Materials Science Forum Vols. 182-184 (1995) pp. 259-262

ABSORPTION AS OPTICAL ACCESS TO ACCEPTOR CONCENTRATIONS AND COMPENSATION MECHANISMS IN ZnSe EPILAYERS

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Keywords: ZnSe, MBE, N-Doping, Compensation

The optical properties of N-doped ZnSe epilayers grown by molecular-beam epitaxy are investigated. Photoluminescence, photoluminescence excitation and absorption results of lifted ZnSe:N glued to quartzglass show the heavy-light hole splitting of the I_1^N and efficient energy transfer processes between I_2 and I_1^N complexes. We demonstrate the possibility to obtain information on the conduction type and the degree of compensation from absorption measurements. For samples with N_A-N_D up to some 10^{16} cm^{-3} compensation around 60% is found. The results indicate the formation of a deep N-related donor in the low doping region.

I. INTRODUCTION

ZnSe-based heterostructures have opened up the prospect of laser diodes working in the blue/green spectral region [1]. MBE growth using free-radical plasma or ECR sources enables net acceptor concentrations (N_A-N_D) up to 2×10^{18} cm^{-3} [2 ,3]. The net acceptor concentration increases linearly with the N concentration, but starts to decrease for N concentrations above some 10^{18} cm^{-3}, which is attributed to the formation of a deep N-related donor. A binding energy of 44 meV is deduced from the DAP luminescence energy [4], whereas the analysis of the temperature dependence of the near band gap luminescence yields 55 meV [5].

The role of selfcompensation in ZnSe:N in the low doping region is not clear, yet. Though net acceptor concentration are routinely determined by capacity measurements, the determination of chemical N concentrations is hampered by the insufficient sensitivity of SIMS measurements. Additionally, SIMS gives only an upper limit for the acceptor concentration N_A and, thus, allows no direct access to the degree of compensation. Recently, methods to deduce the net acceptor concentration from the saturation intensity of the DAP luminescence [6] or from the dynamics of the DAP recombination [7] have been investigated. However, the obtained figures need careful discussion.

Here, we propose an optical method to determine the degree of compensation in thin ZnSe:N epilayers. The optical characterization of ZnSe epilayers is mostly restricted to luminescence measurements due to the GaAs substrate. We extend the characterization to absorption measurements of epilayers lifted from the GaAs substrate. The absorption coefficient is directly proportional to the defect concentration and, additionally, the near band gap absorption depends critically on the charge state of shallow impurities. Thus, absorption allows to monitor recharging of compensated donors and acceptors upon secondary optical excitation. From the absorption results the degree of compensation in either n- or p-conducting samples can be determined.

II. EXPERIMENTAL

The ZnSe epilayers investigated are grown at temperatures between 200 and 300°C using MBE techniques. N doping is performed using a plasma nitrogen source in the low brightness mode giving net acceptor concentrations N_A-N_D up to 3×10^{16}cm^{-3} derived from CV profiling. The as grown ZnSe epilayers with thickness between 0.4 and 3.8μm are glued upside down onto a quartzglass substrate. Subsequently, the GaAs substrate is removed by selective wet chemical etching [8]. Monochromatic absorption measurements are performed dispersing the spectrum of a halogen lamp with a 0.75m double grating monochromator before exciting the sample. For secondary excitation either the sample is placed directly behind the lamp (polychromatic absorption) or an additional high pressure mercury lamp is used. The samples are immersed in superfluid He.

III. EXPERIMENTAL RESULTS

Typical luminescence spectra of nitrogen doped ZnSe epilayers are given in Ref. 9 and 10. Undoped samples show neither DAP nor acceptor bound exciton (A^0,X) (I_1) recombination. For N-doped samples we observe both emissions regardless of the net acceptor concentration. At high doping levels only a broad band in the DAP region is observed and attributed to strong selfcompensation. Results of excitation and time-dependent photoluminescence measurements prove the DAP character of this band indicating the formation of deep donors. However, the luminescence experiments give no direct insight into the degree of compensation in these samples.

To extend the optical characterization we investigated the absorption of ZnSe:N epilayers lifted from the GaAs substrate. Fig.1 shows optical spectra of a 960nm thick sample with N_A-N_D of $3x10^{16}cm^{-3}$ grown at 200°C. Comparing the luminescence of the same sample before and after the lift-off process (bottom part of fig.1) characteristic changes can be stated. The emissions shift towards higher energies and the full width at half the maximum (FWHM) decreases due to the relaxation of strain and the strain gradient in the lifted epilayer which is still glued to quartzglass, respectively. The luminescence peak ? on the low energy tail of the I_1^N vanishes and the I_1^D becomes weaker in the lifted layer. The etch process removes not only the substrate but also the strongly distorted near interface layer. This indicates that both luminescence centers are connected with lattice defects or distortions. Additionally, the relative intensity of the free exciton emission increases in the lifted epilayer indicating a longer lifetime of free carriers and excitons. Recently, time-resolved luminescence measurements proved diffusion across the ZnSe/GaAs interface to be an important recombination channel in thin epilayers [11]. Additionally, removing the interface layer the concentration of recombination centers is diminished.

