PHYSICAL REVIEW B VOLUME 50, NUMBER 4 15 JULY 1994-II

First-principles study of antisite and interstitial phosphorus impurities in ZnSe

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(Received 22 April 1994)

The antisite and interstitial phosphorus defects in ZnSe have been studied by pseudopotential total-energy calculations to investigate their roles in the p-type doping problem of ZnSe. Our calculations suggest that the difficulty in p-type doping of ZnSe with phosphorus is caused by the compensation of shallow acceptors by the antisite defects P_{Zn}, which act as triple donors. A microscopic model for two ionization levels of phosphorus acceptors in ZnSe (one shallow at 84±4 meV and one deep at 0.6–0.7 eV) is also proposed. The shallow acceptor level is attributed to a P substituted at a Se site, while the deep acceptor is assigned to the 2+ charge state of an interstitial P atom near the hexagonal interstitial site.

The wide-band-gap semiconductor ZnSe has been the focus of a great deal of technical and theoretical attention for decades due to its potential applications in optoelectronic devices, such as blue light-emitting diodes and blue diode lasers. Among the numerous obstacles which hindered the applications, the most significant was the inability to obtain highly conductive p-type ZnSe. Recently, however, net acceptor concentrations as high as 1.0×10^{18} cm^{-3} have been achieved in ZnSe:N grown by molecular-beam epitaxy using nitrogen free radicals.[1] Using this doping technique, Haase *et al.*[2] and several other groups have succeeded in demonstrating ZnSe-based semiconductor diodes that lase in the blue-green region of the visible spectrum.

In spite of this success in fabricating low-resistivity p-type ZnSe using nitrogen as the dopant, the origin of the doping difficulties remains unclear. While several explanations have been suggested,[3–7] there is no firm evidence for any of them. The most commonly accepted explanation has been that native defects (e.g., Se vacancies or Zn interstitials) which act as donors are activated as a result of the doping, resulting in compensation of the acceptor impurities. However, a recent study by Laks *et al.*[8] indicates that the native-defect self-compensation mechanism alone cannot explain the doping problem. Therefore, a detailed study of the role of impurities is necessary in order to understand this problem.

We have studied phosphorus and nitrogen impurities in ZnSe, using first-principles pseudopotential total-energy calculations, to investigate the problems associated with p-type doping. Our previous calculations[9] have shown that substitutional nitrogen and phosphorus impurities on the Se site form shallow acceptors. In this paper, we extend our calculations to include antisite and interstitial defects. We find that the antisite defect P_{Zn} plays an important role in the p-type doping problem. When the Fermi level is near the valence-band maximum (VBM), the formation energy of ${P_{Zn}}^{3+}$ is comparable to or lower than that of substitutional phosphorus P_{Se}. This suggests that, in the process of p-type doping of ZnSe with phosphorus, the shallow acceptors are compensated by the antisite defects, which can act as triple donors. In contrast, in the case of nitrogen dopants in ZnSe, the antisite defect N_{Zn} is predicted to have a higher formation energy than N_{Se} for the whole range of Fermi level, in good agreement with the successful fabrication of p-type ZnSe material based on nitrogen doping.

In this work, we employ the ultrasoft pseudopotential approach to density-functional theory in the local-density approximation.[10–12] With this approach we include the highly localized Zn $3d$ states in the *valence shell*, still using a plane-wave cutoff of only 25 Ry. A preconditioned conjugate-gradient method[12] has been used to minimize the Kohn-Sham energy functionals at fixed ionic configurations. A 32- or 33-atom bcc supercell was used for the antisite and interstitial defect calculation, respectively. All atoms were fully relaxed according to the calculated Hellmann-Feynman forces on ions in the unit cell.

