Emergence of Deep Levels in *n*-Type ZnSe under Hydrostatic Pressure

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Photoluminescence is measured in *n*-type ZnSe doped with Ga and Cl under pressures to 100 kbar (at 7 K). For each dopant, the rate of pressure shift of the self-activated band changes at 25–30 kbar from faster than to slower than that of the band gap. The change is evidence that a previously unknown deep donorlike state emerges from the electron continuum. This state probably is related to zinc vacancy-donor complexes, whose levels move lower in the gap with compression.

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Electrically active deep defects in wide band gap semiconductors pose difficult problems for doping and other properties needed for electro-optic applications [1,2]. In ZnSe, several deep defects have been studied at 1 atm by optical, magnetic resonance, and transport methods. These include, e.g., the isolated zinc vacancy V_{Zn} [3], the C_{3v}-relaxed sites of P_{Se} and As_{Se} [4], and complexes involving impurities, vacancies, and interstitials (I) [5,6]. These complexes often participate in donor-acceptor-pair (DAP) recombination yielding self-activated (SA) photoluminescence (PL) bands [7].

ZnSe and many other II-VI solids exhibit strong biases for *n*-type, vs *p*-type, doping [1], but the opposite is true for ZnTe. Proposed explanations of these trends include compensation and trapping by extrinsic or native defects [8,9], impurity solubility limits [10], and shallow-deep bistability [1]. However, the dichotomies for *n*- and *p*-type doping in II-VI solids remain controversial.

Deep states should respond weakly to pressure because they are atomiclike [11,12]. Hence, it is the pressure behavior of the host valence and conduction band edges (VBE) and (CBE) that bears on the doping problem. For example, since the CBE is ~0.6 eV higher in ZnTe than in ZnSe, electron traps that are active at 1 atm in ZnTe may be inactive in ZnSe until pressure (or Te alloying) tunes the CBE to higher energy [1].

We report pressure-PL experiments on Cl- and Ga-doped *n*-type ZnSe. For each dopant, the behavior of the SA emission reveals that (i) the associated deep acceptor state becomes less stable with compression (as found for P_{Se} and As_{Se} in ZnSe [13]) and (ii) a previously unknown deep donorlike state enters the band gap at 25–30 kbar. At 1 atm, the projected energy levels of the latter for both donors studied are ~0.15–0.18 eV above the ZnSe CBE, well within the ZnSe-ZnTe conduction band offset. Hence, these deep states could degrade *n*-type doping in ZnSeTe alloys if their density is high enough. Several origins for these results are examined, the most likely being related to V_{Zn}-donor complexes.

The present ZnSe:Ga and ZnSe:Cl samples were grown in different laboratories by molecular beam epitaxy on (001) oriented semi-insulating GaAs substrates. The Ga-(Cl-) doped epilayers were 3.3 (1.3) μm thick, and contained 1×10^{17} (3×10^{18}) electrons/cm^3 as measured by room temperature Hall effect. They were deposited at 270 °C (320 °C), both under Se-rich conditions.

PL was excited with the 3638 Å line of an Ar^+ laser (5 mW into a 30 μm spot) [13]. Spectra were recorded to 100 kbar at 7 K using a ruby-calibrated diamond-anvil cell (DAC) that was tunable at low temperature. Helium was used as the pressure medium, which was periodically annealed at 120 K to remove possible strain gradients. With this procedure, no plastic deformation in the samples (as indicated by irreversible spectral changes) was seen up to 70 kbar.

The PL spectra measured at various pressures are shown in Figs. 1(a) and 1(b) for the Ga- and Cl-doped ZnSe samples. These spectra can be divided into sharp near band-edge excitonic features and broad "midgap" bands ascribed to stimulated absorption– (SA-) emission processes [7]. In the ZnSe:Ga sample, the principal near-edge PL is due to the Ga_{Zn} neutral donor bound-exciton I_2 peak (2.795 eV at 1 atm) [14]. Similarly, the ZnSe:Cl sample shows a single near-edge I_2 peak (2.798 eV at 1 atm) arising from Cl_{Se} donors [7].

At 1 atm the SA-emission bands have peak positions at 2.28 eV in ZnSe:Ga and 2.04 eV in ZnSe:Cl, and are ~0.23 eV wide. (The oscillations superimposed on each band are interference fringes due to the thin film nature of the specimens.) In *n*-type ZnSe it is common to observe such SA bands in the range 1.7–2.3 eV. This emission is generally assigned to DAP recombination between the intentional shallow donor (here Ga_{Zn} or Cl_{Se}) and deep acceptor states related to zinc vacancies, e.g., isolated

