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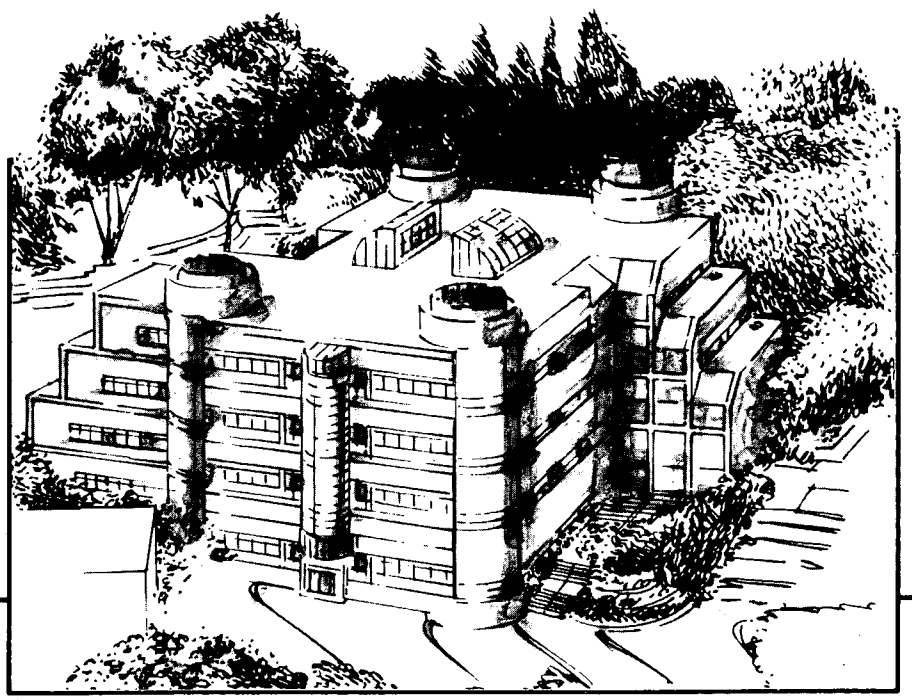

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PHOTOLUMINESCENCE UNDER PRESSURE AND ANNEALING OF NITROGEN-DOPED ZnSe

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ABSTRACT

We report photoluminescence measurements of MBE-grown nitrogen-doped ZnSe under hydrostatic stress. We determined the pressure coefficients of two separate donor-acceptor pair transitions in these samples. The results indicate that the deeper transition is caused by a localized donor that moves further into the band gap with increasing pressure, confirming that it stems from a localized donor. We also show that annealing at temperatures above 325° C produces this donor and results in compensation of the acceptor.

1. Introduction

ZnSe is a technologically important semiconductor because it shows promise as a parent compound for blue light-emitting diodes and lasers. However, difficulty in growing the material with high p-type conductivity is one inherent property limiting its performance. Net acceptor concentrations in p-type, nitrogen-doped ZnSe above 10^{18} cm^{-3} have not been routinely achieved, presumably because of self-compensation. When total nitrogen concentrations exceed 10^{18} cm^{-3}, additional photoluminescence lines appear in the donor-acceptor-pair (DAP) region of the spectrum [1]. These lines have been interpreted as a recombination between a deep, compensating donor and the nitrogen acceptor. Murdin *et. al.* ascribe the defect to a V_{Se} related complex based on magnetic resonance measurements [2].

In this contribution we measure the pressure dependencies of the DAP transitions in both lightly doped and heavily doped samples to elucidate their origin. We show that the DAP peak in highly doped samples involves a deep donor. In addition we find that this deep donor can be produced by annealing the samples. Capacitance-voltage (CV) measurements on the samples show that emergence of the characteristic PL peak during annealing is correlated with a decrease in net acceptor concentration, suggesting that this defect is responsible for the compensation.