The formation energy $F(D^Q)$ of a defect system D^Q in charge state Q is a function of both electron chemical potential (or Fermi level) μ_e and atomic chemical potentials μ_{Zn}, μ_{Se}, and μ_P. However, since each defect system contains a P impurity, we can redefine the formation energy and omit μ_P. Furthermore, using the constraint that $\mu_{Zn}+\mu_{Se}$ is fixed by the total energy E_{ZnSe} of the two-atom unit of bulk ZnSe, we obtain

$$F(D^Q)=E(D^Q)+Q(\mu_e+E_v)-N_{Zn}E_{ZnSe}+(N_{Zn}-N_{Se})\mu_{Se}, \quad (1)$$

where $E(D^Q)$ is the total energy of the supercell for the defect system containing N_{Zn} zinc atoms and N_{Se} selenium atoms. The Fermi level μ_e is measured relative to the valence-band maximum E_v. Thus, when the formation energies of different types of defects are compared, we must consider the energies as a function of the Fermi level μ_e and the Se chemical potential μ_{Se}. However, for a specific type of defect, the relative formation energies for different charge states depend only on the Fermi level; the (thermal) ionization levels are the values of the Fermi level at which energies of competing charge states cross. For charged defects, the

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unit cell was implicitly neutralized with a uniform background charge, following standard practice.[13]

We first consider the antisite defect P_{Zn}. With tetrahedral symmetry, the neutral P_{Zn} has a nondegenerate and a threefold-degenerate level in the band gap (not counting spin). The nondegenerate level, which is near the VBM, is fully occupied by two electrons, while the threefold-degenerate level, which forms deep donor level, is partially occupied by a single electron. Thus, we should check whether charge states ranging from 1− to 5− are possible in n-type ZnSe (acceptor behavior), and whether charge states ranging from 1+ to 3+ are possible in p-type ZnSe (donor behavior). Since we are mainly interested in the p-type material, we only consider 0 (neutral) to 3+ charge states here.

Because of its partially filled degenerate level, the neutral antisite defect is found to undergo a Jahn-Teller (JT) distortion by which the P atom moves about 0.2 Å toward one of the four neighboring Se atoms, lowering the symmetry of the defect from tetrahedral (T_d) to trigonal (C_{3v}). The total energy is lowered by 0.16 eV by the JT distortion. For positively charged defects, the JT distortions are not found, as expected from the fact only nondegenerate gap levels are being depleted. However, substantial breathing relaxations (which preserve T_d symmetry) are found with the change of charge state; the bond lengths between the central P and neighboring Se atoms are 2.50, 2.39, and 2.24 Å for 1+, 2+, and 3+ states, respectively. As ${P_{Zn}}^{2+} \rightarrow {P_{Zn}}^{3+}$, the bond length contracts by 0.15 Å, which is large compared to the typical breathing relaxations induced by phosphorus impurities as the charge state changes. For instance, the bond length between the P atom and neighboring Zn atoms contracts by only 0.04 Å as ${P_{Se}}^{1-} \rightarrow {P_{Se}}^{0}$. The present calculation suggests that, because of these strong relaxations, the states ${P_{Zn}}^{1+}$, ${P_{Zn}}^{2+}$, and ${P_{Zn}}^{3+}$ form a "negative-U system." The reaction $2{P_{Zn}}^{2+} \rightarrow {P_{Zn}}^{1+} + {P_{Zn}}^{3+}$ is exothermic by 0.4 eV, so that the 2+ charge state is a metastable state, decaying either to the 1+ or 3+ state depending on the Fermi level. The calculated thermal depth for the 3+/1+ transition is about 0.71 eV.

We turn now to a consideration of interstitial phosphorous defects. Phosphorous can assume two kinds of tetrahedral interstitial sites. One, which we label $P_{int}(T_{Zn})$, is surrounded by Zn atoms; the other, which we denote $P_{int}(T_{Se})$, by Se atoms. In the breathing-relaxed structure (that is, preserving T_d symmetry), the total energy of ${P_{int}}^{0}(T_{Zn})$ is lower by 0.66 eV compared to ${P_{int}}^{0}(T_{Se})$. Since P_{int} at the T_{Zn} site is more stable than that at the T_{Se} site, we consider only $P_{int}(T_{Zn})$. The P interstitial at T_{Zn} site has a threefold-degenerate level in the band gap, and ${P_{int}}^{0}(T_{Zn})$ contains three electrons on the level.

