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Incorporation of nitrogen in ZnSe grown by metalorganic vapour phase epitaxy

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Abstract

The incorporation processes and efficiencies of nitrogen doping for p-type conductivity in metalorganic vapour phase epitaxy (MOVPE) grown ZnSe/GaAs epilayers are investigated by means of time-integrated and time-resolved photoluminescence (PL) spectroscopy. Two nitrogen-doping methods are compared, plasma-enhanced doping during growth, and ion implantation of nitrogen with annealing after growth. Both types of doped layers exhibit the I_1^N transition from a neutral acceptor bound exciton complex (A_1^0, X), indicating an effective nitrogen embedding on selenium sites. With increasing nitrogen doping rates, a deeper bound exciton line I_1^C appears, lowering the intensity of the I_1^N . An observed reduction of the I_1^N and I_1^C lifetimes for higher nitrogen doping concentrations results from an enhanced overlap of the bound exciton wave functions with those of other impurity centres.

1. Introduction

The fabrication of p-conductive MOVPE ZnSe layers with high reproducibility would open up the exciting prospect of a variety of interesting applications. Low-resistive p-type material with high concentrations of free carriers has to date only been obtained in nitrogen-doped ZnSe grown by molecular beam epitaxy (MBE). Nitrogen concentrations of up to $1 \times 10^{19} \text{ cm}^{-3}$ and free hole concentrations of up to $7.7 \times 10^{17} \text{ cm}^{-3}$ have been reported [1]. The low-temperature photoluminescence spectra of such layers are dominated

by donor–acceptor pair (DAP) recombination with photon energies between 2.623 and 2.695 eV, depending on the growth conditions [2] and the nitrogen concentration [1]. In contrast, material grown by MOVPE suffers from a low activation of the incorporated nitrogen resulting in highly resistive layers as yet. The low activation of the incorporated nitrogen is due to self-compensation mechanisms which are controversially discussed in the literature [2–4]. In the present work we investigate the time-integrated and, for the first time, time-resolved photoluminescence of nitrogen-doped MOVPE ZnSe layers in the energy region of excitons and DAP recombination, yielding information on defects created during growth and doping, their interactions, and the efficiency of p-doping.

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2. Experimental procedure

Two different doping procedures are compared, varying systematically the doping and preparation parameters in order to obtain high nitrogen concentrations and to control the incorporation process. Samples were grown on (100) GaAs substrates at temperatures between 380 and 550°C by plasma-enhanced low-pressure MOVPE using DIPSe (diisopropylselenide), DASE (diallylselenide) or DESe (diethylselenide), and DEZn (diethylzinc) as precursors. In-situ nitrogen doping is performed with a DC nitrogen plasma. Ex-situ nitrogen doping is carried out by ion implantation of nitrogen (dose $1.5 \times 10^{13} \text{ cm}^{-2}$, energy 40–240 keV) and subsequent annealing. SIMS measurements yield nitrogen concentrations around $5 \times 10^{17} \text{ cm}^{-3}$.

For the photoluminescence spectra, the ZnSe layers are excited above the band gap by the 364 nm line of an Ar-ion laser (Spectra). Time-resolved measurements are performed with a dye laser synchronously pumped by an actively mode-locked Nd:YAG laser (Coherent) with a frequency-tripling BBO crystal. The PL signal is analysed using the time correlated single-photon-counting technique and a micro-channel-plate photomultiplier tube. The transients are fitted by convolution of the apparatus response with two exponential functions, one for the luminescence rise (τ_r), and one for the luminescence decay (τ_d).

3. Experimental results

In Fig. 1, time-integrated PL spectra of differently nitrogen doped ZnSe epilayers in the energy range between 2.50 and 2.82 eV are compared with that of a DESe as-grown sample (a). Spectrum (b) in fig. 1 represents the emission behaviour of a DESe sample doped ex situ by ion-implantation with energies of 120 keV and subsequently annealed at 850°C for 30 s. In addition to the structures observed in the as-grown sample, a weak acceptor-bound exciton emission I_1^N at 2.790 eV (on the low energy shoulder of the I_2) and a dominant I_1^C line are observed. Similar