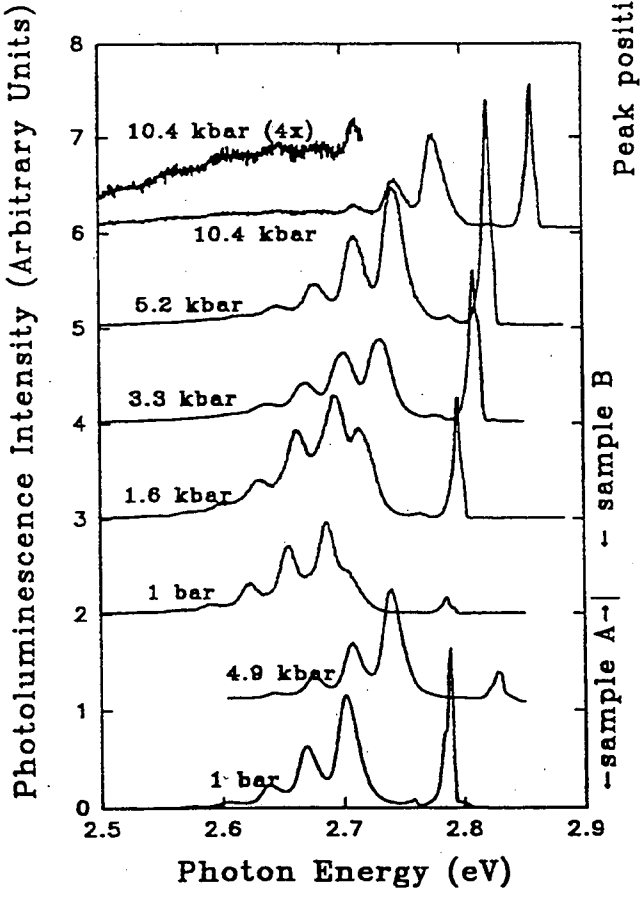
2. Samples and Experimental Procedure

The pressure measurements were performed on two ZnSe samples grown on GaAs substrates by MBE. From CV measurements, sample A was determined to have a net acceptor concentration (N_a-N_d) of 7.4×10^{17} cm^{-3}. For sample B, the total nitrogen concentration was determined by SIMS to be 2×10^{18} cm^{-3}. Annealing studies were performed on a third sample, which had N_a-N_d $=5\times10^{17}$ cm^{-3}.

The samples were excited with a 30 mW He-Cd laser operating at 325 nm and the photoluminescence was analyzed by a SPEX 1404 double monochromator operated with a spectral resolution of 0.5 Å. All spectra were taken at 6 K. The samples were pressurized in a Merrill-Bassett type diamond-anvil cell with liquid N_2 as the pressure medium. The pressure was determined to within ±0.2 kbar by the shift of the R1 ruby line.

Annealing was performed inside an evacuated quartz ampoule in a standard electric furnace at various temperatures for periods of 20 minutes. The N_a-N_d of the annealed samples were then measured by CV. Back-to-back Au contacts were evaporated onto the samples to form the Schottky barriers. The measurements were performed on an HP 4277A LCZ meter.

Fig. 1 Photoluminescence spectra of two nitrogen doped ZnSe samples at various pressures showing acceptor-bound excitons and DAP lines. The weaker structure in the 10.4 kbar spectra is also shown magnified by 4x for clarity.



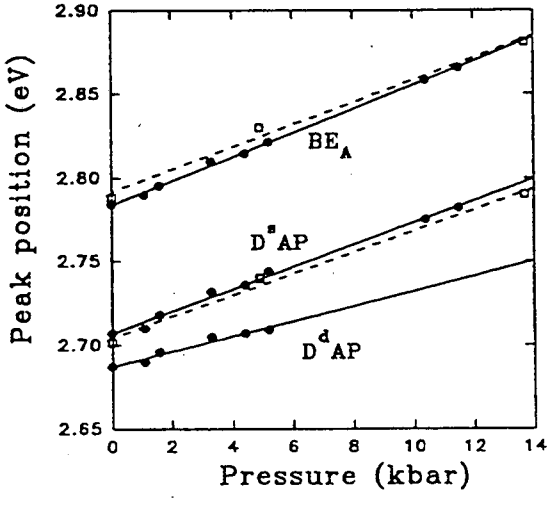


Fig. 2 Pressure dependence of the zero-phonon lines of the DAP transitions and the BE_A of samples A (open squares) and B (closed circles). Lines are linear fits to the data points (sample A→dashed line; B→solid line).

3. Photoluminescence under pressure

The PL spectra of the two samples at various pressures are shown in Fig. 1. The spectrum of sample A at atmospheric pressure is characteristic of lightly doped samples. It exhibits an acceptor-bound exciton (BE_A) at 2.788 eV followed by the DAP line at 2.702 eV and its LO phonon replicas. The same DAP series is present in sample B, however only the zero-phonon line (ZPL) is observable. The rest of the spectrum is dominated by another DAP series with the ZPL at 2.686 eV. We refer to the higher and lower energy DAP emissions as D^sAP (D^s for shallow donor) and D^dAP (D^d for deep donor) respectively. In sample B the D^dAP series masks the LO phonon replicas of the first series; only the ZPL of the D^sAP lines is immediately noticeable as a shoulder on the high energy side.

As the pressure increases, the BE_A and D^sAP peaks of sample A shift toward higher energies but their line shapes do not change appreciably. The pressure dependence of sample B is markedly different. The D^sAP shoulder moves out of the stronger D^dAP peaks (1.6 kbar spectrum). At pressures greater than 3.3 kbar the intensity of the D^dAP peaks decreases, and its peaks become buried within the phonon replicas of the D^sAP lines. At 10.4 kbar the D^sAP lines dominate the high energy side of the spectrum but the D^dAP lines are again observable as a broadened feature. It is evident that the pressure shifts these two DAP features at different rates.

