

**ANNEALING OF NITROGEN-DOPED ZnSe at HIGH
PRESSURES: TOWARD SUPPRESSION OF NATIVE DEFECT
FORMATION**

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Annealing of nitrogen-doped ZnSe at high pressures: Toward suppression of native defect formation

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Abstract. Pressure is shown to have a drastic effect on the annealing characteristics of p-type, nitrogen-doped ZnSe. Samples annealed in vacuum show decreased carrier concentrations and simultaneous formation of deep-donor-related luminescence, while samples annealed under pressure show suppression of this compensating donor. The results are interpreted as an increase in the formation energy of the compensating deep donor under pressure. In addition the samples annealed under pressure show emergence of a new, intense, green luminescence band centered at 2.44 eV. The magnitude of the shift of this peak under applied stress suggests that it results from a recombination involving a deep acceptor.

1. Introduction

Processing of semiconductors for device applications often involves annealing at elevated temperatures. Annealing has the effect of removing damage produced by implantation and activating and diffusing dopants. However, in some instances it also has detrimental effects. Undesired impurities such as transition metals often are unintentionally incorporated. Native crystal defects may also be generated. These two types of defects produce deep levels that trap the free carriers.

For the II-VI semiconductors, annealing often decomposes the crystals at temperatures far below those necessary for regrowth of damaged layers. In nitrogen-doped, p-type ZnSe decomposition initially takes the form of native defects that compensate the shallow, acceptor level [1,2]. Thus in order to implant and activate dopants, novel approaches to annealing that suppress the formation of native defects must be investigated.

In this paper we report the first study of using high pressure to suppress the formation of native defects. Compression of the sample is expected to decrease the concentration of defects that have positive activation volumes. In addition pressure shifts the band extrema and the Fermi level so that the electronic component of the formation energy is changed. We investigate by photoluminescence (PL) and by capacitance-voltage

(CV) measurements the difference in samples annealed under high pressure and those annealed in vacuum. Our preliminary findings show that samples annealed in vacuum are compensated by a deep donor that has a characteristic PL peak while samples annealed under high pressure do not show evidence of this peak. The results are discussed along estimates of the pressure dependence of the formation energy of this defect. We also find the appearance of a new, intense, green band in the luminescence spectrum of samples annealed under pressure.

2. Samples and Experimental Procedure

We studied two nitrogen-doped ZnSe samples grown by molecular-beam epitaxy on semi-insulating GaAs substrates. One (sample A) had an active nitrogen concentration ($N_a - N_d$) of $1.2 \times 10^{17} \text{ cm}^{-3}$; the other (sample B) had $N_a - N_d = 5 \times 10^{17} \text{ cm}^{-3}$. These concentrations were determined by CV measurements. The epitaxial layers were about 2 microns thick.

Photoluminescence spectra were taken at 6 K. The emission was spectrally analyzed by a SPEX 1404 double monochromator operated with a spectra resolution of 0.5 meV and detected by a photomultiplier tube. CV measurements were performed on back-to-back Au Schottky barriers evaporated onto freshly etched surfaces. The measurements were done on a Hewlett Packard 4277A LCZ meter.

Samples annealed in vacuum were sealed in clean quartz ampoules and heated in a furnace. Samples annealed under high pressure were cleaved and lapped into small 200x200x80 micron squares. They were then pressurized in an Inconel diamond-anvil cell with liquid nitrogen as the high pressure medium and heated in a standard electrical furnace. The pressure changed irreversibly during the annealing cycle because of thermal expansion of the cell that deformed the gasket. The pressure after the anneal was often less than 50% of its original value. For each anneal performed at high pressure, the initial pressure of the sample is given.

3. Annealing Results: Donor-Acceptor Pair Luminescence and Compensation

Fig. 1 shows representative PL spectra of sample A (a) as-grown, (b) after annealing in vacuum at 400° C, (c) and after annealing at high pressures (38 kbar) at 400° C. The spectrum of the as-grown sample shows the usual acceptor-bound exciton at 2.787 eV and donor-acceptor-pair (DAP) recombination at 2.698 eV. The latter (hereafter referred to as D^sAP) has been attributed to the recombination between a residual shallow donor and the nitrogen acceptor and is followed by a series of LO phonon replicas. When the sample is annealed another DAP series emerges with a zero-phonon-line at 2.683 eV. Pressure [3] and ODMR [1] studies of this peak have shown it to be caused by a deep donor-to-N acceptor recombination (hereafter referred to as D^dAP). This peak also appears in samples heavily doped with nitrogen. Its occurrence has been correlated with compensation of the nitrogen acceptor [2]. The prevailing ODMR evidence suggests that a V_{Se} -related complex is the deep donor [1]. In the sample annealed under pressure, the

