22nd International Conference on

THE PHYSICS OF SEMICONDUCTORS

Volume 1

Vancouver, Canada

August 15 – 19, 1994

Editor

DAVID J. LOCKWOOD
National Research Council of Canada
Institute for Microstructural Sciences
Ottawa, Canada

World Scientific
Singapore • New Jersey • London • Hong Kong

QUANTITATIVE DETERMINATION OF THE COMPENSATION IN NITROGEN DOPED ZnSe EPILAYERS

A. HOFFMANN, R. HEITZ. B. LUMMER, V. KUTZER, L. ECKEY AND I. BROSER
Institut für Festkörperphysik der TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
and
E. KURTZ, D. HOMMEL, B. JOBST, J. NÜRNBERGER, G. LANDWEHR
Physikalisches Institut der Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

ABSTRACT

The compensation processes in nitrogen doped ZnSe/GaAs heterostructures grown by molecular beam epitaxy (MBE) are investigated. By means of linear transmission spectroscopy the degree of compensation could be determined to be above 60% for samples with N_A-N_D of some 10^{16} cm^{-3}. Deep impurities are mainly responsible for the compensation of p-type N doped ZnSe. Four-wave-mixing experiments yield information about the fine structure of the nitrogen acceptor. The determined coherence time T_2 of the exciton bound to the neutral nitrogen acceptor suggests impurity interactions to govern the dephasing.

1. Introduction

Recently, the possibility to grow p-type ZnSe using nitrogen doping has led to the successful fabrication of blue laser diodes[1]. However, electrical and optical measurements performed on N-doped ZnSe grown by molecular beam epitaxy (MBE) indicate that an increased N-incorporation tends to compensate the p-doping. The hole concentration has its maximum around $10^{18}cm^{-3}$ and decreases at higher N-concentrations[2]. The nature of the compensating defects[3,4] is not fully understood yet. A basic problem is the evaluation of the N concentration as well as of the degree of compensation. Among the optical methods luminescence spectroscopy is commonly employed to characterize ZnSe epilayers, but the luminescence intensity gives no quantitative access to defect concentrations.

In this contribution a simple but powerful method to determine quantitatively the compensation processes in N-doped ZnSe is introduced. The basic idea is that the near

band gap transmission spectrum of ZnSe epilayers depends critically on the charge state of donors and acceptors. Furtheron, four-wave-mixing experiments are presented to yield information about the fine structure of the N-acceptor bound exciton in p-doped ZnSe.

2. Experimental Results and Discussion

Typical luminescence spectra of n-type and weakly p-type samples exhibit bound exciton (BE) and donor-acceptor-pair (DAP) luminescence (fig. 1). From their photon energies the BE emissions are attributed to the decay of excitons bound to a Cl donor (I_2) and to a N acceptor (I_1^N). The energy position of the DAP luminescence around 2.70 eV is consistent with a N acceptor level between 100meV and 110meV. With higher N concentrations N_A-N_D increases ($\geq 1 \times 10^{17}$ cm^{-3}). Instead of BE and DAP luminescences a new broad band appears around 2.63eV. Time-resolved photoluminescence (PL) measurements prove the DAP character of this band. From excitation spectroscopy of the deep DAP luminescence we estimate a N-associated donor level at 53meV (not shown). The acceptor concentrations, determined by means of time-resolved PL of the DAP are in reasonable agreement with N_A-N_D values from CV profiling measurements given in fig. 1. A further increase of the N-concentration results in a blue shift of this broad band, but the shift does not cross the fundamental bandgap. In a similar way, n-type ZnSe epilayers with Cl concentrations of 10^{19} cm^{-3} (lowest spectrum) and higher emit a broad asymmetric luminescence band around the band energy. For the highest Cl concentration the luminescence band is 30meV above the fundamental band gap of undoped ZnSe which is known from semiconductors above the Mott density, such as CdS: In.[5] This effect is explained by a screening of shallow impurities leading to a renormalization of the band gap. We do not observe this behaviour for p-type ZnSe samples and attribute this to compensation effects.

