

Resonant donor defect as a cause of compensation in *p*-type ZnSe: Photoluminescence studies under hydrostatic pressure

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We report the presence, in heavily doped and compensated ZnSe:N, of a resonant donor defect having an activation energy of ≈ 120 – 160 meV. The donor-acceptor pair photoluminescence observed in these materials is quenched at pressures higher than 25 kbar. We attribute this quenching to the shift of a resonant defect level into the band gap. A split N-N interstitial on a Se site is proposed as a strong candidate for the observed defect. We further propose that this species is the dominant donor defect at high *p*-doping levels and, consequently, is responsible for the potential fluctuations observed in this material. Moreover, a very important point shown by the present ZnSe:N data is that different compensating species will dominate in different ranges of N concentrations.

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Wide band-gap semiconductors are of intense interest for many applications, including light-emitting and detecting devices, and high-temperature transistors and sensors. Historically, it has been difficult to achieve good bipolar doping in wide bandgap semiconductors, a continuing puzzle of important fundamental interest. It is generally agreed that either poor solubility^{1,2} or compensation^{2,3} are the most likely culprits. There have been numerous attempts to give microscopic explanations for these problems based either on first-principles theories (see, e.g., Ref. 4, for III-V materials and Refs. 5–11 for II-VI materials) or on semiphenomenological models (see, e.g., Ref. 12 for III-V and Refs. 13,14 for II-VI compounds, respectively).

We concentrate in this work on *p*-type ZnSe. To date, the best acceptor dopant, nitrogen, has not yielded a net acceptor concentration ($[N_A - N_D]$) higher than $\sim 10^{18}$ cm⁻³.^{15,16} It is fascinating that as soon as the total nitrogen concentration exceeds $\sim 10^{18}$ cm⁻³, the material becomes highly compensated. From experimental results, it has been suggested that such behavior could arise from self-compensation by a donorlike complex $[V_{Se}-N_{Se}]$, with an activation energy of 45–50 meV,^{17,18} and/or from a 29.1 meV donor tentatively assigned to nitrogen on an interstitial site.¹⁹ The former is often referred to as a deep donor (as opposed to the nominal shallow donors due to accidental impurities), and gives rise to a donor-acceptor pair (DAP) photoluminescence (PL) peak (often denoted by D^dAP) at about 2.686 eV. However, it is significant that Kimura *et al.*¹⁶ observe this D^dAP PL in ZnSe:N material with a 100% activation ratio (i.e., very low or no compensation). Hence, one can conclude that the $[V_{Se}-N_{Se}]$ defect is not responsible for the compensation in material with doping levels above 10^{18} cm⁻³. The 29.1 meV defect has been observed only in lightly doped ZnSe:N, and it is not expected to dominate at high doping levels.

As to guidance from theory, in view of the well-known result that defect formation energies depend on the Fermi

level,⁶ it is obvious that different defects may dominate at different doping levels. However, in addition, there is no agreement among different calculations² as to the values of the formation energies for different defects. Furthermore, there is little or no correlation between the defects that are predicted theoretically and those that are suggested from the experimental results (for more details see, e.g., Ref. 2).

In this paper we report experimental findings on the effects of hydrostatic pressure on the DAP PL in heavily doped and compensated ZnSe:N epilayers. Our findings point to an important source of strong compensation in heavily doped *p*-type ZnSe—a resonant donor complex involving two N interstitials. We are able to give an estimate for the energy level of this defect. Moreover, we show that this defect can give rise naturally to a nonradiative path that accounts for the PL quenching observed at high pressure.

Cheong *et al.*⁹ and S. Pöykkö *et al.*¹⁰ have predicted that the split interstitial N-N complex occupying a Se site, denoted hereafter by $(N_i-N_i)_{Se}$ when it is in its double charged, has one of the lowest formation energies, and, accordingly, is among the most stable compensating donor defects. Because this defect involves N pairs, it should be important at very high doping densities. Furthermore, its energy level was calculated to lie ~ 120 meV above the bottom of the conduction band. Therefore, this defect is a prime candidate to explain the doping problems in ZnSe:N, since it competes with substitutional shallow acceptors for nitrogen, and in addition it can compensate two of these acceptors. Since the energy level of the defect is resonant with the conduction band (CB), it cannot be observed at 1 atm by any techniques which rely on carrier trapping, e.g., photoluminescence (PL) or deep level transient spectroscopy (DLTS).²⁰ However, if one can “move” the edge of the CB above this energy level, the defect should become “observable.” Fortunately this can be done by applying hydrostatic pressure: It is well known that the bandgap of semiconductors increases with applied pressure, and that almost all of this effect comes from the