The fact that the 2− and 1− states contain 5 and 4 electrons, respectively, in the threefold-degenerate level in the gap makes the system susceptible to a JT distortion which would split the level into a higher nondegenerate and a lower twofold-degenerate level. For these states, we have found relatively small JT effects. The P atom moves by less than 0.1 Å toward one of the four neighboring Zn atoms, lowering the symmetry of the system to C_{3v}. Comparing to the small relaxation of the nearest-neighbor Zn atoms, we have found large outward relaxations of the six second-nearest-neighbor Se atoms; 0.29 Å for 2−, and 0.22 Å for 1− charge state.

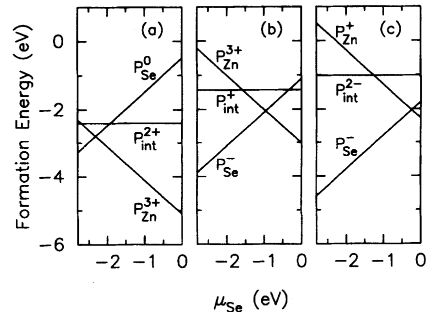

FIG. 1. Formation energies of phosphorus impurities relative to ${P_{int}}^{0}(T_{Zn})$ as a function of the Se chemical potential for three characteristic Fermi levels: (a) 0.0 eV, (b) 0.7 eV, and (c) 1.4 eV above the VBM.

Moving from the 1− to the neutral state leads to an extra JT distortion, thus lowering the symmetry of the system to C_{2v}, since the system reduces its energy by splitting the twofold-degenerate level into a singly occupied higher level and a fully occupied lower level. The JT effect is very small, with the relaxation of each Zn atom less than 0.01 Å. In this charge state, the second-neighbor Se atoms move outward from the P atom by 0.17 Å.

One of the interesting results of the present calculation is that, for the 1+ and 2+ states, the tetrahedral T_{Zn} site is unstable against the sites near the hexagonal interstitial site. In ideal ZnSe, T_{Zn} and T_{Se} sites are separated by 2.45 Å in the [111] direction, and the hexagonal site is midway between these two sites. For the 1+ state, the P atom moves in the [111] direction by about 1.2 Å, almost reaching the hexagonal site. The minimum-energy site is 1.2 eV more stable in energy than the T_{Zn} site. Thus, the P interstitial in ZnSe exhibits some similarities with the Al and self-interstitial defects in silicon, in that the total-energy difference between the hexagonal and tetrahedral site is strongly charge-state dependent.[14]

For the 2+ state, the P atom moves in the [111] direction by about 0.9 Å, passing through the plane formed by three Zn nearest-neighbor atoms. The angle between the [111] axis and the basal bond is calculated to be 95.3°, suggesting that the P and the three Zn's are nearly coplanar. Because of its proximity to the hexagonal interstitial site, we label this defect ${P_{int}}^{2+}(H)$. As a result of the relaxation, the system lowers its energy by 0.63 eV. The calculated thermal depth of the 2+/1+ transition is 0.28 eV. For an optical transition, the transition is so rapid that the instantaneous ionic configuration (that of the 2+ state) is unchanged while it takes place. The energy released as the ions relax back to the stable configuration (that of the 1+ state) after the transition is calculated to be 0.39 eV. Thus, the optical ionization energy of the 2+/1+ transition is found to be about 0.67 eV.

Our results for the total energies of formation of the P_{Se}, P_{Zn}, and P_{int} defects is summarized in Fig. 1. This plot shows the formation energies as a function of μ_{Se} over the range which we estimate to be accessible, based on the heats of formation of bulk Se and bulk Zn. Since different charge states are also considered, Fig. 1 shows the results for three characteristic Fermi levels in p-type material: 0.0 eV, 0.7 eV, and 1.4 eV relative to the VBM.

