PHYSICAL REVIEW B **72**, 075208 (2005)

Photoinduced cation interstitial diffusion in II–VI semiconductors

Gustavo M. Dalpian and Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

(Received 20 May 2005; published 16 August 2005)

The electronic structure, stability, and chemical trend of cation interstitials in II–VI semiconductors are studied through ab initio methods. We find that interstitials in the neutral charge state are more stable in the tetrahedral interstitial site near the cation (T_C), whereas in the $(2+)$ charge state, they are more stable near the anion (T_A). This bistability is explained through the Coulomb coupling and energy-level repulsion in the two different interstitial sites. We show that the diffusion energy barrier changes when the defect charge state changes. We suggest that if electrons or holes are taken from the defect level by light, changing its charge state, the interstitial atom will be able to diffuse almost spontaneously due to a reduced diffusion barrier. These results can help unravel the nature of the recently observed photoinduced migration of interstitials in II–VI semiconductors.

DOI: 10.1103/PhysRevB.72.075208 PACS number(s): 61.72.Ji, 71.55.Gs, 66.30.Lw

I. INTRODUCTION

Photoinduced atomic relaxation of impurities in semiconductor compounds plays an important role in determining the doping limit and stability of semiconductor devices.[1–4] Some of the famous examples, such as the DX-like[2,5] or EL2-like[6–8] impurity centers, have been studied extensively. Recently, in a series of electron paramagnetic resonance (EPR) and optically detected EPR studies, Chow and Watkins revealed that Zn interstitials in ZnSe can stay either on a T_d site surrounded by four nearest-neighbor anions (denoted as T_A) or on a T_d site surrounded by four nearest-neighbor cations (denoted as T_C).[9] In their study the interstitial defects were created by 2 MeV electron irradiation at cryogenic temperatures. They observed that the interstitials can be made to hop back and forth between the two sites by optical excitation. This is an important observation because it is known that a cation self-interstitial is one of the most important intrinsic defects that limits p-type doping.[1] Furthermore, because these defects are highly mobile, it also plays an important role in understanding the degradation mechanism in II–VI semiconductor devices.[10]

However, the mechanism for this optically enhanced migration of Zn_i in ZnSe is not well understood. One explanation proposed by Chow and Watkins[9] is that Zn_i can capture an electron into an excited p state, forming an electronic configuration $4s^2 4p^1$. This would induce a Jahn-Teller distortion, which could provide the initial "kick" to make the interstitial diffuse. The possibility of a DX-like behavior is also suggested. Another possibility would be a reduced or vanishing diffusion barrier in a different charge state for the defect.[11] Although interesting, these conjectures have not been proven experimentally nor theoretically.

In this paper, we study the defect properties of cation self-interstitial Zn_i in ZnX ($X=O$, S, Se, and Te) semiconductor compounds. We calculate their formation energies, transition energy levels, and diffusion energy barriers at different charge states and discuss the chemical trends of Zn_i in these materials. We find that in ZnSe, the light-enhanced diffusion of cation interstitials could, in principle, be explained by a nearly barrierless diffusion path between two charge-dependent minima. In the neutral charge state, the most stable position for the interstitial is at the T_C site, and there is usually a high barrier for it to diffuse into the T_A site. In the double positively charged state, the interstitial is more stable at the T_A site, and the diffusion barrier into the T_C site is highly reduced. Shining light on the sample can change the charge state of the defect, resulting in a diffusion of Zn_i from one metastable site to the other more stable site. This observation is quite general in most II–VI semiconductors and is not limited to self interstitials.

II. CALCULATION METHODS

The calculations in this study were performed using the density-functional theory[12,13] and ultrasoft pseudopotentials,[14] as implemented in the VASP code.[15] We used the local density approximation (LDA) for the exchange-correlation potential.[13] The Zn $3d$ states are treated as valence states. The cutoff energies are 209 eV for ZnS, ZnSe, and ZnTe and 396 eV for ZnO. The Brillouin zone integration for the charge density and total energy calculations are performed using ten special k points for the zinc-blende[16] structure and equivalent k points for the larger supercells.[17] The calculated lattice parameters for ZnO, ZnS, ZnSe, and ZnTe are, respectively, 4.467, 5.303, 5.571, and 5.999 Å. We use the zinc-blende structure for all the materials, and all the internal structure parameters were fully relaxed.

