Compensation of *p*-Type Doping in ZnSe: The Role of Impurity-Native Defect Complexes

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We have examined the possibility that the saturation of the hole concentration observed in the *p*-type doping of ZnSe is caused by the formation of complexes between the substitutional acceptors and charged native defects such as Se vacancies and Zn interstitials. We present a simple model of compensation in which the relevant parameters are computed from first principles. A large lattice relaxation associated with the Se vacancy and the corresponding complex lowers their formation energy significantly. However, the large binding energy of the acceptor–Zn-interstitial complex should make it a more efficient compensator. Under typical growth conditions, our model reproduces the experimentally observed saturation of the hole concentration in the 10^{18} cm^{-3} range.

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Its large band gap and the close matching of its lattice constant to that of GaAs make ZnSe an important material for the development of blue-green diode lasers. Only recently, however, with the use of rf plasma discharge sources of activated nitrogen, has it been possible to achieve a level of *p*-type doping suitable for successful device operation [1]. A problem still hampering further advances is the saturation of the effective acceptor concentration $N_A - N_D$ at approximately 10^{18} cm^{-3} despite the incorporation of nitrogen atoms in excess of [N] = 10^{19} cm^{-3} [2].

A possible explanation for this saturation is the existence of a limit to the solubility of dopants [3]. This argument is supported by the experimental observation [4] of a significantly higher N solubility in ZnTe, a material which does not present *p*-type doping problems. Theoretical calculations [5] have also concluded that the formation energy of a $\mathrm{N_{Te}}$ impurity in ZnTe is lower than that for the $\mathrm{N_{Se}}$ center in ZnSe, leading to an order of magnitude higher nitrogen solubility in ZnTe. Dopant self-compensation through the creation of deep centers [6] and incorporation at an antisite [7] have also been proposed as a reason for the limited doping efficiency of other group-V elements.

In this Letter we consider an alternative possibility: that the observed saturation of the doping level in *p*-type ZnSe arises from the existence of low-energy defect complexes involving the dopant impurity and donor defects such as Se vacancies and Zn interstitials. This model is capable of reproducing the saturation of the hole concentration in the 10^{18} cm^{-3} range with realistic values of its parameters, obtained by first-principles calculations.

The suggestion that the formation of donorlike native defects should be favored in *p*-type doped wide-band-gap semiconductors is based on the premise that their formation energy would be reduced by an amount close to the band-gap energy for every compensated carrier [8]. Despite the appeal of this simple argument, its relevance for the problem of *p*-type doping of ZnSe was questioned after the results of first-principles calculations of defect formation energies led Laks *et al.* [9] to conclude that their concentration would be too low to cause compensation in nearly stoichiometric material.

Two developments have prompted us to reconsider the issue of compensation. The first is our discovery that the doubly ionized Se vacancy (${V_{\mathrm{Se}}}^{2+}$) exhibits a very large lattice relaxation, with a concomitant reduction in its formation energy that makes it the most abundant native point defect in *p*-type ZnSe. The second is the finding that the experimentally observed plateau in the effective acceptor concentration (indicative of zero doping efficiency) can be explained by the existence of complexes in which a negatively charged acceptor impurity is bound to a positively charged donorlike native defect. We have performed first-principles calculations to compute defect formation energies and complex binding energies, and used these values as input for a statistical model of the defect and free-carrier concentration.

Our calculations are based on the local density approximation [10], and employ the first-principles pseudopotential method and a plane-wave basis [11]. In order to keep the computational effort within manageable limits, we place the Zn $3d$ states in the core complex, but account for their sizable overlap with the valence charge density by the introduction of nonlinear core corrections [12]. The resulting scheme has proven reasonably successful in the treatment of systems containing weakly bound d levels [13], in particular for the study of defect formation energies in ZnSe [14]. We use a 32-atom bcc supercell and a plane-wave cutoff of 12 Ry, relaxing up to three atomic shells around individual defects until the Hellmann-Feynman forces are below 0.2 eV/Å.