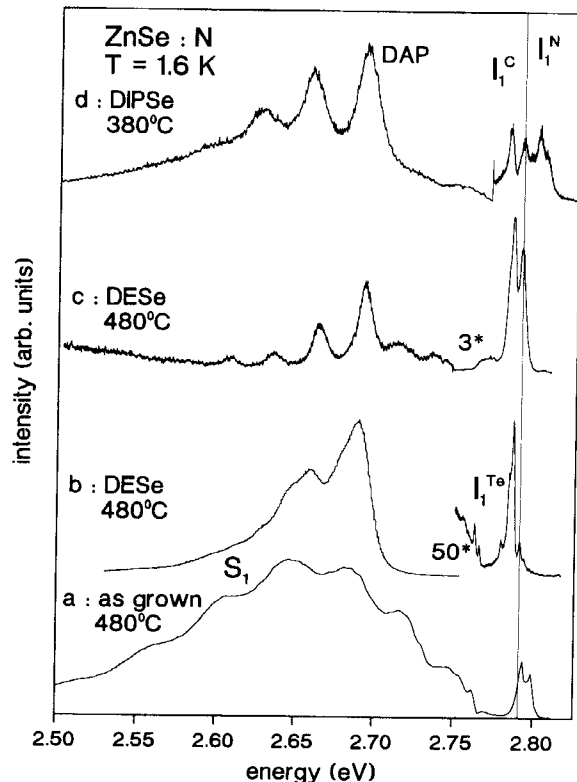


Fig. 1. Luminescence spectra at 1.6 K of differently nitrogen-doped ZnSe epilayers compared to an as-grown sample.

spectra are obtained from plasma-N-doped ZnSe using DESe (c) or DIPSe (d) as precursors. The existence of the I_1^N (recombination of the (A_N^0, X) complex) unambiguously evidences the incorporation of nitrogen on selenium sites in N-doped MOVPE-grown ZnSe layers. This is further confirmed by the energy position of the donor-acceptor pair recombination, yielding an ionization energy of the nitrogen acceptor of 110 meV. Nevertheless, the dominating I_1^C line grows with increasing nitrogen doping rate and indicates compensating defects. The origin of the I_1^C is debated in terms of a deeply bound exciton or a defect related centre to date [5]. We observe this transition in nitrogen-doped but not in undoped MOVPE samples, as the comparison of the spectrum in Fig. 1a with those in Figs. 1b, 1c or 1d clearly reveals.

Around 2.76 eV a doublet of sharp zero-phonon lines (ZPLs) I_1^{Tc} with strong longitudinal

optical (LO) phonon coupling appears in the spectra of Figs. 1a, 1b and 1d. The whole luminescence band is marked by S_1 . In the as-grown sample (a) compared to (b) and (d), no DAP luminescence is to be seen. Using high purity precursors, the S_1 can be diminished as is obvious from spectrum (c) of the DESe-grown sample. In Te-doped ZnSe epilayers, Dhese et al. [6] observed an S_1 band in the same spectral region, which is assigned to recombinations of excitons bound at Te doublets on nearest neighbour anion sites. The periodic structure on the high-energy shoulder reflects the LO phonon energy in ZnSe (31.5 meV). The large FWHM is attributed to the large degree of electron–phonon coupling (insert of fig. 2). This is in agreement with the fact that the DIPSe, DEZn and DESe precursors are contaminated with Te, As, Zn, Sn and B [7]. The transients of this emission are found to be independent of the photon energy, giving a two-exponential decay with time constants of 11.1 and 55.1 ns for the I_1^{Te} doublet as well as for the S_1 band (Fig. 2). A similar dynamical behaviour is known from the Cu-blue luminescence band in ZnS [8], which is attributed to a deeply Cu-bound exciton with two excited states.

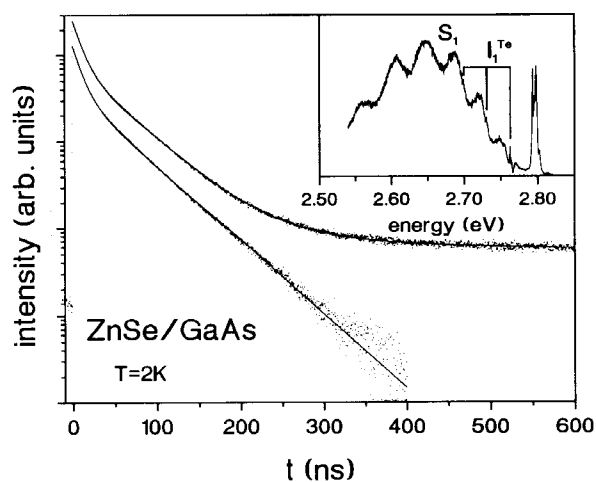


Fig. 2. Transients of the luminescence band S_1 of MOVPE grown ZnSe using DESe as Se precursor and a growth temperature of 480°C. The lower transient is obtained by subtracting the long lived background from the DAP luminescence, clearly revealing a double exponential decay of S_1 . The inset shows the pertaining luminescence spectrum.

