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Influence of compensation on the luminescence of nitrogen-doped ZnSe epilayers grown by MOVPE

R. Heitz [a,*], E. Moll [a], V. Kutzer [a], D. Wiesmann [a], B. Lummer [a], A. Hoffmann [a], I. Broser [a], P. Bäume [b], W. Taudt [c], J. Söllner [c], M. Heuken [c]

[a] *Institut für Festkörperphysik, TU Berlin, Hardenbergstrasse 36, D-14197 Berlin, Germany*
[b] *Institut für Festkörperphysik, Universität Bremen, P.O. Box 330440, D-28334 Bremen, Germany*
[c] *Institut für Halbleitertechnik, RWTH Aachen, Templergraben 55, D-52056 Aachen, Germany*

Abstract

The luminescence of ZnSe grown by metalorganic vapour phase epitaxy and doped by a DC nitrogen plasma is investigated. With increasing N_2 flux the donor–acceptor pair (DAP) band continuously develops into a structureless band peaking at 2.62 eV for highest doping levels. This broad band evolves back into a structured DAP band peaking at 2.698 eV with increasing excitation density. At high N concentrations and at large degree of compensation potential fluctuations become important for the spatially indirect DAP recombination. These fluctuations can easily be screened by optically excited carriers making the experimental conditions decisive for luminescence spectra of strongly doped ZnSe:N samples.

1. Introduction

The growth of p-conducting ZnSe epilayers by metalorganic vapour phase epitaxy (MOVPE) is still an unresolved problem, although recently promising results have been published [1–3]. MOVPE-grown ZnSe:N layers are in general high-resistive leaving photoluminescence as main characterization method [4–6]. In addition to the appearance of the nitrogen acceptor bound exciton emission N doping alters the relative intensity and shape of the donor–acceptor pair (DAP) band. A second DAP band peaking at lower energies appears at higher doping levels and has been attributed to the formation of a deep donor complex consisting out of N and intrinsic defects [7]. For N concentrations above some 10^{18} cm^{-3} the DAP band becomes broad and structureless and experiences a strong red-shift [4–6]. The development of impurity bands has been proposed to explain this behavior, but time-resolved measurements revealed the typical DAP recombination [4]. Recently, a strong influence of excitation density on this band has been reported for MOVPE-grown ZnSe:N [8] and very recently potential fluctuations in compensated material have been proposed to explain the characteristic doping-induced DAP behavior [9].

In this contribution, we report on photoluminescence (PL) and PL excitation (PLE) measurements of MOVPE-grown ZnSe epilayers strongly doped with N. Our results are discussed with respect to the compensated nature of the samples and optical neutralization of charged impurities.

* Corresponding author. Fax: +49 30 314 22064; E-mail: heitz@w422zrz.physik.tu-berlin.de.

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2. Experimental procedure

The epilayers are grown at 330°C with a total reactor pressure of 20 mbar and a VI/II ratio of 0.18 using ditertiarybutylselenide and dimethylzinc triethylamine as Se and Zn sources, respectively [2,3]. N doping by DC plasma-activated N_2 allows to vary the N concentration via the N_2 flux. PL is excited by the UV lines of a HeCd or a Ar^+ laser. PLE spectra are recorded using a tungsten lamp/double grating monochromator combination as tunable light source.

3. Experimental results

Fig. 1 gives a selection of typical PL spectra of N-doped ZnSe epilayers in dependence of the N_2 flux during MOVPE growth recorded at excitation densities of 30 mW cm^{-2}. These spectra evidence a characteristic and continuous development of the spectral shape with increasing N_2 flux (only part of the samples are shown). At low N_2 fluxes a neutral N acceptor bound exciton (I_1^N) emission appears

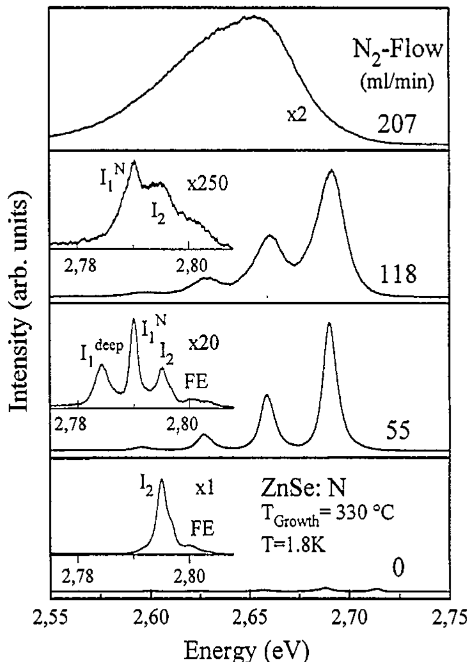

Fig. 1. Low excitation density PL spectra of MOVPE ZnSe:N grown at different N_2 fluxes.