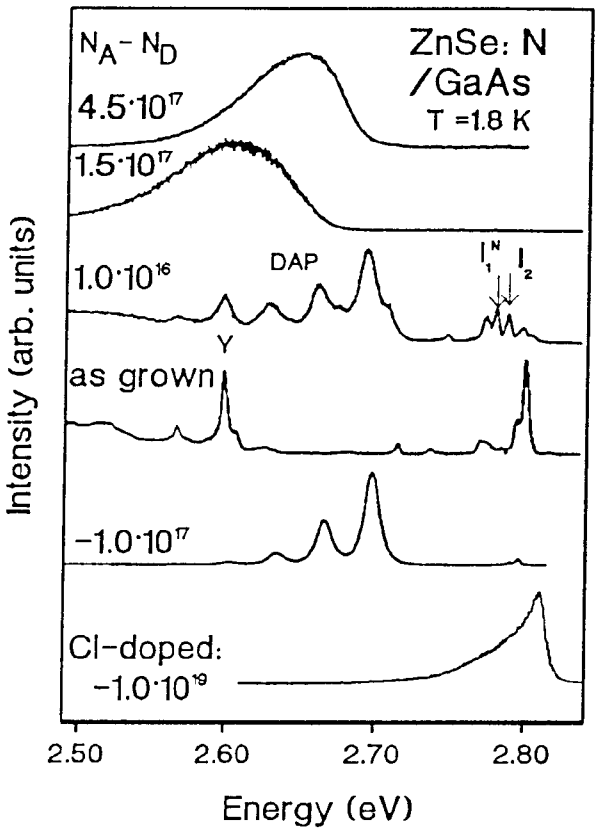

Fig. 1: Luminescence spectra of various ZnSe epilayers near the bandgap

To get a quantitative access to the compensation we use linear absorption spectroscopy. The near band gap absorption depends critically on the concentration as well as on the charge state of shallow defects. In particular, the concentration of neutral shallow impurities can be measured directly from the corresponding I_1 and I_2 bound exciton transmission lines. Using monochromatic light to measure the absorption the "unexcited" epilayer is probed giving the number of uncompensated defects. When

exciting the sample with the total spectrum of a halogen lamp the ionized donors and acceptors are recharged by the highly intense polychromatic light and the total concentration of donors and acceptors is determined from the transmission spectrum. In monochromatic absorption experiments of a ZnSe:N epilayer glued on glass (fig. 2) beside the free A-exciton only the exciton bound to the neutral N-acceptor (I_1^N line) is observed. Using polychromatic excitation the free A-exciton absorption diminishes due to less interactions with charged shallow defects.[6] The I_1^N absorption increases and the I_2 donor bound exciton line appears due to the neutralisation of compensated shallow defects. Employing different excitation densities it is shown that practically all compensated shallow defects are recharged. Using $N_A - N_D = 3x10^{16}$ cm^{-3} derived from CV profiling measurement N_A could be determined in this sample to 1x 10^{17} cm^{-3} by comparison of the absorption coefficients. This result demonstrates a considerable amount of >60% compensated acceptors. The compensating $7x10^{16}$ cm^{-3} donors should establish a more pronounced I_2 -absorption line because of their at least~3 times greater oscillator strength compared to I_1^N. [7] Therefore, we conclude that mainly deep donors contribute to the compensation. We generally observe compensation above 60% and small I_2 - absorption in other epilayers with N-concentrations below 10^{17} cm^{-3} indicating a general effect.

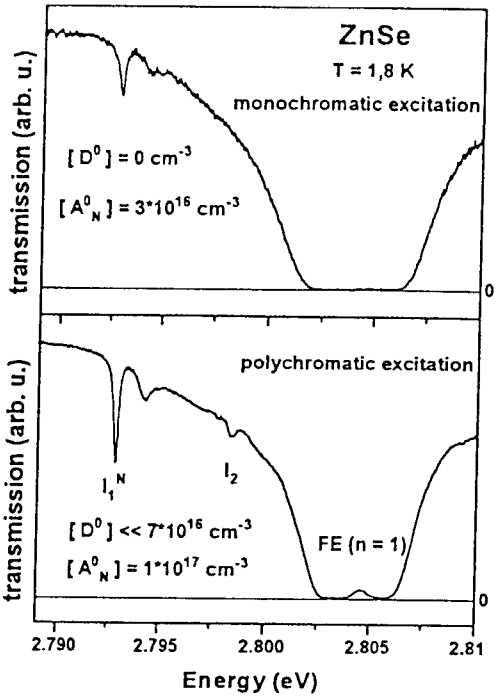

Fig. 2: Mono- and polychromatic transmission spectra of a ZnSe:N epilayer glued on glass