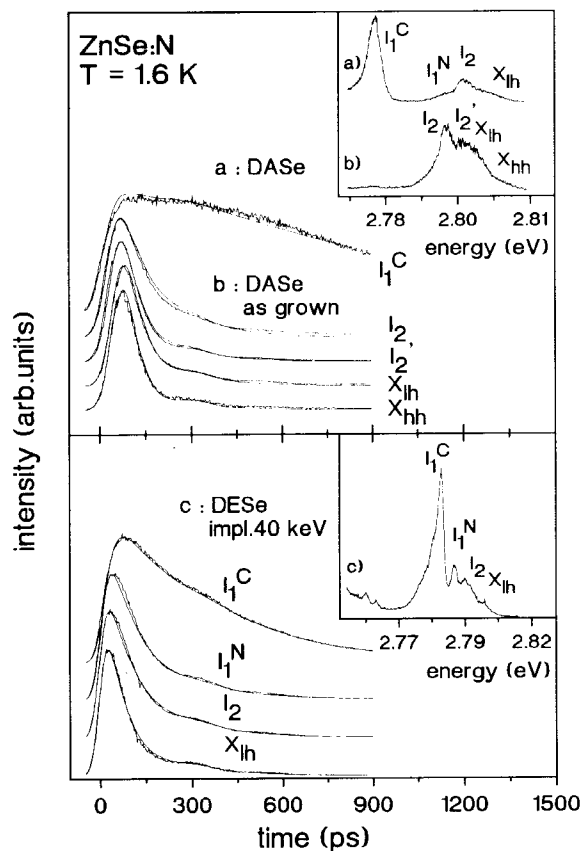


Fig. 3. Transients of different exciton emissions in MOVPE-grown and plasma-doped (a) or N-implanted (c) ZnSe samples compared to those of a DASE as-grown (b) sample.

Fig. 3b shows the transients of the free and bound excitons of the DASE as-grown sample compared to those of in-situ doped (Fig. 3a) and N-implanted (Fig. 3c) samples after interband excitation.

In the excitonic energy region, a typical as-grown spectrum exhibits the strain-split free exciton emissions X_{lh} and X_{hh} and the donor-bound exciton lines I_2 and I_2' (see the luminescence spectrum inset (b) in Fig. 3).

All rise (τ_r) and decay (τ_d) times are in the ps region (see Table 1). The decay times are found to increase with growing binding energy of the bound exciton complex. With increasing nitrogen concentration the decay times decrease, indicating the opening of competing nonradiative re-

Table 1

Rise τ_r and decay τ_d times (in ps) of free and different bound excitons in various ZnSe samples ^a

	MOVPE				MBE [12]		Bulk [11]	
	N-plasma		N-implanted		τ_r	τ_d	τ_r	τ_d
	τ_r	τ_d	τ_r	τ_d				
X_{hh}	–	35			20	100		
X_{lh}	20	45	–	55	80	150		
X							–	30
I_2^{hh}	20	50			110	140		
I_2^{lh}	20	80	–	80	150	200		
I_2^{Lj}							20	40
I_1^{Lj}							50	280
I_1^{N}							50	350
I_1^{ul}					120	300		
I_1^N	20	90	5	90				
I_1^C	20	900	20	260				
I_1^{deep}							100	1020

^a X_i , free excitons; I_2^j , donor bound excitons; I_1^j , acceptor bound excitons; lh and hh, strain split components.

combination channels. However, this effect is also observed for different growth conditions giving rise to different defect backgrounds. Detailed investigations show that ion implantation energies in the range of 40 keV lead to a dominant I_1^N line, whereas higher implantation energies favour the I_1^C emission. From the transients recorded after interband excitation (Fig. 3), it is obvious that there is a drastic reduction of the I_1^N and I_1^C lifetimes, while the lifetimes of the free excitons and the donor bound excitons remain nearly unchanged in comparison with the corresponding transitions in plasma doped samples (see Table 1). This behaviour becomes more pronounced with increasing implantation energy, indicating that defects created during the ion implantation process are responsible. The lifetime of the I_1^C line of 900 ps in plasma-doped ZnSe epilayers using DASE or DESe precursors corresponds well to that of the I_1^{deep} line in bulk material having a similar binding energy [9].

