

Bulk Lattice Instability in II-VI Semiconductors and Its Effect on Impurity Compensation

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From the results of first-principles pseudopotential calculations we identify a new type of low energy lattice instability that is most effective in acceptor passivation in II-VI semiconductors. The instability occurs in the presence of free holes and involves the breaking of *two* host bonds and the creation of a VI-VI dimer bond. The model provides a satisfactory explanation for persistent photoconductivity, its optical threshold, and for the observation of a deep “donor” level in photoluminescence measurements on *p*-doped samples.

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Difficulties in the *p*-type doping of large band-gap II-VI sulfides and selenides were encountered as early as the 1950s [1] and with some notable exceptions persist to the present time. The successful *p*-type doping of ZnSe with a pure N source [2] in 1990 followed by the fabrication of the first blue-green laser diodes [3] has raised hope that problems with other large band-gap II-VI compounds can be similarly solved. For the most part, however, the success with ZnSe has not been duplicated in other II-VI compounds with comparable band gaps. Even for N-doped ZnSe, the hole concentration saturates at $(1-2) \times 10^{18}/\text{cm}^3$, and it is not yet clear whether this is the ultimate doping level or whether higher values can be achieved [4]. The hole concentration drops precipitously with increasing band gap in ZnMgSSe alloys raising doubts as to whether low resistance *p*-type conductance can be obtained in II-VI semiconductors with band gaps larger than in ZnSe [5].

A number of theoretical studies have addressed the fundamental microscopic aspects of doping in wide-band-gap semiconductors. The majority of these studies have dealt with the manner in which dopant solubility [6] or native defects [7,8] such as vacancies, interstitials, and antisites interfere with doping. Laks *et al.* [7] suggested that defect formation energies were too large to explain the doping problems. Including lattice relaxation effects around defects, Garcia and Northrup [8] have recently found that a Se vacancy is the lowest energy native defect in *p*-type ZnSe. The formation energy depends on growth conditions: it is *exothermic* for a Zn-rich environment and is about 0.65 eV for a Se-rich condition. The complexing of the vacancies or interstitials with dopants can substantially reduce the formation energy of these defects [8]. Other studies, particularly our own, have emphasized that, in addition to native defects, large atomic displacements near impurities can play an important and perhaps a dominant role in passivation [9]. The phenomenon of persistent photoconductivity (PPC) recently observed in a N-doped ZnMgSSe alloy [10] is more readily explained by this type of model than with a native defect model, although a more careful study needs to be carried out on lattice defects to check for the possibility of bistability.

In this Letter we examine the effects of lattice relaxation on doping in II-VI semiconductors. The main result of our work is the identification of a new type of low energy lattice instability that is especially effective in acceptor passivation. Unlike previously suggested *DX* or *AX*-like structures [9] that have trigonal symmetry, the new structure has a very low σ_{1h} symmetry. The calculated electronic and optical properties for the new defect are found to be in good agreement with experimental data.

The total-energy calculations were performed using a first-principles pseudopotential approach [11]. Norm-conserving pseudopotentials were generated in the manner of Troullier and Martins [12], and Kleinman-Bylander [13] separable potentials were constructed. The *3d* states of Zn were included in the calculations and a 40 Ry cutoff for the plane wave expansion was used. Partial core corrected pseudopotentials instead of the Zn *3d*-core states (and a 32 Ry cutoff) were utilized in the estimation of the capture barrier between shallow and deep acceptor states. A three-dimensionally periodic 32 atom cell was employed, and the Brillouin zone summations were done with the $\frac{1}{4}(111)$ special *k* point [14]. For pure ZnSe (with no N), the formation energy of the broken-bond state described below was also examined with 64 and 128 atom cells using a 12 Ry cutoff.