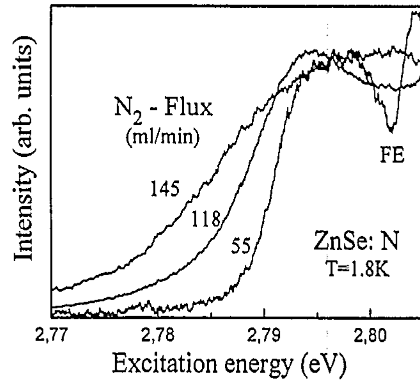

Fig. 2. Low excitation density PLE spectra of the DAP band in MOVPE ZnSe:N grown at different N_2 fluxes.

indicating the incorporation of isolated N on Se sites acting as shallow acceptor. Additionally, a typical DAP luminescence peaking at 2.690 eV appears. With increasing N_2 flux the intensity of excitonic recombination drops due to the increasing number of defects. At highest doping concentrations the DAP band becomes first broader and than structureless and red-shifted up to 80 meV.

For MBE-grown samples [3–5] a similar characteristic development of the PL spectra as shown in Fig. 1 is known to be related to the net acceptor concentration $N_A - N_D$ and the N concentration. At first $N_A - N_D$ follows the chemical N concentration reaching its maximum slightly above 10^{18} cm^{-3}. For N concentrations above 10^{19} cm^{-3} $N_A - N_D$ rapidly decreases [10]. The broad red-shifted band appears if $N_A - N_D$ is saturated and starts to decrease. It is noteworthy that N-doped MOVPE-grown and MBE-grown ZnSe epilayers show the same qualitative behavior, taking into account that all our MOVPE samples are highly resistive. Obviously the N concentration is closely related to the N_2 flux during growth.

The alteration of the PL behavior is matched by a simultaneous change in the excitation spectra of the DAP band. Fig. 2 compares excitation spectra of the DAP band for samples grown at various N_2 fluxes. The spectra show a structureless rise in excitation efficiency just below the excitonic region corresponding to the optical neutralization of donors. With increasing N_2 flux the low energy onset of this band shifts towards lower energies.

Fig. 3a depicts PL spectra of a highly doped ZnSe epilayer (207 ml/min) for excitation densities varying over seven orders of magnitude. With increasing excitation density the structureless and red-shifted DAP band experiences a blue-shift developing resolved LO replica with the ZPL at 2.698 eV. The blue-shift depends logarithmically on the excitation density, and the integrated DAP intensity increases linearly with the excitation density (Fig. 3b). Only above 2 W cm^{-2} the DAP intensity saturates showing the structured shape. Fig. 4 compares low and high excitation density spectra of the 145 ml/min sample. It shows in principle the same behavior, however, above 250 mW cm^{-2} exciton recombination (I_2, I_1^N and I_1^{deep}) appears indicating saturation of defect states. With increasing N_2 flux the excitation density necessary to restore the typical DAP band increases and the lines become broader.

Time-delayed luminescence spectra of the 145 ml/min sample under high excitation conditions strongly support the excitation density dependent measurements. Immediately after excitation normal structured DAP appears which within a few microsecond develops into the broad red-shifted band observed at low excitation densities. Using low excitation densities the DAP recombination is found to be unusually slow taking into account the actual doping level.

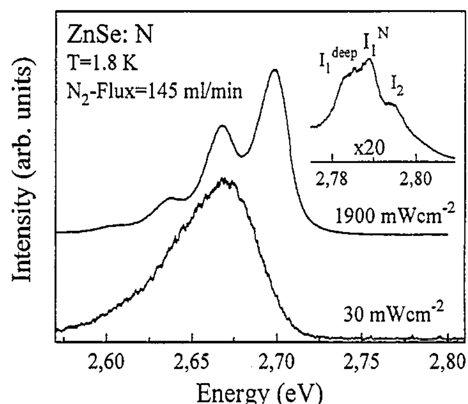

Fig. 4. PL spectra of a 145 ml/min ZnSe:N epilayer at different excitation densities.