The peak positions were determined by curve fitting. The details of the fit are described elsewhere [3]. Fig. 2 shows the pressure dependence of the peak positions of the DAP peaks and the BE_A peak. The points were fitted to straight lines, and the resulting pressure coefficients are shown in Table 1. In both samples, the BE_A and D^sAP lines shift together at about 7 meV/kbar. The line of the free exciton in epitaxial ZnSe shifts at 6.6 meV/ kbar [4]. Thus both the BE_A and D^sAP follow the direct band gap as it increases under stress indicating that this DAP transition results from shallow, hydrogenic donors recombining with the nitrogen acceptor. The D^dAP transition has a smaller pressure coefficient of 4.5 meV/ kbar, indicating that *it is a transition between a deep localized donor and a shallow nitrogen acceptor*. In ZnSe, transitions from shallow donors and free electrons to deep acceptors have pressure coefficients that are larger than the energy gap [5] .

TABLE 1. Pressure coefficients of the BE_A and DAP peaks in meV/kbar.

Feature	Sample A		Sample B			free exciton
	BE_A	D^sAP	BE_A	D^sAP	D^dAP	(ref. [4])
Value	6.7	6.4	6.6	7.2	4.5	6.6

4. Annealing Study

PL spectra of as-grown samples and annealed samples are shown in Fig. 3. Sample C clearly shows emergence of the D^dAP line after annealing. Although the D^dAP line was already present in sample D, annealing generally increases its intensity. For this sample we measured N_a-N_d which is given in the figure. Annealing above 325°C rapidly decreases the net acceptor concentration, qualitatively suggesting that the observed deep donor is responsible for the compensation in the sample.

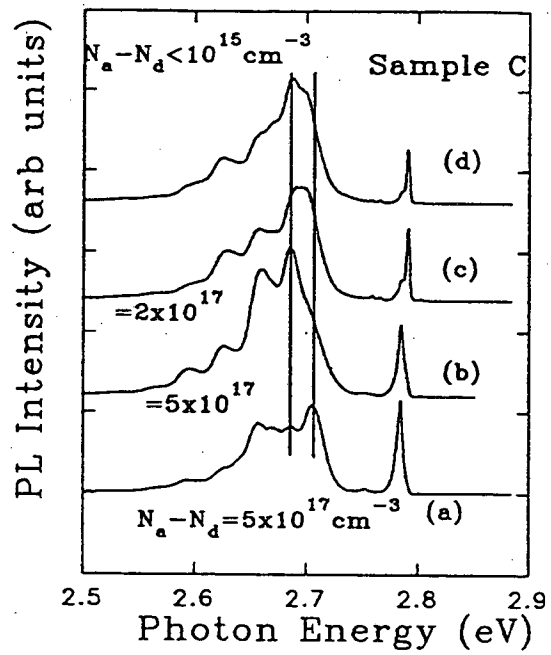


Fig. 3 PL spectra of ZnSe:N (sample C) after various anneals in vacuum: (a) as grown, N_a-N_d= $5x10^{17}$ cm^{-3}; (b) annealed at 300°C for 20 min, N_a-N_d= $5x10^{17}$; (c) annealed at 325°C for 20 min, N_a-N_d= $2x10^{17}$; (d) annealed at 335°C for 20 min, N_a-N_d < $5x10^{15}$. Net acceptor concentrations were measured by CV. Vertical lines indicate positions of D^dAP and D^sAP peaks.

5. Conclusions and Acknowledgments

In summary, hydrostatic pressure shifts the D^sAP peaks at nearly the same rate as the direct energy gap while it shifts the D^dAP peaks at a smaller rate. Therefore the D^dAP lines that appear at higher nitrogen concentration must stem from deep donors. These donors can be produced by annealing the samples in vacuum at temperatures above 325°C and can completely compensate the active acceptors. Since annealing in vacuum can create the defects in large enough concentrations to compensate the dopants at concentrations of 10^{17} cm^{-3} these defects must be native defects or native defect complexes.

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References

[1] I.S. Hauksson, J. Simpson, S.Y. Wang, K.A. Prior, and B.C. Cavenett, Appl. Phys. Lett. **61**, 2208 (1992).

[2] B.N. Murdin, B.C.Cavenett, C.R. Pidgeon, J. Simpson, I. Hauksson, and K.A. Prior, Appl. Phys. Lett. **63**, 2411 (1993).

[3] A.L. Chen, W. Walukiewicz, and E.E. Haller, to appear in Appl. Phys. Lett.

[4] J.A. Tuchman, S. Kim, Z. Sui, and I.P. Herman, Phys. Rev. **B 46**, 13371 (1992).

[5] D.J. Stracham, M. Ming Li, M.C. Tamargo, B.A. Weinstein, J of Crystal Growth **138**, 318 (1994).

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