$ emission, labeled $N_i-\Gamma_{ph}$ and $N_i-2\Gamma_{ph}$, can be seen more clearly. This increase in phonon coupling with temperature is not consistent with DAP recombination, providing further support that the PL from heavily doped ZnSe:N is more complicated than previously thought. Excitation with 325 nm light of a comparable power density increases the relative amplitude of the $N_{iii}$ peak, however, a quenching with increasing temperature is still observed. Previous investigators had interpreted this temperature behavior as a shifting of the composite peak to lower energies with increasing temperature, thus providing supporting evidence for a modified DAP model. We suggest that the apparent peak shift is actually due to the different temperature dependencies of the

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**Table:**

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<th>Temperature (K)</th>
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<tr>
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<td>90</td>
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**Fig. 8:** Temperature dependence of the PL from heavily doped ZnSe:N from 4.8 to 110K. The spectra have been displaced vertically for clarity and have been expanded by the factors shown on the plot.
separate \( N_1 \) and \( N_{II} \) bands.

The average phonon energy for the localized mode associated with the \( N_1 \) band was found to be 69 meV, significantly larger than that of the bulk ZnSe lattice mode (32 meV). This bound phonon energy appears to correspond with the Zn-N\(_{Se}\) localized vibrational mode at 553 cm\(^{-1}\) (68.6 meV), measured using infrared absorption spectroscopy.\(^{17}\) In Fourier transform infrared spectroscopy studies\(^{16}\) conducted at West Virginia University, the 553 cm\(^{-1}\) localized mode has also been detected from several of our heavily doped ZnSe:N epilayers, including the sample described in this PL study. We suggest that the \( N_1 \) emission is related to an electronic transition localized at or near a Zn–N bond. A possible candidate for the defect is the singly ionized selenium vacancy with a nitrogen next-nearest neighbor (\( V_{Se}^+ - Zn - N_{Se}^- \)). This defect complex is neutral. Its electronic behavior can be modeled after a close-associate pair in which the electronic energy levels of the donor (\( V_{Se}^+ \)) and acceptor (\( N_{Se}^- \)) are considerably altered from the energies associated with the isolated defects and the conventional DAP model no longer applies. Note that the charge state of the selenium vacancy in our model is different than the donor model proposed earlier.\(^5\)

Our recent observation\(^4\) of the \( V_{Se}^+ \) center in ZnSe:N epilayers using electron paramagnetic resonance verifies the existence of the singly ionized charge state of the selenium vacancy in compensated material and is consistent with our defect model described above. Since below-band-gap excitation (2.707 eV) drives the \( N_1 \) transition quite efficiently, we conclude that both the ground and excited states of the complex are within the band gap of ZnSe, although their energy positions with respect to the band edges cannot be determined here. The absence of a peak shift for the \( N_1 \) band under increased incident excitation power density and increased temperature is consistent with a close-associate pair defect model.

We recorded the time dependence of the PL from heavily doped ZnSe:N under pulsed excitation from a Q-switched Nd:YAG laser.\(^{19}\) The \( N_1 \) and \( N_{II} \) bands exhibit different decay times, again illustrating the different electronic nature of these two emissions. The \( N_1 \) band has a longer decay time. Using 128 \( \mu \)W/cm\(^2\) average power pulse excitation, a third band with a lifetime shorter than the system resolution of 3.5 ns was observed at 2.65 eV. We label this third PL band \( N_{III} \). The energy difference between \( N_{II} \) and \( N_{III} \) is about 50 meV. Further, the short lifetime suggests \( N_{III} \) involves either band-to-band, band-to-impurity, or excitonic transitions. Excitonic transitions are unlikely at this high doping level (>\( 10^{19} \) cm\(^{-3}\)). We suggest that the \( N_{III} \) band is (\( e, A_0^\circ \)) recombination related to the isolated substitutional nitrogen acceptor. The energy difference between \( N_{II} \) and \( N_{III} \) is consistent with the deep donor ionization energy found in heavily doped samples. Thus, \( N_{II} \) is the only component which appears to be related to the deep donor observed by others.

**SUMMARY**

The PL from heavily doped ZnSe:N epilayers is composed of two distinct bands \( N_1 \) and \( N_{II} \). The emission peak of \( N_1 \) is insensitive to incident power or temperature over the ranges studied. A 69 meV localized phonon of \( N_1 \) is observed. We propose that the dominant PL band \( N_1 \) is recombination related to a \( V_{Se}^+ - Zn - N_{Se}^- \) close-associate pair. The \( N_{II} \) band displays characteristics which do not allow us to rule out the conventional DAP model related to a 50 meV deep donor and nitrogen acceptor. A third band \( N_{III} \) observed under high-power pulsed excitation, is consistent with (\( e, A_0^\circ \)) recombination where the acceptor is most likely \( N_{Se}^- \). Previous studies of ZnSe:N had not been able to select between candidate donor models. Our PL study provides strong evidence that singly ionized selenium vacancy complexes form in heavily doped ZnSe:N and play a dominant role in compensation.

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