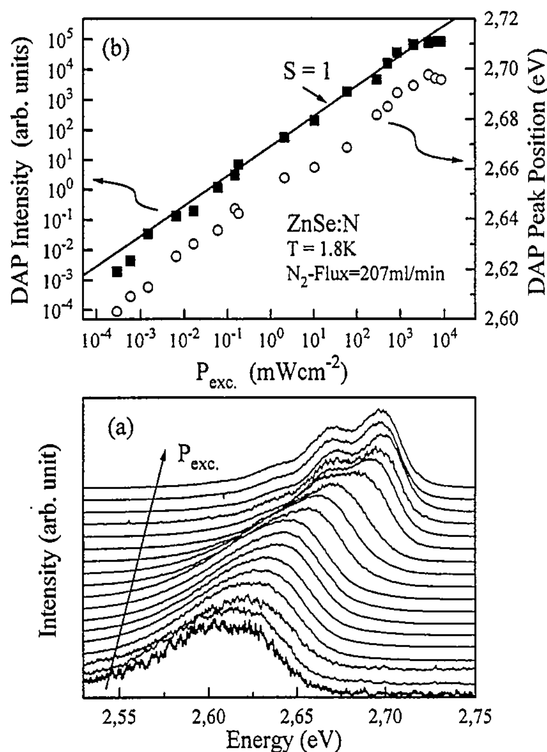

Fig. 3. (a) PL spectra of a 207 ml/min ZnSe:N epilayer for different excitation densities. (b) DAP peak position and integrated intensity as function of excitation density.

4. Discussion

The continuous development of the spectral shape with increasing N concentration as well as the continuous restoring effect of high excitation densities observed for the DAP band in highly N-doped ZnSe epilayers indicate severe changes in the samples. In principle, the formation of a more or less continuous spectrum of deep defects due to lattice imperfections at higher N concentrations might be an explanation. However, our results show that both high N concentrations *and* strong compensation are necessary preconditions to obtain the broad red-shifted DAP band.

In highly compensated samples most (all for semi-insulating samples) shallow impurities are ionized leading to strong electric fields. The random distribution of the impurities leads to long range potential fluctuations whose amplitude and characteristic length depend on the concentration of charged defects. The theory of potential fluctuations in compensated semiconductors has been developed by

Shklovskii and Efros [11] and successfully applied to explain the behavior of the DAP band in strongly doped GaAs [12] which is analogous to that observed for ZnSe:N.

The long range potential fluctuations lead to a reduction and smearing out of the energy of spatially indirect DAP transitions. Thus, with increasing doping concentration *and* compensation level, i.e. with increasing amplitude of the potential fluctuations, the DAP band becomes broader and shifts towards lower energies. Additionally, the "artificial" separation of neutralized donors and acceptors slows down the DAP recombination. This model is supported by the excitation spectra, Fig. 2. With increasing N concentration the onset of the excitation shifts towards lower energies which might be attributed to the increasing contribution of spatially indirect absorption in conjunction with the increasing band bending.

It is clear that the excitation density has a pronounced influence on the spectral shape of the DAP band. At lowest excitation densities donors in the potential minima of the conduction band and acceptors in maxima of the valence band will be preferably populated leading to a maximum red-shift. At slightly higher excitation densities the probability to populate defects outside the immediate minima and maxima increases leading to a blue-shift of the broad DAP band. At highest excitation densities the photogenerated carrier concentration is sufficient to screen the electric fields restoring the flat band situation. The normal structured DAP band with its ZPL at 2.698 eV reappears (Figs. 3 and 4).

Similar results have been found for MBE-grown ZnSe:N layers [9]. The close resemblance between the optical spectra of MBE- and MOVPE-grown ZnSe:N epilayers indicates that the development of defects is in principle the same in both growth processes. However, we like to stress that the broad red-shifted band depends on both N concentration *and* the degree of compensation giving no direct access to the nature of the compensating defect. It is not possible to discern between the various proposed deep donors having binding energies between 35 and 55 meV [5–7]. Transitions involving shallow donors have a higher probability than those involving deep ones and, thus, dominate the spectra at high excitation densities. In fact our MOVPE-grown samples have a high Cl concentration acting as shallow donors [2,3]. Thus, the formation of the red-shifted DAP band occurs at lower N concentrations than in MBE-grown layers.

5. Conclusions

Our luminescence investigations show characteristic changes in the exciton spectrum and of the DAP band with increasing N_2 flux during MOVPE growth proving an increasing N acceptor concentration. The broadening and red-shift of the DAP band at highest N concentrations is related to potential fluctuations arising from the statistical distribution of compensated defects giving rise to a strong influence of the excitation density due to optical neutralization of defects. Thus, the characteristic red-shift of the DAP band is an indicator for strong compensation in the samples connected with the enhanced generation of donors for high N concentrations but does not depend critically on the type of donor. The analysis of luminescence spectra of ZnSe:N has to take into account the effect of band bending, especially, since HeCd laser excitation is often sufficient to alter the spectral shape considerably.

Acknowledgements

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