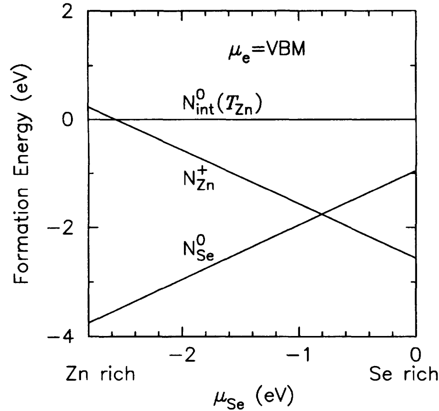

FIG. 2. Formation energies of nitrogen impurities relative to $N_{int}{}^0(T_{Zn})$ as a function of the Se chemical potential for the Fermi level at the VBM.

The calculation suggest that, when the Fermi level is near the valence-band edge as a result of phosphorus doping, the formation energy of the antisite defect P_{Zn} in the 3+ or 2+ charge states is comparable to or lower than that of the substitutional P_{Se} in the neutral or 1− charge state. Therefore, when shallow acceptors ($P_{Se}{}^0$) are created, they are compensated by the donors (P_{Zn}). Since, near the valence-band edge, the stable charge state of the antisite defect is 3+, three acceptors are compensated by a single antisite defect. According to the calculations by Laks *et al.*[8] on the native defects in ZnSe, the concentrations of the native defects are very low (of order 10^{10} cm^{-3} at $T=600$ K in material doped p-type with 10^{18}-cm^{-3} dopants) in stoichiometric ZnSe. Thus, at least for stoichiometric ZnSe, the equilibrium state is most likely determined by the concentrations of the dopant-associated defects. In the equilibrium state for which the concentrations of $P_{Zn}{}^{3+}$ and $P_{Se}{}^{1-}$ are the same order of magnitude, the calculated Fermi level lies at 0.4–0.5 eV above the VBM.[15]

In the equilibrium state, $P_{Zn}{}^{3+}$ and $P_{Se}{}^{1-}$ are the dominant impurities, and small concentrations of $P_{Se}{}^0$ and positively charged $P_{int}(H)$ with other intrinsic defects such as Zn interstitials and Zn vacancies are expected. For $E_F=0.4$ eV, we expect about 10^{16} cm^{-3} un-ionized acceptors ($P_{Se}{}^0$) at $T=600$ K in a material with 10^{19}-cm^{-3} dopants. When the Se chemical potential is near its minimum allowed value, the formation energy of $P_{Se}{}^0$ becomes lower than that of P_{Zn}, indicating that the compensation of shallow acceptors by P_{Zn} would be suppressed. However, in this nonstoichiometric Zn-rich condition, compensation by Zn interstitials acting as double donors is expected instead.[3,8] Thus, the p-type doping would probably not improve.

We have also calculated the formation energies of nitrogen defects in ZnSe, and found that the formation energy of substitutional nitrogen (which forms a shallow acceptor) is lower than the energies of the corresponding nitrogen antisite and interstitial defects. These results suggest that nitrogen should be a more robust acceptor than phosphorus. The relative formation energies of nitrogen impurities when the Fermi energy is at the VBM is shown in Fig. 2. Details of the nitrogen defect calculations will be published elsewhere.

To date, photoluminescence studies of P-doped ZnSe have revealed two kinds of phosphorus acceptor ionization energies. One is a deep center with an ionization energy of 0.6–0.7 eV,[16–19] and the other is a shallow acceptor at 84±4 meV.[19] The origins of the shallow and especially the deep acceptor remain unclear. Watts and co-workers[16,17] suggested that the origin of the deep center was a P ion substituted at a Se site (P_{Se}) which induced a JT distortion to form a deep-acceptor center whose symmetry was lowered from T_d to C_{3v} by the distortion. They estimated that the bond length between the P atom and one of the four nearest-neighbor Zn atoms was increased by ~ 0.5 Å, such that the P and other three Zn's tend toward an almost coplanar arrangement, with an angle of 96° between the axial and basal bonds. Our previous calculation,[9] which predicted the ionization energy of substitutional P acceptors in ZnSe to be $\lesssim 0.1$ eV, supports the existence of a shallow acceptor state associated with substitutional P impurity in ZnSe. However, our results were not consistent with the assignment of the deep acceptor center to substitutional P_{Se} as proposed by Watts and co-workers.