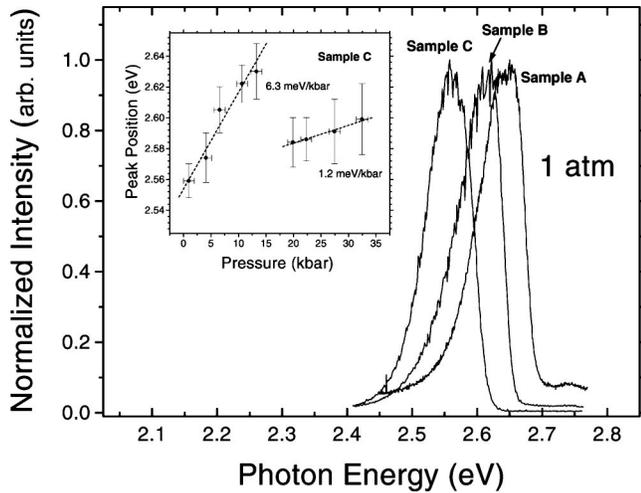


FIG. 1. CW PL spectra from the investigated samples at 1 atm. The inset shows the peak energy for the sample C PL band as a function of applied pressure.

movement of the CB edge (see Ref. 21 and citations therein).

In the present high pressure experiments, we report results on three heavily doped and compensated ($[N] \sim 10^{19} \text{ cm}^{-3}$, with $(N_A - N_D) \leq 2 \times 10^{17} - 5 \times 10^{17} \text{ cm}^{-3}$) ZnSe:N epilayer samples grown by molecular-beam epitaxy (MBE). All of these samples have been studied extensively before at ambient pressure, and their descriptions can be found elsewhere.^{22–24} We employed a ruby-calibrated diamond-anvil cell (DAC), tunable in the pressure/temperature ranges 0–300 kbar/7–300 K, with liquid helium as the pressure transmitting medium. A detailed account of the experimental system can be found in Ref. 25. Samples, $\sim 75 \times 75 \times 30 \text{ } \mu\text{m}^3$ in size, were prepared by standard cleaving and substrate lapping procedures. The PL was excited using $\sim 5\text{--}30 \text{ mW}$ UV light from an Ar^+ (364 nm) or a Kr^+ (356 nm) laser, focused into a spot of $\sim 40 \text{ } \mu\text{m}$ diameter. The experiments were performed at temperatures of 8–12 K, and the He pressure medium was annealed intermittently at 100 K to remove strain gradients.²⁵

The PL spectra observed at 1 atm for the three ZnSe:N epilayer samples are shown in Fig. 1 and are attributed to DAP PL (see, Ref. 24 and references therein). In each case, the PL intensity scale is normalized to unity at the peak maximum. These DAP spectra show the expected behavior for highly doped and compensated ZnSe:N—namely samples with higher doping levels exhibit PL peaks that are shifted more to the red.²⁴ For pressures below 10–13 kbar (see inset in Fig. 1) the rates of pressure shift for these DAP PL peaks are all similar to that for the ZnSe band-gap E_G [$dE_G/dP \sim 6.5 \pm 0.2 \text{ meV/kbar}$ (Refs. 25 and 26)]. However, at higher pressures, the rates of shift for the PL peaks all decrease sharply compared to dE_G/dP (and acquire some sample dependence). Thus, unlike the “usual” shallow DAP and exciton PL in ZnSe (and most other semiconductors) doped at low and medium levels, these deeper DAP PL bands tend not to follow the shift of the bandgap at high pressures. They also broaden significantly, and, as a consequence, it is hard to make definite conclusions about the peak

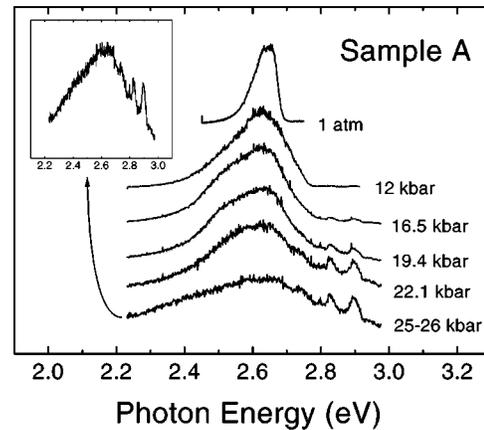


FIG. 2. CW PL spectra from Sample A as a function of applied pressure. Two high-energy peaks observed at high pressures are from the diamond cell (see also text).

shifts at pressures higher than 10–13 kbar.²⁷ Such behavior is quite intriguing and merits further study.