The defect calculations[18] are modeled by setting the interstitial atom in the center of a periodic 64-atom supercell. For the charged state, a uniform background charge is added to keep the charge neutrality in the supercell. The formation energy of a cation interstitial defect α in a q charge state $[\Delta H_f(\alpha,q)]$ is calculated using the following equation:[19–21]

$$\Delta H_f(\alpha,q) = \Delta E(\alpha,q) - \mu_c + qE_F, \tag{1}$$

where $\Delta E(\alpha,q) = E(\alpha,q) - E(\mathrm{host}) - E(c) + q\epsilon_{\mathrm{VBM}}$ (where VBM is valence band maximum). Here, $E(\alpha,q)$ is the total energy of the supercell with defect α in charge state q; $E(\text{host})$ is the energy of the supercell without the defect; $E(c)$ is the energy of the cation (Zn) in its metallic ground state; and ϵ_{VBM} is the energy of top of the valence band. In Eq. (1), μ_c is the chemical potential of the cation (to be zero at the metallic phase) and E_F is the Fermi energy (to be zero at VBM). The VBM for charged states is corrected by aligning the average potential in a region far from the defect. The transition energy level $\epsilon(q,q')$ is the Fermi energy, at which the defect in charge states q and q' have the same formation energy, i.e.,

$$\Delta\epsilon(q,q') = [\Delta E(\alpha,q) - \Delta E(\alpha,q')]/(q'-q). \tag{2}$$

Our calculated band gaps at the special k point are 2.06, 3.17, 2.48, and 2.01 eV, respectively, for ZnO, ZnS, ZnSe, and ZnTe, which are smaller than the experimental band gaps of 3.35, 3.78, 2.82, and 2.39 eV. To correct this well-known LDA band-gap error, we add a constant energy to the conduction-band minima (CBM), equal to the difference between the experimental and calculated band gaps. We also assumed that the defect level has mostly the CBM character and thus shifts by the same amount as the CBM.[21] Defect formation energies are also corrected: for neutral defects, as there are two electrons occupying the level in the gap, the formation energy will be corrected by two times the shift of the CBM. For single positively charged defects, it will be corrected by one time the shift of the CBM, whereas for double positively charged defect, there will be no change in the formation energy because the energy level in the gap is empty. We have tested the above assumptions by increasing the band gap through pressure. We find that, indeed, the difference of single-electron levels of Zn$_i$ at T_A and T_C is not sensitive to the band-gap increases under pressure.

III. RESULTS AND DISCUSSION

We first calculate the formation energies of cation interstitial point defects at high-symmetry T_A and T_C sites for ZnO, ZnS, ZnSe, and ZnTe in different charge states. The formation energies at $\mu_{\text{cation}}=0$ and $E_F=0$ for these defects are given in Table I. To obtain the results at the anion-rich limit ($\mu_{\text{anion}}=0$), one needs to subtract the formation energies of the II–VI compounds from the value shown in Table I. Our calculated formation energies for ZnO, ZnS, ZnSe, and ZnTe are −3.45, −2.04, −1.39, and −0.80 eV, respectively.

We have observed the following chemical trends: (i) for ZnS, ZnSe, and ZnTe in the neutral charge state, the interstitial defect is more stable at the T_C site. The stability (the energy difference between the T_C and T_A sites) decreases as the ionicity increases from ZnTe to ZnSe to ZnS. (ii) for the (2+) charged state, the interstitial defect is always more stable at the T_A site. The stability increases when the ionicity increases. (iii) For the single (+) charged state, it follows the same trend as in the neutral charged state, but the energy differences between the T_C and T_A sites are much smaller than those in the neutral charge state.[22]

TABLE I. Formation energies for interstitial defects at $\mu_{\text{cation}}=0$ and $E_F=0$. T_A means a tetrahedral interstitial near the anion and T_C near the cation. Formation energies are in electron volts. The numbers in the parentheses are the equilibrium nearest-neighbor Zn$_i$-anion (cation) bond lengths. The calculated ideal cation-anion bond lengths for pure compounds are 1.934, 2.296, 2.412, and 2.598 Å, respectively, for ZnO, ZnS, ZnSe, and ZnTe. All distances are in angstroms.

	ZnO	ZnS	ZnSe	ZnTe
$T_A(0)$		5.18 (2.529)	3.91 (2.632)	3.38 (2.765)
$T_A(+)$		2.41 (2.406)	1.86 (2.532)	1.79 (2.694)
$T_A(2+)$	0.16 (1.921)	−0.52 (2.314)	−0.27 (2.449)	0.35 (2.652)
$T_C(0)$		4.89 (2.402)	3.50 (2.478)	2.83 (2.604)
$T_C(+)$		2.38 (2.461)	1.73 (2.545)	1.59 (2.668)
$T_C(2+)$	0.85 (2.284)	0.05 (2.520)	0.17 (2.604)	0.65 (2.707)

ZnO is a particular case and different from the other ZnX compounds. We find that Zn$_i$ in ZnO is only stable in the (2+) charge state.[20] This is because the conduction band minimum state of ZnX contains a significant amount of anion s character. Because the O s level is very low in energy, the CBM of ZnO is also very low in energy. Because of this, the defect levels created by Zn$_i$ in ZnO are above the CBM. Consequently, the interstitial will be stable only in the (2+) charge state, and it will prefer to be located in the T_A interstitial site.

