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Bistability of Cation Interstitials in II-VI Semiconductors

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ABSTRACT

The stability of cation interstitials in II-VI semiconductors is studied using *ab initio* methods. We find that interstitials in the neutral charge state are more stable in the tetrahedral interstitial site near the cation, whereas in the (2+) charge state, they are more stable near the anion. The diffusion energy barrier changes when the defect charge state changes. Therefore, if electrons/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.

1. Objectives

Recently, Chow and Watkins¹ revealed that cation interstitials in II-VI semiconductors can stay either on a tetrahedral site surrounded by four nearest-neighbor anions (denoted as T_A) or on a tetrahedral site surrounded by four nearest-neighbor cations (denoted as T_C). They observed that the interstitials could be made to hop back and forth between the two sites by optical excitation. This is an important observation because it is known that cation self-interstitials are one of the most important intrinsic defects that limit p-type doping in semiconductors. Furthermore, because the interstitials are highly mobile, they also play a crucial role in understanding the degradation mechanism of II-VI semiconductor devices such as CdTe solar cells.

In this work, we study the defect properties of cation self-interstitial Zn_i in ZnX ($X= O, S, Se, \text{ and } Te$) 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 materials². We find that the light-enhanced diffusion of cation interstitials can be explained by a nearly barrier-less 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 (2+) 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 behavior is found to be quite general in most II-VI semiconductors such as in CdTe.

2. Technical Approach

The calculations in this study were performed using the local density approximation (LDA) and ultrasoft pseudopotentials, as implemented in the VASP code².

The calculated lattice parameters for ZnO, ZnS, ZnSe, and ZnTe are, respectively, 4.467 Å, 5.303 Å, 5.571 Å, and 5.999 Å. We use the zinc-blende structure for all the materials, and all the internal structure parameters are fully relaxed. The defect calculations are modeled by putting 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.

Our calculated band gaps at the special \mathbf{k} point are 2.06 eV, 3.17 eV, 2.48 eV, and 2.01 eV, respectively, for ZnO, ZnS, ZnSe, and ZnTe, which are smaller than the experimental band gaps of 3.35 eV, 3.78 eV, 2.82 eV, and 2.39 eV. To correct this well-known LDA band gap error, we add a constant energy to the conduction band minimum (CBM), equal to the difference between the experimental and calculated band gaps. We also assume that the defect level has mostly the CBM character, and thus shifts by the same amount as the CBM. Defect formation energies are then corrected for neutral and single positively charged defects.

3. Results and Accomplishments

We first calculated the formation energies of cation interstitial point defects at T_A and T_C sites for ZnO, ZnS, ZnSe, and ZnTe in different charge states. The results are shown in Table 1. We observed the following chemical trends. (1) 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. (2) For the (2+) charged state, the interstitial defect is always more stable at the T_A site. The stability increases when the ionicity increases. (3) For the single (+) charged state, the stability 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. This

Table 1. Calculated formation energies (in eV) for cation interstitial defects at different sites and in different charge states.

	ZnO	ZnS	ZnSe	ZnTe
$T_A(0)$	—	5.18	3.91	3.38
$T_A(+)$	—	2.41	1.86	1.79
$T_A(2+)$	0.16	-0.52	-0.27	0.35
$T_C(0)$	—	4.89	3.50	2.83
$T_C(+)$	—	2.38	1.73	1.59
$T_C(2+)$	0.85	0.05	0.17	0.65

bistability can be explained by the Coulomb coupling and energy level repulsion in the two different interstitial sites. ZnO is a particular case and is different from the other ZnX compounds. We find that Zn_i in ZnO is only stable in the (2+) charge state because the CBM of ZnO is much lower than the other ZnX compounds. Consequently, the interstitial will be stable only at the T_A site.

These results 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, the interstitial can hop from one equilibrium position to another. To explain this effect, we calculated the diffusion barrier of these interstitial impurities in different charge states. The diffusion path is a straight line between T_A and T_C along the $\langle 111 \rangle$ direction, passing through the hexagonal site (H). In Fig. 1 we show the variation of the formation energy as the interstitial atom moves. We find that 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 variations of these defects. As the formation energy of the defect at the starting point increases, the energy barrier decreases. Our results also confirmed that the energy barriers for the cation interstitial diffusion are relatively small, therefore, these defects are quite mobile in these II-VI semiconductors.

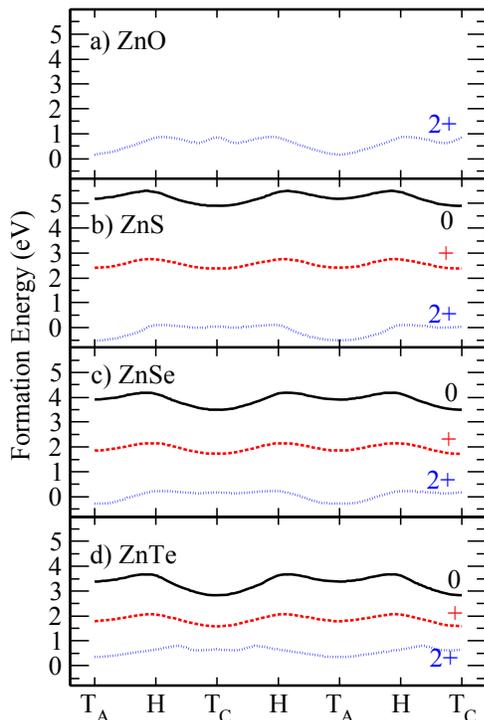


Fig. 1 Diffusion barriers of the cation interstitials for different charge states in the studied materials.

4. Conclusions

We studied the photoinduced migration of cation interstitials in II-VI semiconductors. We 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. 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 experimentally observed photoinduced migration of the interstitials.

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