Considering the crystal as a multicomponent thermodynamic system, the formation energy of a native defect [15] can be written as

$$\Omega = E_s - n_{\mathrm{Zn}}\mu_{\mathrm{Zn}} - n_{\mathrm{Se}}\mu_{\mathrm{Se}} - n_e\mu_e , \qquad (1)$$

where E_s is the calculated total energy of the supercell containing n_{Zn} Zn atoms and n_{Se} Se atoms, and n_e is the number of electrons that have to be transferred from a reservoir at chemical potential (Fermi level) μ_e to the defect to achieve a given charge state. Taking into account the constraints $\mu_{\rm Se} + \mu_{\rm Zn} = E_{\rm ZnSe}$, $\mu_{\rm Se} \leq \mu_{\rm Se}({\rm bulk})$, and $\mu_{\rm Zn} \leq \mu_{\rm Zn}({\rm bulk})$, which represent, respectively, the equilibrium of a pair of atoms with a formula unit of the bulk, and the condition of no precipitation of bulk Se or bulk Zn, the range of variation of the Zn and Se chemical potentials, and hence the stoichiometry of the system can be described by a single parameter λ which varies between zero and one:

$$\mu_{\rm Zn} = \mu_{\rm Zn}({\rm bulk}) - \lambda \Delta H\,, \qquad (2)$$

$$\mu_{\rm Se} = \mu_{\rm Se}({\rm bulk}) - (1 - \lambda)\Delta H\,. \qquad (3)$$

In these equations, ΔH is the heat of formation of ZnSe, which we calculate to be 1.66 eV, in good agreement with the experimental value of 1.65 eV [16]. The formation energy of a defect of charge q thus depends on two parameters,

$$\Omega(\lambda, \mu_e) = \Omega^0 + \lambda(n_{\rm Zn} - n_{\rm Se})\Delta H + q\mu_e\,. \qquad (4)$$

It is customary to refer μ_e to the valence band edge. Then Ω^0 represents the formation energy of the defect under extreme Zn-rich conditions ($\lambda = 0$) in a hypothetical p-type regime for which the Fermi level is at the top of the valence band. In this connection, it should be noted that the treatment of charged defects involves an estimation of the proper lineup of the band structure of the defect supercell with that of the bulk [17]. Particularly for doubly and triply ionized defects, this introduces uncertainties of a few tenths of an eV in the formation energies.

Recently, it has been shown [18] that the As vacancy in GaAs can exhibit a triply ionized state (${V_{\rm As}}^{3+}$) characterized by a large lattice relaxation. We studied the possibility of a similar behavior in the case of the Se vacancy in ZnSe. As Table I shows, there is, in fact, a large relaxation energy (1.6 eV) associated with ${V_{\rm Se}}^{2+}$. The distortion of the lattice structure around the defect is very similar to that around ${V_{\rm As}}^{3+}$, with the neighboring Zn atoms moving outward by 0.51 Å. It is interesting to note (Fig. 1) that $V_{\rm Se}$ is a negative-U defect, but what is more relevant to the problem of compensation of p-type ZnSe is that the large relaxation energy turns ${V_{\rm Se}}^{2+}$ into the donorlike defect with the lowest formation energy (Table I), even below the doubly charged Zn interstitial previously proposed as such by Laks *et al.* [9].