These general chemical trends can be understood as follows. In the neutral charge state, two defect electrons are localized at the interstitial site. To reduce the Coulomb repulsion between the electrons, the interstitial would prefer to be at a site with fewer electrons, thus it is more stable at the T_C site. On the other hand, when the interstitial is (2+) charged, it will prefer to be at a site with more electrons to enhance Coulomb binding, thus it is more stable at the T_A site.

The strong Coulomb interaction between Zn$_i$ and the host elements is also apparent by studying the nearest-bond-length variation at different sites and charge states (Table I). We observed that when one changes from the neutral to the (2+) charge state, at a T_A site, the Zn$_i$-anion distance decreases, whereas at the T_C site, the Zn$_i$-cation distance increases. This is because the anion is negatively charged. As the charge state of Zn$_i$ becomes more positive, the Zn$_i$-anion bond length decreases to enhance the Coulomb attraction. On the other hand, the cation is positively charged; as the charge state of Zn$_i$ becomes more positive, the Zn$_i$-cation bond length increases to reduce the Coulomb repulsion.

To further understand these chemical trends, in Fig. 1 we plot the single-particle levels introduced by the neutral defects. As we can see from these energy levels, at the T_C site the defect level couples more to the empty cation conduction-band states above it, so its level is lower than that at T_A site, where it couples more to the occupied anion valence states below.[23] In the neutral charge state, as this defect level is doubly occupied for ZnS, ZnSe, and ZnTe, the T_C site will have lower energy because the T_C energy level is lower. For the (2+) charge state, these levels are empty, thus the T_A site is more stable because the coupling between the occupied host states and the empty defect level lowers the energy of the host energy levels. For ZnO it is always more

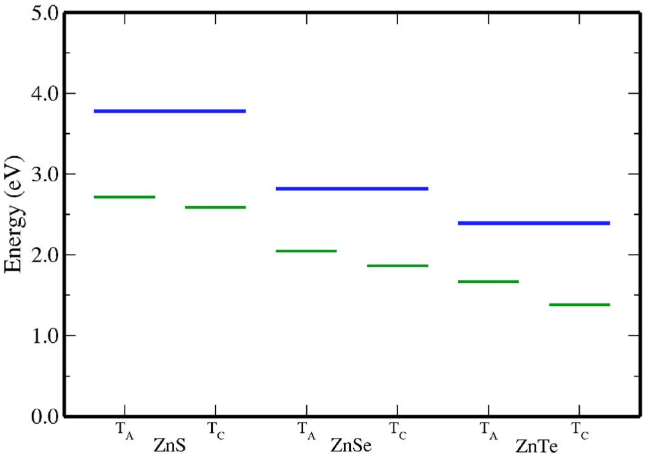

FIG. 1. (Color online) Single-particle electron energy states for interstitial defects in II–VI compounds. The energy levels (thin lines) are for neutral defects. T_A means a tetrahedral interstitial near the anion and T_C near the cation. The thicker lines represent the conduction-band minima of each material.

stable at the T_A site because it can only exist in the (2+) charge state.

In Fig. 2 we show the calculated transition energy levels for Zn_i in ZnX compounds. The energy levels are plotted in an absolute scale. The valence band offsets in this figure were taken from Ref. 24; the conduction-band offsets are obtained by adding experimental band-gap differences to the valence-band offsets. For ZnS, ZnSe, and ZnTe, due to the bistability of Zn_i at the different charge states, we find that the (+) charged state is not stable at equilibrium. When Fermi energy increases, Zn_i will transfer directly from the (2+) charge state to the neutral charge state, i.e., they are negative-U systems. Our calculated U is very small for ZnTe, whereas for ZnS and ZnSe, we found $U=-0.39$ eV and $U=-0.23$ eV, respectively.