The original motivation for considering a large-lattice-relaxation model came from work on *DX* centers in *n*-type AlGaAs alloys [15]. We tested a structurally similar type of lattice relaxation (accompanied by the capture of two holes into a deep state) for As- and P-doped ZnSe and suggested that the problems with *p*-type doping were associated with large atomic relaxations and that N was likely to be immune to such a phenomenon [16]. More detailed theoretical studies have shown that N does prefer to stay in a tetrahedrally coordinated state in ZnSe [17] and in MgSe [18]. The trigonal state with large lattice relaxation in N-doped ZnSe is 0.3 eV higher in energy than the tetrahedral effective-mass state [17]. In principle, N should be an excellent dopant in ZnSe and other II-VI semiconductors. Doping saturation in N-doped ZnSe and the observation of PPC in ZnMgSSe alloys

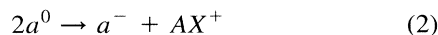
[10] indicate, however, the possibility of other types of instabilities.

One possibility is that the large lattice relaxation instead of occurring at N takes place at some other place in the lattice. For trigonally symmetric distortions along the [111] bond axis leading to the rupture of host bonds we found that the bond breaking energy was significantly reduced in the presence of free holes [19]. For ZnSe, the +2 charged state of the broken-bond state was found to have an energy of 0.3–0.4 eV. However, this state did not give a clear minimum in the total energy and the atoms slowly relaxed back to their ideally bonded positions. In the following, we report on a lower symmetry and lower energy type of bond rupture mechanism that leads to either a stable or a metastable state. The electronic structure for this new defect leads to a much more satisfactory explanation of experimental data.

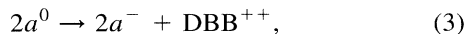
The ideal zinc blende crystalline structure and a new lattice defect labeled as the “double broken bond” (DBB) state are shown in Figs. 1(a) and 1(b), respectively. The symmetry of the DBB complex is σ_{1h} ; i.e., there is a single mirror reflection plane. As can be seen, two Zn-Se bonds are broken and a Se-Se dimer bond is formed. The N impurity maintains a fourfold coordinated geometry, which previous theoretical studies have shown it favors [17,18]. If the N atom of the complex is replaced by a Se atom, the lattice distortion would place one electron in each of the two Zn dangling bonds thereby making the DBB state a double donor. With N present as shown in Fig. 1(b), the complex is only a single donor, which can passivate a second N atom not associated with the complex. The overall passivation reaction can be represented by



where a^0 and a^- denote neutral and negatively charged tetrahedrally coordinated N impurity atoms and $a^- \oplus \text{DBB}^{++}$ is the complex in Fig. 1(b). Denoting the $a^- \oplus \text{DBB}^{++}$ complex by AX^+ for convenience, the passivation reaction



shows more clearly the negative- U character of the passivation and its similarity with the reaction $2d^0 \rightarrow [d^+ + DX^-]$ for donor impurities in III-V alloys [15]. The favorable Coulombic interaction between the positively and negatively charge components of the $a^- \oplus \text{DBB}^{++}$ complex and the reduction of the large bonding strain caused by the N substitutional atom make the reaction in Eq. (1) more favorable than the corresponding one given by



where the two impurities represented by a^- are far from the DBB^{++} state. When N is part of the DBB complex, the total energy is lowered by nearly 0.2 eV (as compared to the situation where N is a more distant neighbor of the impurity). The energy of the broken-bond state in the presence of free holes in the valence band maximum was checked by additional calculations using 64 and 128 atom