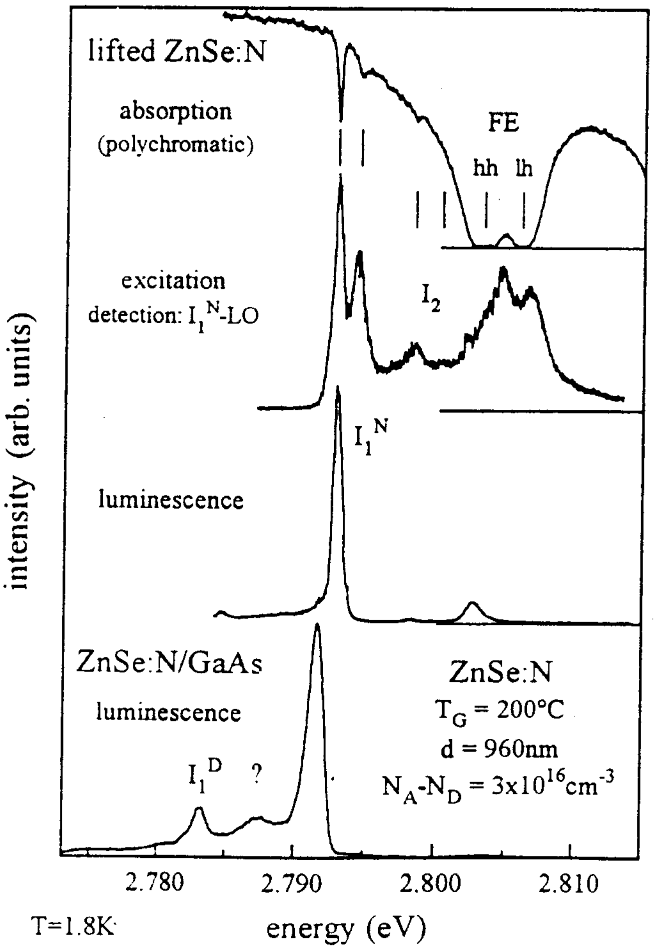

Fig. 1: Optical spectra of a lifted ZnSe:N epilayer glued to quartzglass compared to the luminescence of the ZnSe:N/GaAs heterostructure.

In absorption, besides the free exciton a weak neutral donor bound exciton (I_2) and a strong I_1^N absorption are observed. For the I_1^N we found FWHM's down to 250µeV. The compressive strain caused by the quartzglass results in a splitting of the excitonic states clearly resolved in absorption. The splitting of the (A^0,X) and the (D^0,X) complex is found to be smaller than that of the heavy-light hole splitting of the free exciton. However, decreasing splittings caused by strain relaxation after some cooling cycles prove their heavy-light hole origin. Luminescence excitation spectra recorded on the first LO phonon replica of the I_1^N emission show the same structures. It is obvious that the I_1^N is efficiently excited via the free exciton absorption. However, the occurrence of the I_2 resonance in the excitation spectrum indicates efficient energy transfer processes, which are probably the reason for the weak I_2 emission. Energy transfer processes from donor to acceptor bound exciton complexes [12] are favored by the comparatively high acceptor concentration in our ZnSe:N epilayers.

The excitonic absorption of ZnSe:N epilayers shows remarkable differences depending on the experimental conditions, fig. 2. Monochromatic absorption (full lines) reveals strong free exciton absorption as well as either the I_2 in a n-type sample (a) or the I_1^N in p-type samples (b, c). Varying the excitation density by a factor 10 does not change these spectra, proving that the monochromatic excitation causes no detectable distortions of the equilibrium population of impurity states. In polychromatic absorption (dotted lines) reduced free exciton absorption but increased bound exciton absorption is observed. The additional broad band excitation recharges compensated defects increasing the concentration of neutral shallow defects. By varying the excitation density or using a second UV-excitation source it is proven that the recharging effects are practically saturated under the used experimental conditions. A decreased concentration of ionized shallow defects corresponds to a reduced scattering probability for free excitons [13]. Therefore, the observed decrease in free exciton absorption confirms the recharging of the major part of compensated defects. Depending on the conductivity type monochromatic absorption exhibits *either* a weak I_2 *or* a weak I_1^N corresponding to uncompensated shallow defect concentration. On the contrary, polychromatic absorption shows *both* the I_2 *and* I_1^N corresponding to the increased concentration of neutral shallow defects, which practically equal the total concentration of the shallow defects under our experimental conditions.

IV. DISCUSSION

The absorption coefficient α of an impurity transition is proportional to the impurity concentration N [14]

$$\int \alpha(\nu)\,d\nu = \frac{\lambda^2}{8\pi}\frac{g_{ex}}{g_{gr}}\frac{N}{\tau}, \qquad (1)$$

with λ the transition wavelength, g_i the degeneration and τ the lifetime.