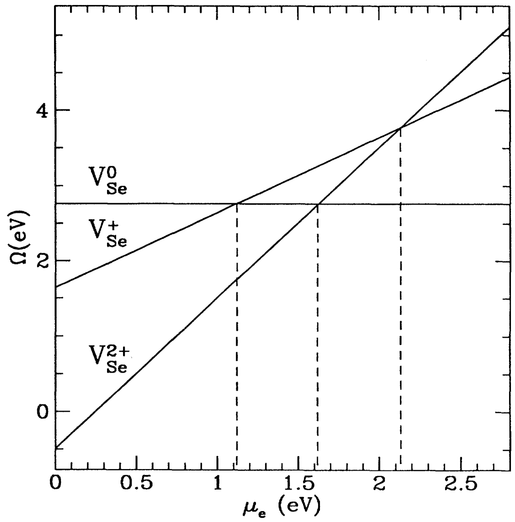

FIG. 1. Formation energies of the three charge states of the Se vacancy as a function of the position of the Fermi level (for $\lambda = 0$). The broken lines indicate the position of the transition levels [$(+|2+) = 2.13$ eV, $(0|2+) = 1.62$ eV, $(0|+) = 1.12$ eV]. Since the ${V_{\rm Se}}^+$ state is never the most stable, the Se vacancy is a negative-U defect.

TABLE I. Formation energies in eV of selected native defects and complexes in ZnSe [see Eq. (4)]. Also given are the relaxation energies, defined as the energy lowering brought about by lattice distortion. For defects containing As, the formation energy corresponds to $\mu_{\rm As} = \mu_{\rm As}({\rm bulk})$ (Ref. [15]).

Defect	Ω^0	Relaxation energy
${V_{\rm Se}}^0$	$2.76 + \lambda\Delta H$	0.15
${V_{\rm Se}}^+$	$1.64 + \lambda\Delta H + \mu_e$	0.14
${V_{\rm Se}}^{+2}$	$-0.49 + \lambda\Delta H + 2\mu_e$	1.61
${\rm Zn}_i{}^{+2}$	$-0.18 + \lambda\Delta H + 2\mu_e$	0.70
${\rm As_{Se}}^-$	$1.22 + \lambda\Delta H - \mu_e$	0.14
$({\rm As_{Se}}\text{-}V_{\rm Se})^+$	$0.46 + 2\lambda\Delta H + \mu_e$	1.56
$({\rm As_{Se}}\text{-}{\rm Zn}_i)^+$	$-0.19 + 2\lambda\Delta H + \mu_e$	0.52

To test whether a low-energy vacancy could by itself play a role in the mechanism of compensation, we used a simple statistical model to compute the hole concentration p in the presence of a hypothetical number N_A of singly ionized acceptor impurities (e.g., ${X_{\rm Se}}^-$, where X is a group-V element) and the resulting concentration of doubly charged vacancies. The position of the Fermi level is determined by the charge neutrality condition,

$$p + 2[{V_{\rm Se}}^{2+}] = N_A\,, \qquad (5)$$

with the equilibrium concentrations given by

$$[{V_{\rm Se}}^{2+}] = N_s \exp[-\Omega(\lambda, \mu_e)/k_BT]\,, \qquad (6)$$

$$p = \frac{2}{\sqrt{\pi}} N_v \mathcal{F}_{1/2}(-\mu_e/k_BT)\,. \qquad (7)$$

Here $N_s = 2.2 \times 10^{22}$ cm^{-3} is the number of Se sublattice sites per unit volume, N_v is the effective valence density of states, and $\mathcal{F}_{1/2}$ is the Fermi-Dirac integral. For a typical growth temperature $T = 600$ K, it is easy to show that a decrease in the doping efficiency starting in the neighborhood of $N_A = 10^{18}$ cm^{-3} can be achieved if $\lambda = 0.4$, that is, under moderately Zn-rich conditions. Experiments, however, show not just a reduced doping efficiency but an eventual saturation of the hole concentration.