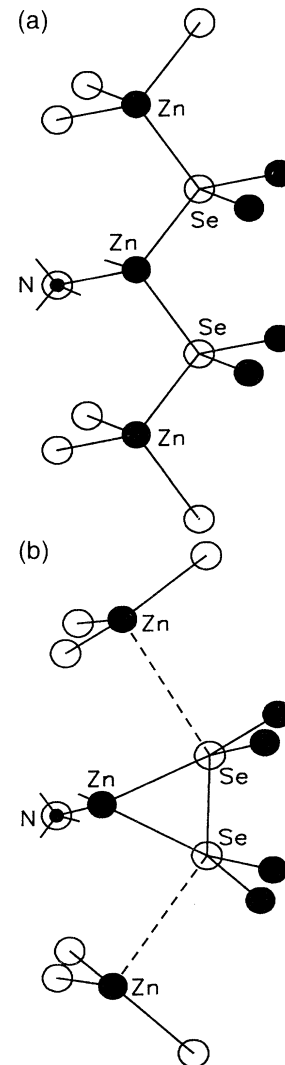


FIG. 1. The ideal zinc blende lattice for ZnSe is shown schematically in (a). The double-broken-bond (DBB) state resulting from the breaking of two Zn-Se bonds and the formation of a Se-Se bond is shown in (b).

cells. The formation energy is found to converge to better than 0.1 eV for a 64 atom cell.

The Se-Se dimer bond length in Fig. 1(b) is calculated to be 2.4 Å; i.e., each Se atom moves by 0.8 Å along a [011] axis. The small size of N makes the dimer bonding easier since the strain energy is released by the short bond length between the common Zn atom of the dimers and the N impurity. The calculated Zn-N bond length of 1.94 Å is 0.07 Å shorter than that for a tetrahedrally coordinated substitutional N. Each of the two threefold coordinated Zn atoms resulting from the lattice distortion is found to undergo a distortion into a nearly planar bonded configuration.

The N-induced AX^+ center in ZnSe has two unoccupied electronic levels in the gap. The lowest energy one is a midgap state that has an antibonding electronic charge

distribution between the two Se atoms as can be seen from Fig. 2(a). Occupation of this level by one electron, e.g., through optical excitation, breaks the Se-Se dimer and restores the two broken Zn-Se bonds to their original state. Once the bonds are restored, the formation of the AX center is prevented by an energy barrier corresponding to the bond breaking energy. This result suggests that in II-VI compounds, where the reaction in Eq. (2) is exothermic, persistent photoconductivity should be observed. The optical threshold E_{opt} for PPC for the DBB state is calculated to be at least 1.1 eV in ZnSe, and if the 2.04 eV calculated gap is expanded to the 2.8 eV experimental value it is about 0.4 eV larger. The 1.1–1.5 eV range for E_{opt} is, by a factor of 2, in better agreement with the 1.65 eV experimental value [10] (for a ZnMgSSe alloy that has a band gap a few tenths of an eV larger than ZnSe) than for any other model we have examined. The energy barrier needed to create the DBB state is calculated to be nearly 0.5 eV.

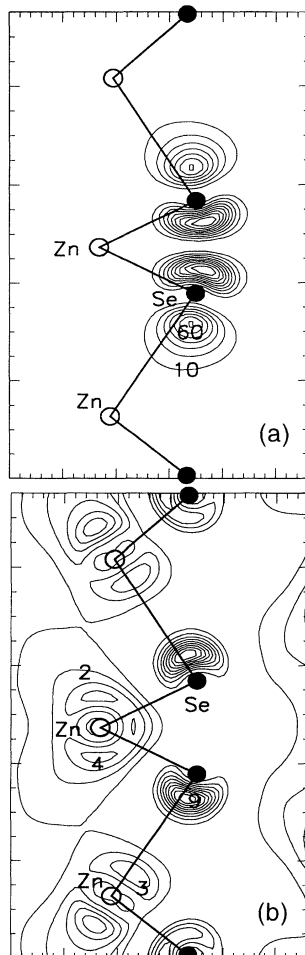


FIG. 2. The electronic charge density for the empty midgap state of the DBB configuration for ZnSe is shown in (a). Electronic excitation into this level destabilized the DBB state. The charge density for the empty “deep donor” state near the conduction band is shown in (b).

For ZnSe, the formation energy of AX centers is endothermic and no significant PPC is expected, in agreement with the experimental data [10]. As in the case of DX centers in III-V alloys, our theory predicts that optical excitation releases *two* holes for each AX^+ that is converted to a tetrahedrally coordinated N. The experimental observation of PPC in N-doped ZnMgSSe provides very strong evidence for bistability in II-VI semiconductors. We believe that the structural model proposed here is the one most appropriate for the explanation of this phenomenon.