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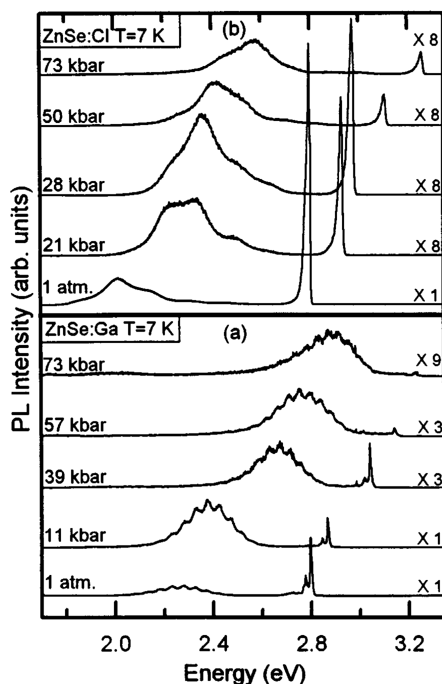


FIG. 1. Observed PL spectra for the ZnSe samples doped with (a) Ga and (b) Cl.

$V_{Zn}^{=}$ or second nearest-neighbor V_{Zn}-donor complexes (A centers) [5–7,15].

Figures 1(a) and 1(b) show that all of the observed PL features shift to higher energy with increasing pressure. The I_2 peaks essentially follow the ZnSe band gap, as expected [13,16]. However, the SA bands respond quite differently, requiring two pressure coefficients to describe their behavior in each sample (see below). Pressure produces few line-shape changes, except minimal broadening of the I_2 peaks, and distortions of the SA bands (mainly in ZnSe:Cl) due to changing overlap between the band maximum and the thin film fringes. The peak energy of each SA band was obtained by fitting with a Gaussian line shape and applying a wavelength-dependent correction for the system response (determined using a calibrated blackbody source). The intensity of all the PL features tends to weaken gradually with pressure; this was reversible below 70 kbar.

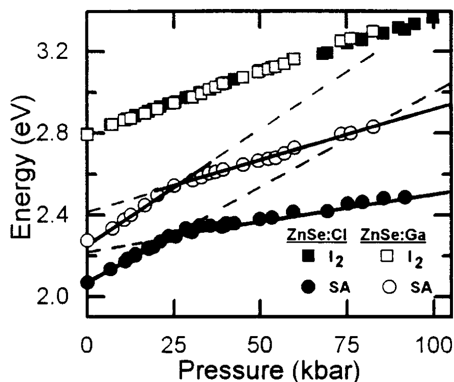


FIG. 2. Peak energies of the SA bands (corrected for system response) and I_2 lines vs pressure in both samples. $E_A \approx 0$ at the projected crossing of $E_{SA}^{<}$ with I_2. The energy of the D level above the CBE at 1 atm is $\sim(E_{SA}^{>} - E_{SA}^{<})$ projected to $P = 0$.

TABLE I. Pressure shift of PL features and deep-level binding energies.

[meV/kbar]	ZnSe:Cl I_2	ZnSe:Cl SA	ZnSe:Ga I_2	ZnSe:Ga SA
$\partial E^{<}/\partial P$	6.6 ± 0.2	9.1 ± 0.5	6.3 ± 0.2	11.1 ± 0.5
$\partial E^{>}/\partial P$	6.6 ± 0.2	2.7 ± 0.5	6.3 ± 0.2	5.0 ± 0.5
$\partial E_A/\partial P$	-2.2 ± 0.7		-4.2 ± 0.7	
$\partial E_D/\partial P$	6.4 ± 1.0		6.1 ± 1.0	

The peak energies of the observed I_2 lines and SA bands are plotted versus pressure for both samples in Fig. 2. The linear slopes obtained from a best-fit analysis of these data are given in Table II. The small difference in the pressure shifts of the exitonic peaks is typical for ZnSe [13,16], and not important here. The SA bands initially shift to higher energy faster than the direct gap. If this trend continued, the band maxima would cross the gap energy at ~105 and ~220 kbar in the Ga- and Cl-doped samples, respectively (see Fig. 2). *Instead, the pressure coefficients of the SA bands decrease strongly at 25 kbar in ZnSe:Ga and 28 kbar in ZnSe:Cl.*

Similar behavior is not observed for the I_2 lines (Fig. 2), and none of the PL features (I_2 lines or SA bands) exhibit related intensity changes. The latter result is seen in Fig. 3, where the intensity ratio of the two types of features varies smoothly in the 20–35 kbar range. Also, similar behavior has not been found in the p-type and undoped samples studied thus far [13].