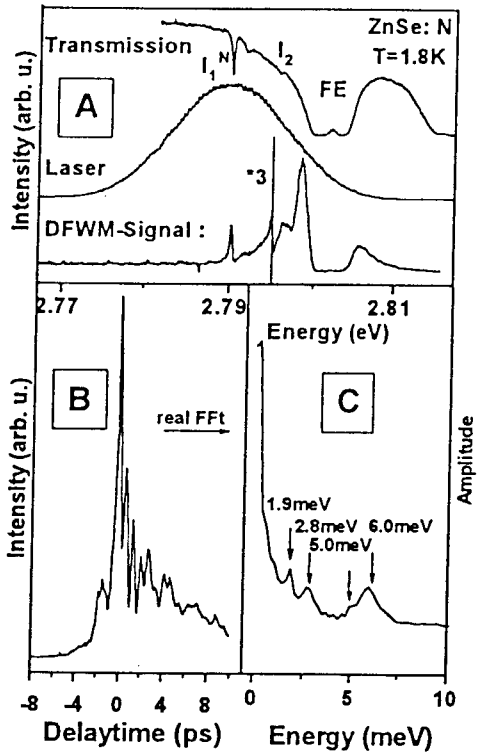

Fig. 3: DFWM signals of a ZnSe:N epilayer for explanation see text

To elucidate the problem of oscillator strength's more quantitatively, we performed time-resolved photoluminescence experiments, where we found an increase in lifetime for the bound excitons when we extend the investigation from ZnSe:N/GaAs epilayers to ZnSe: N glued onto glass. This indicates the existence of competing strain induced nonradiative relaxation channels that determine the lifetime of the transition. It is interesting that this also affects the coherent dynamics of the bound exciton absorption. Fig.3A gives degenerate-four-wave-mixing (DFWM) spectra for a N-doped ZnSe-

epilayer excited by broadband fs-pulses. The upper part compares spectrally resolved the linear transmission, the laser spectrum and the DFWM signal at zero delay. The transmission exhibits the absorption of free excitons (FE) as well as of excitons bound to neutral nitrogen acceptors (I_1^N) and to neutral donors (I_2.) Since the ZnSe epilayer is fixed on a glass substrate the thermal stress leads to a splitting of the different exciton lines. The DFWM signal is recorded spectrally resolved on the I_1^N transition in dependence on pulse delay. It shows a typical quantum beat structure (fig. 3B) [8]. The energy separation of the interfering states is determined by a Fourier transformation (fig. 3C). This enables us to get information about the fine structure splitting of the nitrogen acceptor and about the dephasing times of states which are involved in the interference processes. For example, we attribute the peak at 1.9 meV in the beat spectrum to a beating between strain split lh- and hh- components of the I_1^N. With resonant picosecond excitation we observe a T_2-time of about 80ps for the I_1^N. This value is drastically shorter than expected from energy relaxation time T_1 = 600 ps measured by time-resolved photoluminescence at the I_1^N-line. In regard of the high total impurity concentration in these samples, we suggest impurity interactions to be resposible for the reduced dephasing time at the I_1^N. Further analysis of the DFWM-results at ZnSe: N epilayer will be given in a forthcoming paper.

3. Conclusion

The analysis of transmission spectra of nitrogen doped ZnSe epilayers under different excitation conditions yields an reliable access to impurity concentration and compensation. In the net acceptor concentration range between 10^{15} - 10^{17} cm^{-3} , we could demonstrate that the ratio between compensated and uncompensated nitrogen acceptors amounts 2:1. Mainly, deep defects are responsible for the compensation. DFWM experiments in the fs-range yield as result the fine structure of the exciton complex formed at the to neutral nitrogen acceptors and give additionally information about the dephasing mechanism.

4. References

1. J. Qiu, J.M. DePuydt, H. Cheng, and M. A. Haase, Appl. Phys. Lett. 59 (1991), 2992
2. Z. Yang, K.A: Bowers, J. Ren , Y. Lansari, J.W. Cook, J.F. Schetzina, Appl. Phys. Lett. 61 (1992), 2671
3. I.S.Hauksen, J. Simpson, S.Y. Wang, K.A. Prior, and B.C. Cavenett Appl. Phys. Lett. 61 (1992), 2208
4. D.J. Chadi and K.J. Chang, Appl.Phys. Lett. 55 (1989), 575
5. Ch. Fricke, R. Heitz, A. Hoffmann, and I. Broser, Phys. Rev. B 49 (1994), 5313
6. K.-H. Pantke, H. Over, and I. Broser, phys. stat. sol. 159 (1990), 437
7. E.I. Rashba and G.E. Gurgenishvili, Sov. Phys.-Solid State 4 (1962), 759
8. K.-H. Pantke and J.M. Hvam, Int. J. Mod. Phys. B 7 (1993)