Guided by the present calculation and the experimental results of Watts and co-workers[16,17] we propose a model in which the shallow acceptor level is due to substitutional P_{Se}, while the deep acceptor level is ascribed to the 2+ charge state of the P interstitial near the hexagonal site, $P_{int}{}^{2+}(H)$. Several pieces of information suggest that the latter defect can be a good candidate for the deep acceptor center observed by Watts and co-workers. First, $P_{int}{}^{2+}(H)$ is an electron paramagnetic resonance (EPR) -active deep center, which is consistent with the observation of a strong EPR signal by Watts *et al.*[16] We find it to have a nondegenerate half-occupied level near the bottom of the band gap, with the hole in this level strongly localized by a large lattice distortion. Second, the ionization levels of the defects are in good accord with experiment. The calculated optical depth of 0.67 eV agrees with the experimental depth of 0.6–0.7 eV. Reinberg *et al.*[17] found that the 1.91-eV luminescence thermally quenches with a thermal activation energy of 0.3 eV, consistent with our calculated thermal depth of 0.28 eV. Third, the ionic structure of the $P_{int}{}^{2+}(H)$ is actually rather similar, in many ways, to the structure proposed by Watts and co-workers.[16,17] Both the $P_{int}(T_{Zn})$ and P_{Se} defects start with four equidistant Zn neighbors to the P in the high-symmetry state. According to our calculation, the angle between the [111] axis and the basal P-Zn bonds relaxes to 95.3°, which is quite similar to the 96° estimated by Watts and co-workers. Of course, there is a significant difference in that we find the relaxation to be so large for $P_{int}{}^{2+}(H)$ that the P atom passes through the plane formed by the three neighboring Zn atoms. Thus, perhaps the complement of 95.3° should really be compared with the 96°. However, since the structure of Watts and co-workers was extracted from a configuration coordinate model that turned out to be doubtful,[18] we do not believe this discrepancy is very serious.

Perhaps the most serious problem with our assignment of the EPR center is that it appears to conflict with the conclusion of Watts *et al.*,[16] based on their observed g values, that the defect structure is derived from a threefold set of p states in the configuration p^5. Our structure derives, instead, from a p^1 configuration of $P_{int}{}^{2+}(T_{Zn})$. However, the argument in

favor of p^5 over p^1 seems to rest on an assumption about the sign of the spin-orbit interaction, which may be anomalous for interstitial defects. Moreover, our relaxation is sufficiently large that the perturbation analysis used may not be valid. In the EPR spectrum, Watts and co-workers observed small "satellites" arising from the interaction of six Se nuclei with the applied magnetic field. For the field along a [111] axis, these were divided into two groups of three equivalent nuclei. The assignment P_{Se} of Watts and co-workers for the EPR center fails to explain these "satellites" fully, as the substitutional P has 12 next-nearest Se neighbors. However, ${P_{int}}^{2+}(H)$ has six next-nearest neighbor Se atoms, divided into two groups of three Se atoms due to the symmetry-lowering distortion. Thus, our assignment appears to be more consistent with the observed spectrum.

In summary, we have performed pseudopotential total-energy calculations of antisite and interstitial phosphorus defects in order to study their role in the p-type doping problem of ZnSe. The results indicate that the difficulty in p-type doping of ZnSe with phosphorus dopants is most likely caused by compensation of the shallow substitutional P_{Se} acceptors by antisite P_{Zn} donors. In the case of nitrogen, the formation energy of the antisite defect is higher than that of the shallow acceptor, and thus such compensation would not be expected. Finally, we propose a model for two acceptor levels associated with P impurities in ZnSe: a shallow acceptor level due to substitutional P_{Se} and a deep acceptor level associated with the $2+$ charge state of an interstitial P atom near the hexagonal site $[{P_{int}}^{2+}(H)]$. This model appears to be in good accord with available spectroscopic information, provided that our unorthodox assignment of the deep acceptor level can be shown to be quantitatively consistent with the EPR experiment of Watts and co-workers. We hope to have stimulated future work to investigate this point more closely.

This work was supported by NSF Grant No. DMR-91-15342. Cray YMP time was provided by the National Center for Supercomputing Applications under Grant No. DMR920003N.

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