The near band gap absorption in a ZnSe epilayer depends critically on the concentration of shallow impurities as well as their charge state. The prominent I_1 and I_2 absorptions are attributed to the formation of bound exciton complexes at neutral shallow acceptors and donors, respectively [15]. Therefore, the integrated absorption coefficient is a measure of the concentration of neutral acceptors and donors, respectively. Consequently, the comparison of the I_1^N and I_2 absorption coefficient under monochromatic and polychromatic excitation yields the conductivity type of the layer as well as the degree of compensation $(N-N^0)/N$ giving the part of compensated acceptors and donors in p- and n-type layers, respectively.

For the two p-conductive samples investigated we obtain (60±5)% (960nm) and (65±5)% (3800nm) compensation of

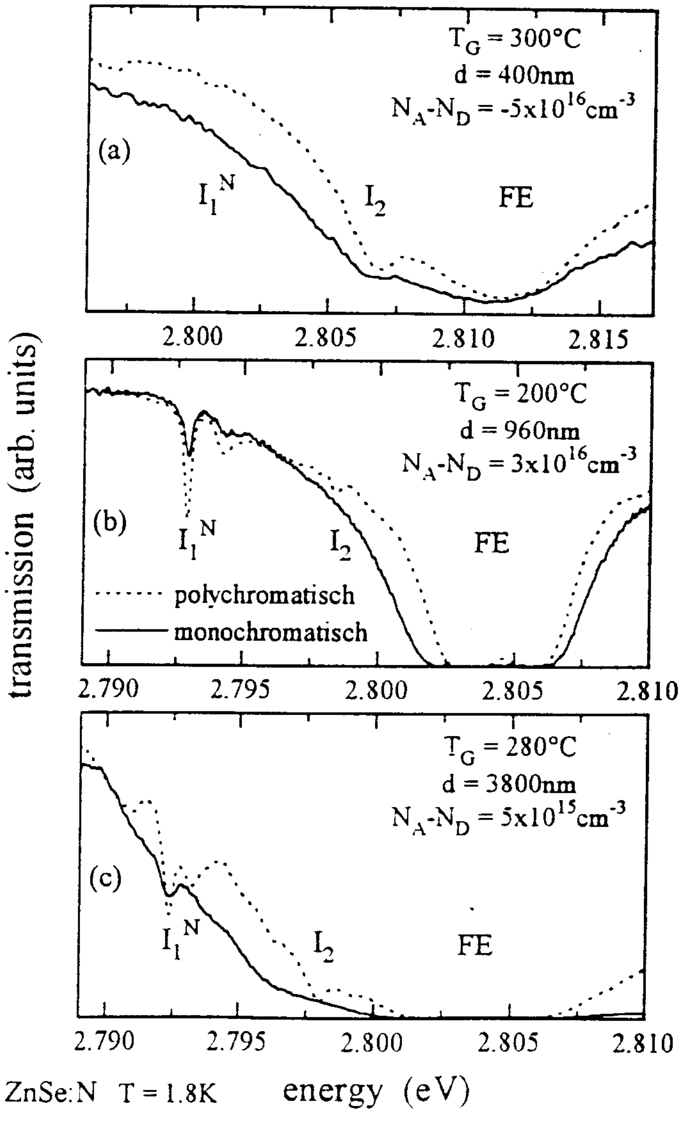

Fig. 2: Monochromatic and polychromatic recorded absorption spectra of three different lifted ZnSe:N epilayers glued to quartzglass.

the N acceptors. Using the net acceptor concentration N_A-N_D determined by CV profiling these figures correspond to total N acceptor concentrations of $8x10^{16}cm^{-3}$ and $1.4x10^{16}cm^{-3}$ in these epilayers, respectively. Obviously, N doping gives about 40 % uncompensated acceptors in the low doping region. The integrated absorption coefficient of the I_2 observed in polychromatic absorption allows to estimate the shallow donor concentration too. From the recombination dynamics of bound excitons in bulk ZnSe [16] it is known that the lifetime of the I_1 is about 10 times that of the I_2. Using equation (1) and comparing the I_1^N and the I_2 absorption coefficients we estimate the shallow donor concentration to $1.5x10^{15}cm^{-3}$ for both samples. This concentration is much to low to account for the observed compensation, but can explain the slightly higher compensation in the sample having the lower net acceptor concentration (3800nm). Thus, the compensation in the low doping regime is due to deep donors obviously generated by N-doping, probably the same known from the high doping regime [4,5].

Analyzing the data of the thin n-type layer grown under almost the same conditions like the p-type ones we obtain (50±5)% compensation corresponding to a shallow donor concentration of $1.0x10^{17}cm^{-3}$. From the I_1^N absorption we can estimate a N acceptor concentration of $4x10^{16}cm^{-3}$ explaining the compensation. The high shallow donor concentration is probably due to a Cl contamination of the reactor.

IV. CONCLUSION

In the present paper we emphasized the potential of absorption measurements on lifted ZnSe:N epilayers for the evaluation of compensation processes connected with N doping. For ZnSe:N epilayers a compensation of 60 % is found in the low doping regime caused by a deep N-related donor, which is tentatively identified with the deep donor causing devastating compensation at high N concentrations.

In principle the proposed absorption method allows to discriminate between semiinsulating, p- and n-conductive epilayers and allows to trace the origin of compensation. However, the method is restricted to the low doping region, since otherwise no bound exciton resonances can be resolved.

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