A truly null doping efficiency can be explained by the formation of complexes involving negatively charged acceptor impurities ${X_{\rm Se}}^-$ and positively charged vacancies [19]. Although a low formation energy of the native defect is essential, the relevant parameter controlling compensation by complexes is the binding energy E_b in the reaction

$$X_{\mathrm{Se}}{}^{-} + V_{\mathrm{Se}}{}^{2+} \rightleftharpoons (X_{\mathrm{Se}}\text{-}V_{\mathrm{Se}})^{+} + E_b\,. \tag{8}$$

In order to obtain an estimate of E_b we performed a first-principles calculation of the formation energy of the $(\mathrm{As}_{\mathrm{Se}}\text{-}V_{\mathrm{Se}})^{+}$ complex [20] finding (see Table I) a binding energy of approximately 0.3 eV. Figure 2(a) shows that for relatively high doping levels the concentration of such $(X_{\mathrm{Se}}\text{-}V_{\mathrm{Se}})^{+}$ complexes practically equals that of the active dopants, achieving total compensation and effectively pinning the Fermi level. The number of $V_{\mathrm{Se}}{}^{2+}$ defects also saturates as their formation energy is linked to μ_e. Thus the free-carrier concentration levels off despite the continuing incorporation of dopants [Fig. 2(b)] [21].

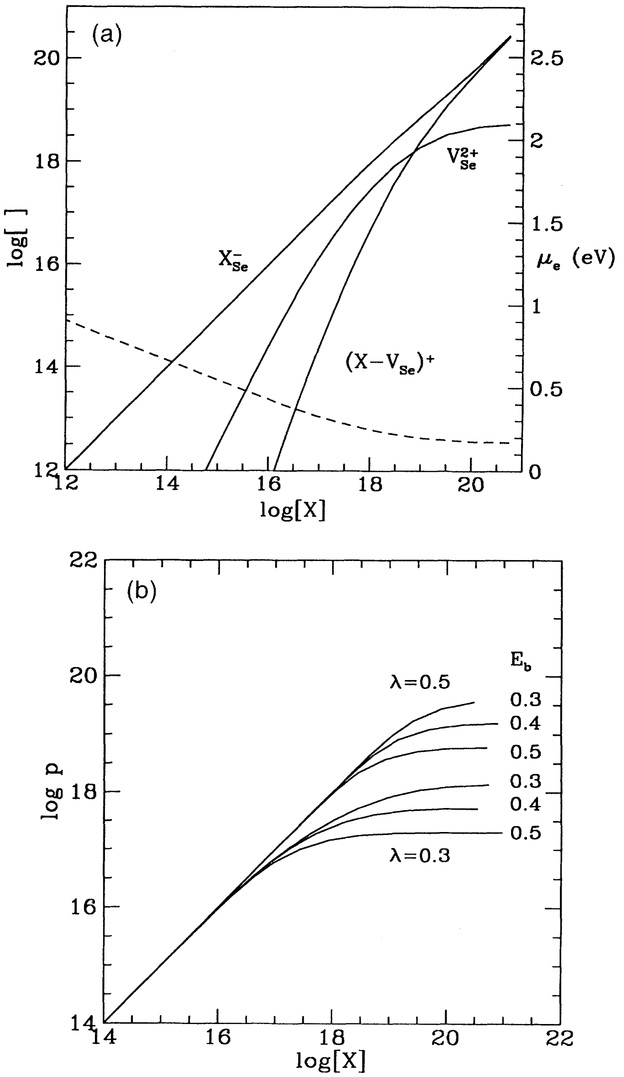

FIG. 2. (a) Dopant acceptor, vacancy, and dopant-vacancy complex concentration (left-hand logarithmic scale) and Fermi level (broken line, right-hand scale) as a function of the total impurity concentration (for $\lambda = 0.3$ and $E_b = 0.3$ eV). (b) Logarithmic plot of the free hole vs total impurity concentration for a range of values of λ and the binding energy E_b of the $(X_{\mathrm{Se}}\text{-}V_{\mathrm{Se}})^{+}$ complex.