The results above show that the cation interstitial has charge-induced bistability in these II–VI semiconductors; thus, under optical excitation, when the charge state of the defect changes, it can hop from one equilibrium position to another. To explain this effect, we calculated the diffusion barrier of these impurities in different charge states. The diffusion path is a straight line between TA and T_C along the ⟨111⟩ direction, passing through the hexagonal site (H). In these calculations, we fixed the position of the interstitial atom and of an atom located far from it. All the other atoms were allowed to relax. We used five intermediate positions in order to get the diffusion barriers. In Fig. 3 we show the variation of the formation energy as the interstitial atom moves. It is easy to see from the figure the most stable interstitial sites for different charge states. In Table II we give the calculated diffusion barriers for all systems in different charge states. As the charge state changes from (0) to (+) to (2+), the diffusion barrier increases when starting from the T_A site, but decreases when starting from the T_C site. Furthermore, the diffusion barrier increases with the ionicity when starting from the T_A site, but decreases when starting from the T_C site. These trends are consistent with the energy

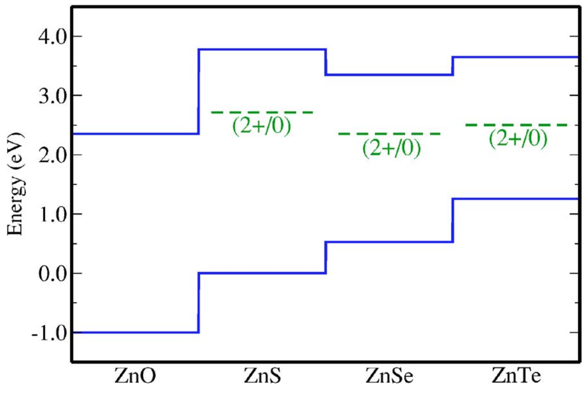

FIG. 2. (Color online) Transition levels of Zn_i in ZnX compounds. The transition level for ZnO is inside the conduction band. We plotted the energy level in an absolute scale using the calculated valence-band offsets from Ref. 24.

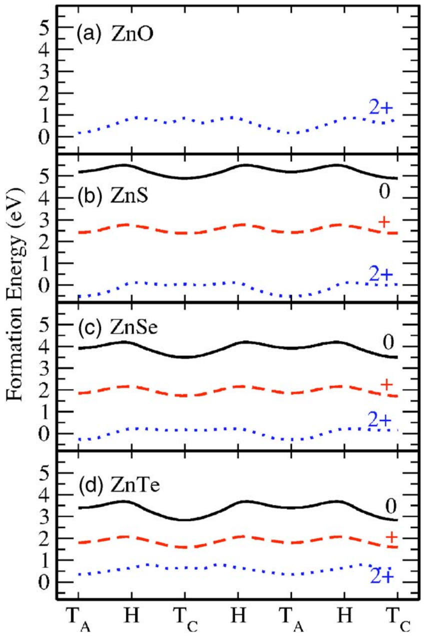

FIG. 3. (Color online) Diffusion barriers for different charge states in the studied materials. The formation energies are calculated at $\mu_{\mathrm{cation}}=0$ and $E_F=0$.

TABLE II. Calculated diffusion barriers for different configurations and charge states.

Starting point	Charge state	ZnO	ZnS	ZnSe	ZnTe
T_A	(0)		0.27	0.24	0.24
T_A	(+)		0.33	0.29	0.27
T_A	(2+)	0.68	0.63	0.49	0.45
T_C	(0)		0.56	0.65	0.80
T_C	(+)		0.36	0.42	0.47
T_C	(2+)	0.00	0.06	0.05	0.15

variations of these defects. As the formation energy of the defect at the starting point increases, the energy barrier decreases.

Our results indicate that the energy barrier for the cation interstitial self-diffusion can be relatively small, which is consistent with the observation that these defects are quite mobile. They could also explain some of the experimentally observed photoinduced transitions between the two interstitial defects. Taking ZnSe as an example, for *p*-type or intrinsic samples, the Zn_i is more stable in the T_A site with a $(2+)$ charge state. The energy barrier to move from the T_A site to the metastable T_C site is 0.49 eV. When light shines on the sample, one or two electrons can be excited to the defect level either directly or through the conduction bands, thus Zn_i can change to $(+)$ or neutral charge states. Our calculations show that at $(+)$ or neutral charge states the T_C site is more stable, therefore Zn_i will hop from the T_A to T_C site with reduced energy barriers of 0.29 and 0.24 eV, respectively. On the other hand, for an *n*-type sample with the Fermi energy close to the CBM, the stable equilibrium structure for Zn_i is at the T_C site with a neutral charge state. The energy barrier to move from the T_C site to the metastable T_A site is 0.65 eV. When light shines on the sample, one or two electrons can be excited from the Zn_i defect level to the conduction band, and Zn_i can change to $(+)$ or $(2+)$ charge states. Our calculations show that at a $(2+)$ charge state, the T_A site is more stable; therefore, Zn_i will hop from the T_C to the T_A site with an energy barrier of about only 0.05 eV (i.e., this process can occur almost spontaneously). This mechanism can explain why the Zn interstitial moves under illumination in ZnSe. Furthermore, although our discussion above is for ZnSe, we expect that the behavior of photoinduced cation interstitial diffusion should also occur in the other II–VI compounds (e.g., CdX).[19]