We, however, concentrate on the more striking behavior shown in Fig. 2. For all three ZnSe:N samples, it is found that the DAP PL intensity drastically decreases with pressure above 20–25 kbar. This is clearly illustrated by comparing the strength of the DAP peaks in Fig. 2 to that of the features at the high-energy end of the spectra. These latter features are from the diamond anvils, and since the strength of this emission does not change appreciably with pressure, it can be used as a reference for the PL intensity of the ZnSe. Based on this comparison, we conclude that the DAP PL is essentially quenched above 25 kbar. It is important to note that this quenching is reversible (i.e., the PL intensity increases again on reducing the pressure below 25 kbar), so structural damage to the samples can be excluded.

It is instructive to contrast these findings with the results of previous high-pressure PL experiments on ZnSe samples with light to moderate nitrogen doping.^{28,29} For a ZnSe:N epilayer with $[N_A - N_D] \sim 10^{16} \text{ cm}^{-3}$, Weinstein *et al.*²⁸ observed that the line shape of the usual shallow DAP PL became distorted at pressures above 24 kbar, but no strong decrease in intensity was found to at least 53 kbar. In another study on samples with $[N_A - N_D] \sim 10^{17} \text{ cm}^{-3}$, Chen *et al.*²⁹ also found distortions in the shallow DAP PL line shape (here at somewhat lower pressures), but again no strong quenching was apparent. Considered together, these results indicate that the concentration of the nonradiative defects responsible for the PL quenching in ZnSe:N increases sharply with the N content. A very important corollary to these results is that the dominant compensating donor species can likewise depend on the range of N concentration.

The most straightforward explanation of the observed pressure-induced PL quenching is that it is due to a nonradiative defect level, which is resonant with the conduction continuum at ambient pressure, enters the ZnSe bandgap at higher pressure, and rapidly increases in density for N concentrations above 10^{18} cm^{-3} . To estimate the energy above the CB edge of the (resonant) level, we make the following reasonable assumptions: (1) the conduction band edge shifts

with the full gap pressure coefficient; (2) the resonant donor level is associated with a localized state and, therefore, is pressure insensitive^{28,29} (see, also Ref. 30); (3) the PL at 1 atm involves a donor with a binding energy of 45 meV,^{17,18} and this binding energy does not change appreciably with pressure. Combining these assumptions with the observed threshold pressure for quenching, we estimate that the energy of the resonant level at ambient pressure is ≈ 120 – 160 meV above the conduction band edge in heavily doped ZnSe:N. Considering that the $(N_i-N_i)_{Se}$ complex is calculated to have an energy level 120 meV above the conduction band edge, and that this defect has a low formation energy,^{9,10} we postulate that the $(N_i-N_i)_{Se}$ defect is responsible for the photoluminescence quenching under pressure observed here in heavily doped ZnSe:N.

The next important question is, how does the PL quenching occur? We suggest the following. After the resonant level of the $(N_i-N_i)_{Se}$ complex moves into the band gap, the complex becomes a highly efficient electron trap. Moreover, since the complex should be a double donor (i.e., localize two electrons), there is a high probability that it will give rise to a strong Auger recombination channel (see, e.g., Ref. 31). An Auger process would be quite efficient in quenching the photoluminescence, particularly if the paired interstitial complexes are present in sufficient concentration. In fact, paired interstitial complexes are expected to be dominant at very high doping levels, and, therefore, only in heavily doped materials should there be enough of these defects to quench

the photoluminescence, while at lower doping levels they might modify the PL spectra only slightly. These expected properties of the $(N_i-N_i)_{Se}$ defect are in essential agreement with all of the available data.

In summary, we have observed pressure-induced quenching of the DAP PL band at threshold pressures of 20–25 kbar in three heavily doped and compensated ZnSe:N samples. This behavior is attributed to a localized double donor state that is resonant with the conduction continuum at 1 atm, but is driven into the band gap by applied pressure. Auger recombination due to the double donor is suggested as the PL quenching mechanism. We estimate that the active level for this defect should lie ~ 120 – 160 meV above the conduction band edge at 1 atm in ZnSe:N. A strong candidate for this donor defect in ZnSe:N is the $(N_i-N_i)_{Se}$ complex, a split interstitial N-N pair on a Se site. The present pressure results on heavily N-doped ZnSe, compared to earlier findings on ZnSe:N with lower doping, emphasize that the dominant donor defect is a function of the N concentration. It is hoped that the ideas raised by these pressure results will stimulate further experimental and theoretical work on the nature and energy structure of defect complexes in II-VI materials.

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¹G.F. Neumark, Phys. Rev. Lett. **62**, 1800 (1989).

²G.F. Neumark, Mater. Sci. Eng., R **21**, 1 (1997).