In Fig. 4 time-resolved investigations of the donor–acceptor pair (DAP) luminescence are presented. The inset of Fig. 4 shows the emission spectrum of a DIPSe plasma-doped ZnSe epilayer grown at 380°C compared with that of a

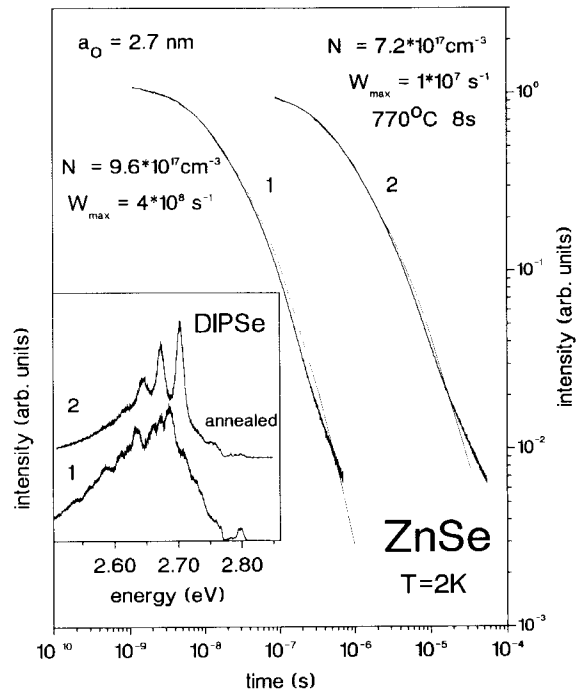


Fig. 4. Transients of the DAP luminescence in plasma-doped ZnSe epilayers grown with a DIPSe precursor at 380°C. Sample 1 has not been annealed, whereas sample 2 has been annealed for 8 s at 770°C. The inset shows the related DAP luminescence.

sample which was subsequently annealed for 8 s at 770°C. It is evident here that annealing leads to an increase of the DAP luminescence in comparison with the exciton emissions and S_1 band. The decay of the DAP recombination yields information on doping concentration and on compensation mechanisms. Using the statistical model of Thomas and Hopfield [10], we determined an acceptor concentration of $9.6 \times 10^{17} \text{ cm}^{-3}$ without and of $7.2 \times 10^{17} \text{ cm}^{-3}$ after annealing. This indicates that this annealing temperature has a weak influence on the incorporation of shallow impurities in MOVPE-grown ZnSe epilayers. However, the decrease of W_{max} , which is a measure of the transition probability, demonstrates that the deep defect concentration is strongly reduced.

4. Discussion

It is important to point out that both plasma doping and ion implantation lead to an efficient nitrogen doping of MOVPE-grown ZnSe layers. The occurrence of the I_1^{N} line, corresponding to the radiative recombination of an (A_{N}^0, X) complex, as well as the donor–acceptor pair recombination energy, indicate an incorporation of nitrogen atoms on selenium sites. These centres act as neutral acceptors and are required for p-type ZnSe. Nevertheless, all investigated nitrogen-doped MOVPE layers are highly resistive, indicating the simultaneous generation of compensating deep donors during the doping process. The dependence of the bound exciton lifetimes on the implantation energy confirms this interpretation.

A prominent feature of our nitrogen doped ZnSe epilayers is the I_1^{C} line, which is not present in undoped samples. A strong increase of the I_1^{C} intensity by two orders of magnitude takes place with increasing nitrogen doping rates, indicating a correlation between the I_1^{C} and nitrogen. However, we observe the same transition in undoped hot-wall epitaxy (HWE) grown ZnSe epilayers and bulk ZnSe crystals [11], too, but not in ultra-pure MBE samples [12]. Since the intensity of the I_1^{C} line depends more critically on growth parameters than on the various dopants, we assign this