The results displayed in Fig. 2(b) correspond to a range of binding energies $E_b = 0.3-0.5$ eV, again under moderately Zn-rich conditions. It is clear that the larger the binding energy, the earlier the plateau in the hole concentration sets in. The vacancy and the impurity are second-nearest neighbors in the complex (which also means that the symmetry is greatly reduced). It would seem reasonable to assume that a complex in which the constituents are closer together will have a larger binding energy. One such complex (suggested in Ref. [3]) is formed by $\mathrm{Zn}_i{}^{2+}$ (Zn interstitial in the tetrahedral T_{Se} site) and $X_{\mathrm{Se}}{}^{-}$. The calculated binding energy (approximately 1.2 eV for X = As) is indeed quite large. Thus, despite the slightly larger formation energy of the Zn interstitial when compared to the Se vacancy, the $(X_{\mathrm{Se}}\text{-}\mathrm{Zn}_i)^{+}$ complex has a lower formation energy than the vacancy-impurity one (see Table I) and is a more efficient compensator: Figure 3 shows that a plateau in p in the 10^{18} cm^{-3} range, very much like those experimentally observed [2], appears for $\lambda \sim 0.7$. Of interest for its experimental identification is that the $(X_{\mathrm{Se}}\text{-}\mathrm{Zn}_i)^{+}$ complex has C_{3v} symmetry.

The actual doping level achieved before the doping efficiency drops to zero depends quite sensitively on the parameter λ, which is determined in practice by the Se:Zn flux ratio and the temperature. A rough estimate for λ can be obtained as follows. For the typical growth conditions (e.g., $P_{\mathrm{Se}}/P_{\mathrm{Zn}} = 2$ in Ref. [22]) an experimental surface phase diagram of ZnSe(100) [23] shows either coexistence of Zn-covered $c(2 \times 2)$ and Se-covered (2×1) reconstructions or only the latter. Then we can use our previous theoretical estimate of the

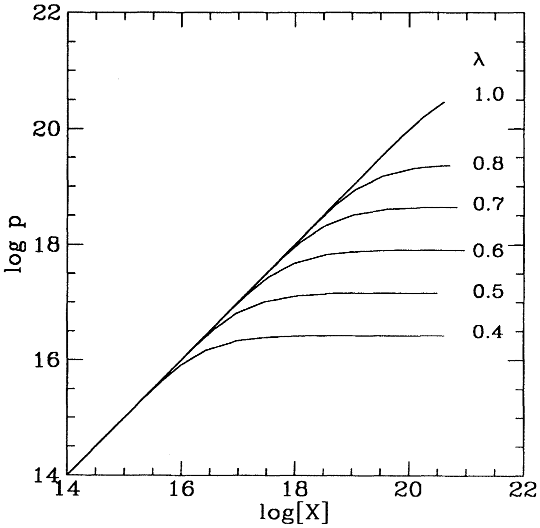

FIG. 3. Logarithmic plot of the free hole vs total impurity concentration for $E_b = 1.2$ eV and a range of values of λ illustrating compensation by $(X_{\mathrm{Se}}\text{-}\mathrm{Zn}_i)^{+}$ complexes.

stability of the Se-covered (2×1) reconstruction [24] to find that $\lambda \gtrsim 0.7$.

Figure 3 suggests that the maximum hole concentration could be easily increased from its current level in the 10^{18} cm^{-3} range ($\lambda \sim 0.7$) by carrying out the growth of ZnSe under more Se-rich conditions (toward $\lambda = 1$). However, it should be kept in mind that the degree of solubility of the acceptor dopant also depends on λ [3], with the most favorable conditions for incorporation being those of a Zn-rich regime ($\lambda \sim 0$). These conflicting requirements might imply that the achievement of high p-type doping levels in ZnSe necessitates a nonequilibrium incorporation of acceptor impurities.

In summary, we have examined the issue of compensation of p-type doping in ZnSe by native defects, proposing that the experimentally observed saturation in the free-carrier concentration is due to the formation of complexes between the acceptor impurities and low-energy donor native defects. The stability of the dopant–Se-vacancy complex is increased by a large lattice relaxation, but the significantly higher binding energy of the dopant–Zn-interstitial complex should make it more abundant. Under the typical equilibrium conditions, our model reproduces the saturation of the effective acceptor concentration in the 10^{18} cm^{-3} range observed experimentally.

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