The second unoccupied gap level for the AX center has an energy between 50 and 100 meV below the conduction band minimum. Its charge density shown in Fig. 2(b) reveals substantial contribution from the Zn dangling bond orbitals and also from the dimerized Se atoms. This state behaves as a trap for electrons excited into the conduction band minimum. There is experimental evidence from photoluminescence and optically detected magnetic resonance data that a “deep donor” level at 45–55 meV below the conduction band (as compared with 29 meV for the hydrogenic state) occurs upon *p*-type doping in II-VI semiconductors [20]. This state was previously associated with the dangling bonds on Zn neighbors of a Se-site vacancy. Our model, although quantitatively different than a vacancy model, can explain the Zn dangling bond origin of this state.

We have examined the energetics of the reaction in Eq. (2) for N-doped ZnS, ZnSe, ZnTe, and for assumed zinc blende forms of MgS, MgSe, and MgTe. For the latter three compounds the reaction is strongly exothermic, with ΔE in Eq. (2) ranging from -0.3 eV in MgS and MgTe to -0.5 eV in MgSe. This indicates that Mg based II-VI compounds with a high Mg content cannot be doped *p*-type even in the absence of any native defects. The reaction is found to be endothermic by about 0.17 ± 0.1 eV for ZnTe and by nearly 0.1 ± 0.1 eV for ZnSe. The latter energy is substantially below the 0.65 eV value estimated for the lowest energy native defect, i.e., an *isolated* SE vacancy (V_{Se}^{+2}) in ZnSe, under *Se-rich* growth conditions [8,21]. The larger formation energy of the DBB state in ZnTe as compared to ZnSe is consistent with experimental data which show that ZnTe can be *p* doped to extremely high levels [22,23] exceeding in some cases $10^{20}/\text{cm}^3$.

An important question is whether our model can explain doping saturation effects in a II-VI semiconductor such as ZnSe. We have stated that DBB formation is endothermic in ZnSe and at first sight this might indicate that there should be no doping saturation. However, the reaction energy for DBB in Eq. (1) takes the initial ground state of the acceptor to be the a^0 state, i.e., the neutral bound effective-mass state where the hole has a binding energy of about 80–100 meV. This is the proper state to take in the limit of low doping densities. At higher doping levels where the Fermi level drops to the valence band maximum (VBM) or below, the a^0 state in Eqs. (1)–(3) should be replaced by a free hole state at the Fermi level.

This lowers the formation energy of the DBB state and can easily make the reaction exothermic, thereby providing an effective mechanism for doping saturation.

The passivation of N impurities by DBB defects as proposed here is consistent with recent experimental data on the participation of some type of defect complex. Particle-induced x-ray emission studies [24] indicate that N remains on a substitutional site even in heavily doped ZnSe and that Zn and Se atoms are on "slightly distorted" substitutional sites. Local vibrational mode studies also point to the conclusion that N is on a substitutional site [25,26]. Experimental evidence for some type of point defect generation with increasing N concentration in ZnSe has come from a broadening of the Raman spectra with doping and from a larger reduction in lattice constant than can be explained by a shorter Zn-N bond length [27]. As discussed above, the calculated Zn-N bond length for the DBB defect is 0.07 Å shorter than for substitutional N thus providing a possible explanation for the larger than expected lattice constant reduction with doping [28].

The DBB state could be especially important when the covalent bonding radius of the impurity is significantly smaller than the atom it replaces. The Se-Se dimer bond in Fig. 1(b) pushes an adjacent Zn atom towards N, significantly reducing the strain energy in this bond. The DBB state discussed above in connection with acceptor passivation may also be important for donor passivation. In this case the dimer bonds take place between cations (instead of the Se atoms in Fig. 1). The DBB state provides an additional channel for donor passivation, which can be competitive with the usual DX mechanism. We are examining this possibility for halogen donor impurities in several II-VI semiconductors.

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