The slope changes in Fig. 2 for the SA bands may have two origins given the DAP nature of this recombination. Compression either causes the deep acceptor state involved in the SA process to shift below the VBE and become unstable against shallow acceptors or it causes a new deep donorlike state (hereafter D) to enter the band gap. The first alternative is unlikely since it would require, contrary to our results, quenching of the SA bands and the appearance of shallow DAP lines ~0.13 eV

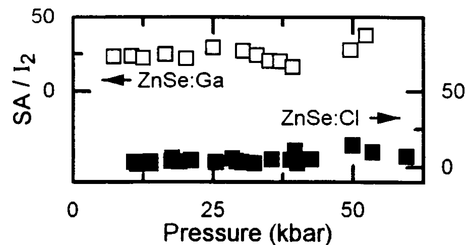
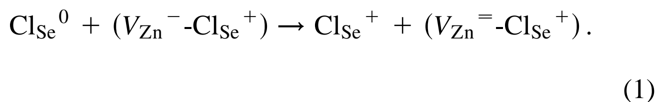


FIG. 3. Integrated intensity of the SA bands relative to the I_2 peaks vs pressure.

below the band gap [7]. In contrast, the second alternative is consistent with our findings since it permits the continued presence of broadband PL in the same energy range, but should lead to a decrease in pressure shift due to the D state.

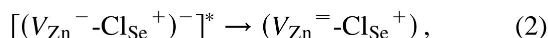
Let us consider a more detailed model of the SA emission. At low pressure, the pertinent DAP processes involve V_{Zn}-donor (A-center) complexes [6,7], as e.g., in ZnSe:Cl,



$$Cl_{Se}{}^{0} + (V_{Zn}{}^{-}\text{-}Cl_{Se}{}^{+}) \rightarrow Cl_{Se}{}^{+} + (V_{Zn}{}^{=}\text{-}Cl_{Se}{}^{+}) . \quad (1)$$

A similar reaction applies for ZnSe:Ga except that the donor is Ga_{Zn} and, for the 2.28 eV (1 atm) band found in our sample, the A' center (known to be similar to V_{Zn}-Ga_{Zn}) is involved [14,15].

An attractive candidate for the D state is an antibonding, or mixed character, excited level of the vacancy-donor complex. At high pressure, an electron could be trapped nonradiatively by such a state, and PL then would occur via the internal transition,



$$[(V_{Zn}{}^{-}\text{-}Cl_{Se}{}^{+})^{-}]^{*} \rightarrow (V_{Zn}{}^{=}\text{-}Cl_{Se}{}^{+}) , \quad (2)$$

with an analogous reaction for ZnSe:Ga. This hypothesis accounts in a simple way for the decrease in pressure shift of the SA bands, since *both* levels involved in such an internal transition will depend primarily on the atomiclike potential of the deep defect. Hence, the transition energy should be less sensitive to pressure than when (below 25–30 kbar) one of the participating levels stems from a hostlike shallow donor state.

Alternate origins for the D level are possible. It might be due to other residual impurities, or to native point defects. But these possibilities seem questionable, the former because similar decreases in pressure shift occur in Cl- and Ga-doped specimens from different laboratories, and the latter because this behavior is thus far absent in undoped and group-V doped ZnSe samples [13]. Recently, a DAP series having a pressure shift smaller than the gap was identified in the *near-edge* PL spectrum (~2.7 eV at 1 atm) of ZnSe:N [17]. However, this cannot explain our results since the levels involved are active at 1 atm. It also seems unlikely that the D state arises from the isolated Cl_{Se} or Ga_{Zn} donors, for then the intensity and shift of the I_2 peaks also should undergo abrupt changes near 25–30 kbar. But this does not occur, implying that the D state originates at a different site than the shallow donors and probably has a lower concentration.

The last comments also apply for DX centers, since their density should be half that of the shallow donors. Recent calculations [1,18] find that the DX center is unstable for Cl in ZnSe, and metastable for Ga in ZnSe. In the latter case, the formation reaction at 1 atm is endothermic by 0.5 eV (per captured electron pair). The D level in ZnSe:Ga is extrapolated to lie ~0.15–0.18 eV above the CBE at 1 atm (Fig. 2), somewhat low to be identified with the calculated Ga DX center. Hence, the changes in pressure shift of the SA bands in Cl- and Ga-doped ZnSe are probably not related to DX centers.

The pressure shifts of the SA band maxima E_{SA} below (<) and above (>) the slope changes in Fig. 2 allow one to estimate how the binding energies of the associated deep levels depend on pressure:

$$\frac{\partial E_A}{\partial P} \approx \frac{\partial E_g}{\partial P} - \frac{\partial E_{SA}{}^{<}}{\partial P} ,$$

$$\frac{\partial E_D}{\partial P} \approx \frac{\partial E_{SA}{}^{<}}{\partial P} - \frac{\partial E_{SA}{}^{>}}{\partial P} . \quad (3)$$

Here, E_g is the band gap, and E_A and E_D refer to the optical (not thermal) ionization energies of the A-center complex and D state relative to the VBE and CBE, respectively [19]. Table II gives the results using $\partial E_g/\partial P \approx 6.9 \pm 0.2$ meV/kbar [16].