line to a point-defect-related centre. Detailed investigations of undoped ZnSe samples clearly correlate the I_1^{C} intensity with an increasing Se/Zn ratio, supporting an interpretation as radiative recombination of an (A^0, X) complex formed at a deep acceptor based on a zinc vacancy. Thus, the dominating I_1^{C} line in nitrogen-doped MOVPE samples indicates the creation of zinc vacancies during nitrogen incorporation even in the case of in-situ plasma doping. Undoped MOVPE samples show no I_1^{C} line (Fig. 1a) indicating a sufficient quality of these layers. Nevertheless, the generation of deep acceptors does not prevent p-conductivity, which may be due to deep donors formed, e.g., by Te incorporation during growth using DEZn or DIPSe as precursors. Further progress in p-conductivity of MOVPE-grown ZnSe epilayers requires undoubtedly the reduction of the number of I_1^{C} related centres by the optimization of doping parameters and purified precursors. A further point is to diminish the growth temperature to 300°C, which is usual for MBE samples.

The lifetimes of the free and bound exciton complexes are sensitive to the defect concentration and thus give information on the defect concentration in the investigated layers. The formation of bound exciton complexes at shallow donors and acceptors is a major recombination channel for free excitons [9], limiting the free exciton lifetimes in doped crystals. For bound exciton complexes, both the screening of the electrostatic interaction at high doping concentrations [13] and the introduction of competing non-radiative recombination channels by energy transfer processes in the presence of deep centres lead to a reduction of their lifetimes. The longest excitonic lifetimes in ZnSe have been observed in ultra-pure MBE samples to date (see Table 1). Even in high purity bulk material, the free as well as the donor bound exciton lifetimes are strongly reduced, whereas the acceptor bound exciton lifetimes can be explained by the entirely radiative decay of the undisturbed complexes [11] with the model of Rashba and Gurgenshvili [14]. The comparatively short excitonic lifetimes observed for nitrogen-doped MOVPE samples result from a large concentration of disturbing defects. This

effect is especially pronounced for the I_1^N and the I_1^C complexes in nitrogen-implanted samples, indicating a large number of deep defects. The excitonic lifetimes become even shorter using higher implantation energies. Thus, it seems to be reasonable that zinc vacancies created during the implantation process form deep acceptors and are responsible for the large concentration of deep defects.

5. References

- [1] J. Qiu, J.M. DePuydt, H. Cheng and M.A. Haase, *Appl. Phys. Lett.* 59 (1991) 2993.
- [2] I.S. Hauksson, J. Simpson, S.Y. Wang, K.A. Prior and B.C. Cavenett, *Appl. Phys. Lett.* 61 (1992) 2208.
- [3] A. Ohki, Y. Kawaguchi, K. Ando and A. Katzui, *Appl. Phys. Lett.* 59 (1991) 671.
- [4] D.J. Chadi and K.J. Chang, *Appl. Phys. Lett.* 55 (1989) 575.
- [5] P.J. Dean and J.L. Merz, *Phys. Rev.* 178 (1969) 1310.
- [6] K.A. Dhese, J.E. Nicholls, P.J. Wright, B. Cockayne and J.J. Davies, *J. Crystal Growth* 126 (1993) 179.
- [7] Data Sheet, Morton International, USA.
- [8] A. Hoffmann, A. Franz, A. Ismail, F. Asch and I. Broser, *Mater. Sci. Forum* 38–41 (1992) (1989) 525.
- [9] R. Heitz, C. Fricke, A. Hoffmann and I. Broser, *Mater. Sci. Forum* 83–87 (1992) 1241.
- [10] D.G. Thomas, J.J. Hopfield and W.M. Augustyniak, *Phys. Rev.* 140 (1965) A 202.
- [11] G. Kudlek, U.W. Pohl, Ch. Fricke, R. Heitz, A. Hoffmann, J. Gutowski and I. Broser, *Physica B* 185 (1993) 325.
- [12] G. Kudlek, Ch. Fricke, N. Presser, R. Heitz, A. Hoffmann, J. Gutowski and I. Broser, in: *Proc. 21st Int. Conf. on Physics of Semiconductors, Beijing, 1992* (World Scientific, Singapore, 1992) p. 1168.
- [13] Ch. Fricke, U. Neukirch, R. Heitz, A. Hoffmann and I. Broser, *J. Crystal Growth* 117 (1992) 783.
- [14] E.I. Rashba and G.E. Gurgenshvili, *Sov. Phys.-Solid State* 4 (1962) 759.