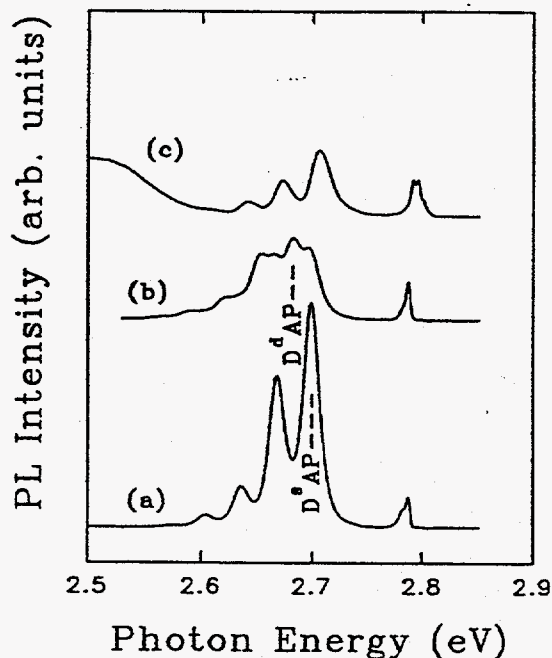


Fig. 1 PL spectra of ZnSe:N (sample A) under different annealing conditions: (a) as-grown, (b) annealed in evacuated ampoule at 400°C for 20 min, (c) annealed at 38 kbar of pressure at 400°C for 20 min.

D^dAP peaks are absent and the D^SAP peaks shift slightly toward higher energy.

To correlate the occurrence of the D^dAP peak with compensation we annealed sample B at various temperatures and analyzed them with both PL and CV measurements (Fig. 2). Although this sample already had evidence of the D^dAP peak before heat treatment, one can clearly see an increase in the D^dAP intensity relative to the D^SAP peak intensity. The measured concentrations of net acceptors are given in the figure. We find a rapid decrease in $N_a - N_d$ when this sample is annealed above 325° C and an increase in D^dAP intensity at these temperatures. Thus the appearance of the D^dAP peak signifies the onset of compensation in annealed samples.

The effect of pressure on annealing can be qualitatively understood by estimating the formation energy of the compensating defect. The concentration of a native defect in a solid is given by the Arrhenius type expression,

$$C \propto \exp\left(\frac{-G}{kT}\right) \quad (1)$$

where

$$G = E + PV^* - TS \quad (2)$$

is the change in the Gibbs free energy that is required to form the defect. Here P is the pressure, V^* is the activation volume, T is the temperature, and S is the change in the entropy. Internal energy, E , has two components

$$E = E_0 - (E_d - E_F) \quad (3)$$

where E_0 is the formation energy of the neutral defect and $-(E_d - E_F)$ is the electronic part [4] of the formation energy that the native donor gains when it gives an electron from

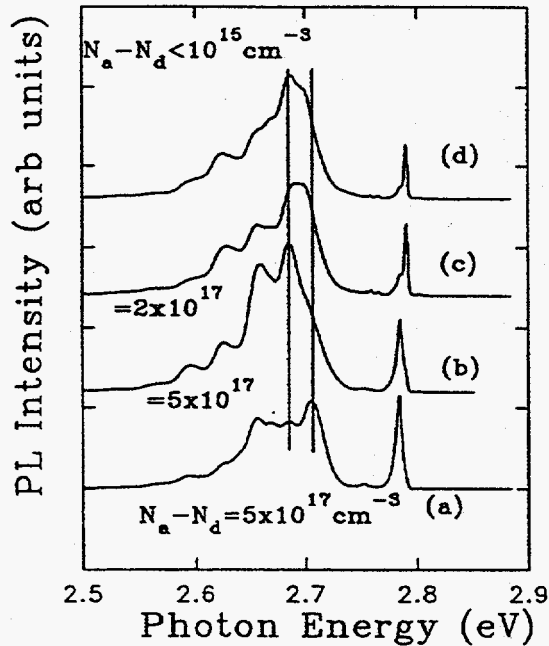


Fig. 2 PL spectra of ZnSe:N (sample B) after various anneals in vacuum: (a) as grown, $N_a - N_d = 5 \times 10^{17} \text{ cm}^{-3}$; (b) annealed at 300°C for 20 min, $N_a - N_d = 5 \times 10^{17}$; (c) annealed at 325°C for 20 min, $N_a - N_d = 2 \times 10^{17}$; (d) annealed at 335°C for 20 min, $N_a - N_d < 5 \times 10^{15}$. Net acceptor concentrations were measured by CV technique. Vertical lines indicate positions of deep DAP and shallow DAP peaks.