The increase in E_D with pressure shows that the D state is becoming a deeper electron trap due to the strong upward shift of the CBE. In contrast, the decrease in E_A implies that pressure tends to destabilize the deep-acceptor ground state of the relevant V_{Zn}-donor complex. Similar results were found for the C_{3v}-relaxed deep-acceptor states of P_{Se} and As_{Se} in ZnSe [13]. The projected pressure at which $E_A \rightarrow 0$ is ~105 kbar for ZnSe:Ga (Fig. 2), but is outside the zinc blende stability range for ZnSe:Cl and the other samples studied [13]. Thus, it might have been possible to detect a deep-to-shallow transition of the A' center in ZnSe:Ga if plastic deformation above 70 kbar were avoided.

Chadi and co-workers proposed (and supported by total energy calculations on DX centers) that deep donorlike antibonding states should respond to pressure like the conduction band mean position [12,18]. They suggest

$$\frac{\partial (E_g - E_{AB})}{\partial P} \approx \frac{1}{8}\left\{\frac{\partial E_g}{\partial P} + 3\frac{\partial E_X}{\partial P} + 4\frac{\partial E_L}{\partial P}\right\}, \quad (4)$$

where E_X and E_L are the X- and L-indirect gaps and E_{AB} is the binding energy of the deep antibonding level. For ZnSe, this implies $\partial E_{AB}/\partial P \sim 3$–$5$ meV/kbar [18,20], marginally similar to $\partial E_D/\partial P \sim 6 \pm 1.0$ meV/kbar in Table II. Hong *et al.* [11] calculate pressure shifts for the deep states of many point defects in zinc-blende solids using a tight-binding model that neglects lattice relaxation and Coulomb splittings. Their results for ZnSe range from -1 to $+2$ meV/kbar (relative to the VBE), e.g., $+0.8$ meV/kbar for the T_2 level of V_{Zn}. This differs somewhat from $\partial E_A/\partial P \sim -2$ to -4 (± 1) meV/kbar in Table II for V_{Zn}-donor complexes.

The above discrepancies suggest that lattice relaxation accounts for a substantial part of the pressure dependence

in E_A and E_D. Since the corresponding deep states participate in PL (unlike the DX center in GaAs), large configuration barriers probably are absent. Therefore a model may apply similar to that given by Watkins [3,5] for the 1.72 eV DAP emission involving C_{3v} distorted isolated $V_{Zn}^{=}$ acceptors in electron irradiated ZnSe. The strong decrease in E_A observed here then indicates that pressure weakens the linear Jahn-Teller relaxation term [21].

A high density of D states could degrade n-type behavior in ZnSe at pressures above 25–30 kbar, where this level emerges from the conduction band. Since similar behavior was found for donors substituting on group II and group VI sites, it is likely that analogous D states exist for other common donors in ZnSe. If our hypothesis for the D state [related to Eq. (2)] is right, the effect at equilibrium should not surpass the 1 atm compensation. This is because electron trapping would proceed via an excited state of the existing A-center (V_{Zn}-donor) complexes, and these are not expected to have a high density [9]. However, if the D state is due to a separate trap, whose density might be increased by adding Te, Mg, etc., the impact on n-type doping in the corresponding alloys could be much larger. In any case, the emergence of the D state is likely to shorten the electron lifetime, especially if lattice relaxation enhances the trapping cross section.

Experiments on Cl doping in ZnSe/ZnTe short-period superlattices show that the electron density drops sharply for an average Te concentration above $x_{av} \sim 20\%$ [22]. A linear interpolation of the CBE with x_{av} would suggest that the offending deep trap lies ~0.12 eV above the ZnSe CBE at 1 atm. This is temptingly close to the projected position of the D level, ~0.15–0.18 eV above the CBE. However, the $ZnSe_{1-x}Te_x$ system exhibits large band gap bowing, which leads to ambiguity in deciding the separate positions of the CBE and VBE vs x. If most of the bowing is actually taken up by the CBE [1], the D level could still be a resonant state in $ZnSe_{0.8}Te_{0.2}$ at 1 atm and, hence, unable to degrade n-type doping.

In summary, the pressure shift rates of the SA bands in Cl- and Ga-doped ZnSe change at 25–30 kbar, from faster then to slower than the band-gap shift. For each dopant, we find that the deep acceptor ground state of the V_{Zn}-donor complex becomes less stable with pressure, and that a deep donorlike state (D) enters the gap. An attractive choice for the D state is an excited state of the V_{Zn}-donor complex. At 1 atm both D levels are well positioned, ~0.15–0.18 eV above the CBE, to degrade n-type doping in ZnSeTe alloys. However, the need for a high density of D states, and the band gap bowing in the ZnSeTe system may prevent this.

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