³G.F. Neumark, R.M. Park, and J.M. DePuydt, Phys. Today **47** (6), 26 (1994).

⁴J. Neugebauer and C.G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).

⁵D.B. Laks, C.G. Van de Walle, G.F. Neumark, and S.T. Pantelides, Phys. Rev. Lett. **66**, 648 (1991).

⁶C.G. Van de Walle, D.B. Laks, G.F. Neumark, and S.T. Pantelides, Phys. Rev. B **47**, 9425 (1993).

⁷A. Garcia and J.E. Northrup, Phys. Rev. Lett. **74**, 1131 (1994).

⁸K.W. Kwak, D. Vanderbilt, and R.D. King-Smith, Phys. Rev. B **52**, 11 912 (1995).

⁹B.-H. Cheong, C. H. Park, and K. J. Chang, Phys. Rev. B **51**, 10 610 (1995).

¹⁰S. Pöykkö, M. J. Puska, T. Korhonen, and R. M. Nieminen, Mater. Sci. Eng., B **47**, 1 (1997).

¹¹S. Pöykkö, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **57**, 12 174 (1998).

¹²S.B. Zhang, S.H. Wei, and A. Zunger, Phys. Rev. Lett. **84**, 1232 (1999).

¹³S.B. Zhang, S.H. Wei, and A. Zunger, J. Appl. Phys. **83**, 3192 (1998).

¹⁴Y. Marfaing, J. Cryst. Growth **138**, 305 (1994).

¹⁵J. Qiu, J.M. DePuydt, H. Cheng, and M.A. Haase, Appl. Phys. Lett. **59**, 2992 (1991).

¹⁶K. Kimura, S. Miwa, C.G. Jin, L.H. Kuo, T. Yasuda, A. Ohtake,

K. Tanaka, T. Yao, and H. Kobayashi, Appl. Phys. Lett. **71**, 1077 (1997).

¹⁷I.S. Hauksson, J. Simpson, S.Y. Wang, K.A. Prior, and B.C. Cavenett, Appl. Phys. Lett. **61**, 2208 (1992).

¹⁸T.A. Kennedy, E.R. Glaser, B.N. Murdin, C.R. Pidgeon, K.A. Prior, B.C. Cavenett, Appl. Phys. Lett. **65**, 1112 (1994).

¹⁹E. Tournié, P. Brunet, and J.-P. Faurie, Appl. Phys. Lett. **74**, 2200 (1999).

²⁰Such a defect, of course, contributes to compensation and should “reveal” itself in electrical measurements; however, the latter do not provide any information on the origin of compensating defects.

²¹S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

²²I. Kuskovsky, G.F. Neumark, V.N. Bondarev, and P.V. Pikhitsa, Phys. Rev. Lett. **80**, 2413 (1998).

²³I. Kuskovsky, D. Li, G.F. Neumark, M. Moldovan, N. Giles, V.N. Bondarev, and P.V. Pikhitsa, J. Cryst. Growth **184/185**, 525 (1998).

²⁴I. Kuskovsky, D. Li, G.F. Neumark, V.N. Bondarev, and P.V. Pikhitsa, Appl. Phys. Lett. **75**, 1243 (1999).

²⁵M. Ming Li, D. J. Strachan, T.M. Ritter, M. Tamargo, and B. A. Weinstein, Phys. Rev. B **50**, 4385 (1994).

²⁶J.A. Tuchman, M. Kim, Z. Sui, and I.P. Herman, Phys. Rev. B **46**, 13 371 (1992).

²⁷The current experimental data do not exclude the appearance of another weak PL band. However, there is no clear evidence for such an effect.

- ²⁸B.A. Weinstein, T.M. Ritter, D. Strachan, M. Li, H. Luo, M. Tamargo, and R. Park, *Phys. Status Solidi B* **198**, 167 (1996); T.M. Ritter, B.A. Weinstein, R.M. Park, and M.C. Tamargo, *Phys. Rev. Lett.* **76**, 964 (1996).
- ²⁹A. Chen, W. Walukiewicz, and E.E. Haller, *Appl. Phys. Lett.* **65**, 1006 (1994).
- ³⁰It is important to understand that deep impurities do not necessarily mean defects that have energy levels deep in the band gap [see, e.g., P.Y. Yu and M. Cordona, *Fundamentals of Semiconductors* (Springer-Verlag, Berlin, 1996), p. 149]. We follow here their terminology, which defines deep impurities (centers) as localized defects, whose energies cannot be calculated by means of the “effective-mass approximation.” The most intriguing examples are resonant defects, whose energy levels fall into the bands.
- ³¹G.F. Neumark, *Phys. Rev. B* **7**, 3802 (1973).