its donor level (E_d) to the Fermi level (E_F). The activation volume, V^* , for creation of a Se vacancy-interstitial pair is not known. We make a rough estimate of V^* by using the activation volume of V_{Ga} in GaAs, which is reported to be about 20 \AA^3 [5]. The PV^* term would then increase the formation energy by about 12 meV/kbar. This increase is partly counteracted by the electronic contribution, which decreases the formation energy. Since E_F can be assumed to remain pinned by the nitrogen acceptors, the pressure dependence of the electronic contribution is then the separation between the deep donor state and the nitrogen acceptor, i.e. the pressure dependence of the D^{dAP} peak. We previously measured this value to be 4.5 meV/kbar [3]. Thus, overall pressure increases the formation energy of this defect by about 7.5 meV/kbar. At the annealing pressures of about 40 kbar, the increase is 300 meV. At 400°C the concentration of this native defect would be decreased by a factor of about 100.

Our estimate indicates that pressure creates a large increase in the pressure-volume term in the Gibbs free energy and thus suppresses the formation of this compensating native defect. This result is reflected qualitatively in the PL spectra where we witness suppression of the characteristic D^{dAP} peak when the samples are annealed under pressure.

4. Annealing Results: Broad Green Luminescence

We also find that annealing at high pressures produces an intense broad green luminescence. A representative spectrum is shown in Fig. 3. It is composed of three

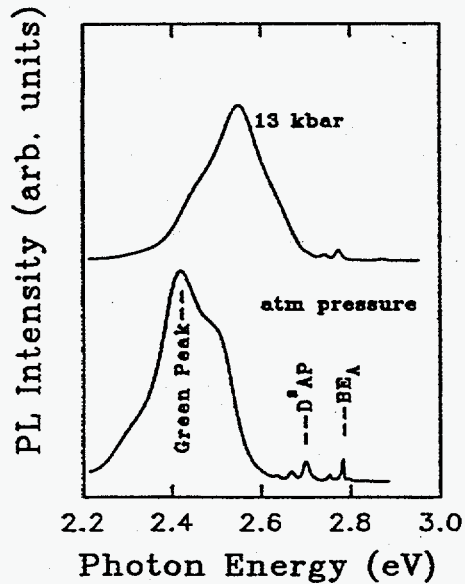


Fig. 3 PL spectra of ZnSe:N after annealing at 20 kbar at 390° C for 40 min. Upper (lower) spectrum was taken at 13 kbar (atm. pressure).

broad peaks at energies of about 2.33, 2.44 and 2.51 eV. We annealed many samples at temperatures between 300 and 400° C and pressures between 10 and 40 kbar and find the following trends in the intensity of this luminescence: (i) the three peaks occur in samples annealed above 300°C, (ii) higher temperatures, higher pressures, and longer anneal times all enhance the peak intensity, and (iii) the peaks are not observed when n-type samples are annealed. It seems that pressure enhances the incorporation of the defect or impurity that is responsible for this luminescence.

To further characterize the peaks we measured their shifts under applied hydrostatic pressure. A spectrum taken at 13 kbar is also shown in Fig. 3. All three peaks increase at rates that are larger than that of the direct energy gap. The central green peak shifts at 10.2 meV/kbar. Without deconvoluting the peaks, the pressure coefficients of the weaker two peaks cannot be determined accurately. The direct energy gap of ZnSe shifts at 6.6 meV/kbar [3]. It is known that transitions between the conduction band and deep acceptor states in ZnSe have pressure coefficients between 10 and 13 meV/kbar [6]. From this argument we tentatively assign each peak in the series to a deep acceptor incorporated into the crystal. The weaker peak at 2.33 eV may correspond to the well studied "Cu-green" peak which involves a shallow donor and a Cu-related acceptor. We have not been able to find spectra in the literature that even remotely resemble the other two broad features.

5. Conclusions

We have shown that pressure strongly effects the annealing characteristics of p-type, nitrogen-doped ZnSe. It suppresses the formation of one compensating, native defect mainly by increasing the pressure-volume term of the formation energy. However it also

introduces additional defects into the crystal that give rise to a characteristic green luminescence band that we tentatively identify as arising from deep acceptor states. It is striking that annealing in vacuum produces deep donors while annealing under pressure creates deep acceptors. Although further measurements of the pressure annealed samples are required in order to determine whether pressure annealing increases the p-type activity, our current results are promising and show that pressure can be used to affect the concentrations of compensating defects.

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