Experimentally, Zn_i is observed in ZnSe by optically detected electron-paramagnetic reasonance (ODEPR) when the Zn_i is at $(+)$ charge state. Although we have shown that the $(+)$ charge state is not stable at equilibrium, it can exist under nonequlibrium condition, such as in ODEPR, when Zn_i does not have enough time to reach equlibrium. Using our calculated results in Table I and Eq. (2), we find that for ZnSe the $(+/2+)$ transition for Zn_i at the T_A site is 0.69 eV below the CBM, whereas at the T_C site, the level is at 1.26 eV below the CBM. This is consistent with the experimental values of 1.0 and 1.6 eV below the CBM, respectively, especially regarding the energy separation between the two levels at the two different interstitial sites.[9] However, we also want to point out that although we have shown the existence of bistability and reduced diffusion barriers for different charge states, and proposed that this mechanism should be important to understanding the observed photoinduced migration in ZnSe, there are still some discrepancies between our calculated values and the experimental data. For example, we find that at a $(+)$ charged state Zn_i is more stable at the T_C site, whereas the experimental analysis suggests that it is more stable at the T_A site. Further experimental and theoretical work is needed to clarify these discrepancies.

IV. SUMMARY

We have studied the electronic structure and stability of Zn interstitial defects in II–VI semiconductors to provide insights into the observed photoinduced migration of interstitial Zn in ZnSe. Our results show that, in the neutral charge state, the more stable site for the interstitial is near the cations, whereas for the $(2+)$ charge state, it is near the anions. Similar behavior is also expected for other materials, such as III–V semiconductors. This bistability is explained through the Coulomb coupling and energy-level repulsion in the two different interstitial sites. We show that the diffusion energy barrier changes when the defect charge state changes and suggest that this is the origin of the experimentally observed photoinduced migration of the interstitials. We expect that this photoinduced enhancement of interstitial defect migration should also occur in other II–VI and III–V compounds.

ACKNOWLEDGMENT

The work at NREL is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. DE-AC36-99GO10337 to NREL.

---

[1] S. B. Zhang, S.-H. Wei, and A. Zunger, J. Appl. Phys. **83**, 3192 (1998).

[2] D. J. Chadi, Phys. Rev. Lett. **72**, 534 (1994); C.-H. Park and D. J. Chadi, Phys. Rev. B **52**, 11884 (1995).

[3] J. Nisilaa, K. Saarinen, P. Hantojarvi, A. Suchocki, and J. M. Langer, Phys. Rev. Lett. **82**, 3276 (1999).

[4] R. Biswas and Y. P. Li, Phys. Rev. Lett. **82**, 2512 (1999).

[5] F. J. Espinosa, J. Mustre de Leon, S. D. Conradson, J. L. Pena, and M. Zapata-Torres, Phys. Rev. Lett. **83**, 3446 (1999).

[6] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1999).

[7] J. Dabrowski and M. Scheffler, Phys. Rev. Lett. **60**, 2183 (1988).

[8] G. A. Baraff and M. A. Schluter, Phys. Rev. B **45**, 8300 (1992).

[9] K. H. Chow and G. D. Watkins, Phys. Rev. Lett. **81**, 2084 (1998);Phys. Rev. B **60**, 8628 (1999).

[10] S. Guha, J. M. DePuydt, M. A. Hasse, J. Qiu, and H. Cheng, Appl. Phys. Lett. **63**, 3107 (1993).

[11] A. M. Stoneham, Rep. Prog. Phys. **44**, 1251 (1981).

[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[13] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[15] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); G. Kresse and J. Furthmller, *ibid.* **54**, 11169 (1996).

[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[17] S. Froyen, Phys. Rev. B **39**, 3168 (1989).

[18] S.-H. Wei, Comput. Mater. Sci. **30**, 337 (2004).

[19] S.-H. Wei and S. B. Zhang, Phys. Rev. B **66**, 155211 (2002).

[20] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[21] S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
[22] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blochl, and S. T. Pantelides, Phys. Rev. B **45**, 10965 (1992).
[23] R. W. Janse, D. S. Wolde-Kidane, and O. Sankey, J. Appl. Phys. **64**, 2415 (1988).
[24] S.-H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).