First-principles investigation on diffusion mechanism of Zinc in n-GaSb

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Abstract

According to previous investigations, Zn diffusion in GaSb is mediated by dissociative mechanism or kick out mechanism. However, little work has been carried out to explain why Zn diffusion is mediated by these two different diffusion mechanisms. This work concentrated on the effect of diffusion sources (pure Zn and ZnGa alloy) on the diffusion mechanism mediating Zn diffusion in n-GaSb. First-principles method was employed to calculate the formation energies and migration barriers for interstitial Zn in all possible charges states at two tetrahedral sites. It was found that diffusion sources can influence the site of interstitial Zn, resulting in different diffusion mechanisms. Interstitial Zn is stable at anion-surrounded tetrahedral site under pure Zn condition, while stable at cation-surrounded tetrahedral site under ZnGa alloy condition. The results of diffusion activation energies demonstrated that kick out mechanism plays a dominant role for Zn diffusion in n-GaSb under ZnGa condition, and that under pure Zn condition, dissociative mechanism plays a dominant role at the beginning of the diffusion process and then kick out mechanism becomes dominant.

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Keywords: First-principles; Zn diffusion mechanism; diffusion source; interstitial Zn site; diffusion activation energy

1. Introduction

GaSb, with a narrow direct band gap (0.82eV at 0 K), is a promising material for photodiodes [1], photodetectors [2], thermal photovoltaic cells [3] and so on. P-type dopant is usually used to diffuse into Te-doped GaSb to form p-n junction in the fabrication of the photovoltaic devices. Zinc is the most commonly used p-type dopant in III-V materials due to its high solubility, high diffusivity and low ionization energy [4]. An understanding of the mechanism of Zn diffusion in n-GaSb is very important to accurately predict the Zn diffusion profiles for fabricating high-efficiency photovoltaic devices.

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According to previous work, two mechanisms govern Zn diffusion: dissociative mechanism [5] and kick out mechanism [6]. Many researchers have investigated Zn diffusion in GaSb [7-12] based on these two mechanisms. However, they do not have consistent answers on the dominant mechanism mediating Zn diffusion. First-principles method can be used to study the microscopic physical process in Zn diffusion. Nevertheless, previous first-principles researches of impurity diffusion in semiconductors have concentrated mainly on calculating formation and migration energies [13, 14], few of them dealt with the factors resulting in dissociative mechanism and kick out mechanism.

This work is aimed to microscopically illustrate why Zn diffusion is mediated by different diffusion mechanisms with respect to different diffusion sources (pure Zn and ZnGa alloy). First-principles method was employed to calculate formation energies and migration barriers for interstitial Zn (in all possible charge states) at two tetrahedral sites. The activation energies of kick out process and dissociative process were calculated to determine which diffusion mechanism plays a dominant role for Zn diffusion in n-GaSb.

2. Computational Model and Method

The calculation model is based on a periodic 2×2×2 supercell of GaSb [15], which consists of 64 atoms in the supercell. In the model, the effect of Te doping on Zn diffusion is neglected due to its low concentration compared to that of Zn. When using pure Zn as diffusion sources, large amounts of Ga vacancies will form due to the evaporation of Ga atoms from the surface of GaSb because of its high self-diffusivity. We assumed that the concentration of Ga vacancies in the surface region is high and approximately equals to that of Zn. The concentration of Zn in the surface region is approximately 3.5×10^{20}/cm^{3} [16], namely 1%. Therefore, we constructed a model with a Ga vacancy at the center of the supercell (the concentration of Ga vacancies is 1.5%) to represent GaSb under pure Zn condition. When using ZnGa alloy as diffusion sources, Ga from the diffusion sources will suppress the evaporation of Ga atoms. Then we assumed that the concentration of Ga vacancies is low and approximately equals to the equilibrium value. The equilibrium value of Ga vacancies is approximately 1×10^{15}/cm^{3} [17], namely 3×10^{-6}%, which could be neglected in our 64-atom supercell. Therefore, we used a model without Ga vacancy to represent GaSb under ZnGa condition.

All the calculations in this work were performed using the Cambridge Sequential Total Energy Package (CASTEP) code, which is based on density functional theory and plane-wave pseudopotential method [18]. For the exchange-correlation function, the Perdew-Burke-Ernzerhof function for solids (PBESOL) [19] in the general gradient approximation (GGA) was adopted. Ultrasoft pseudopotential was used to describe the interaction between valence electron and ion core. The valence electron configurations for Ga, Sb and Zn were considered as 3d^{10}4s^{2}4p^{1}, 5s^{2}5p^{3} and 3d^{10}4s^{2}, respectively. Before doing supercell calculations, the convergence tests of the total energy with respect to the plane-wave cut-off energy and k-point sampling have been carefully examined. In the calculation, the set of cut-off energy was 350eV, and the Brillouin-zone was sampled using a Monkhorst-Pack grid of 2×2×2 k points. The atomic coordinates were allowed to relax using energy minimization under constant volume condition. The convergence thresholds of energy and force acting on each atom were 1×10^{-5} eV and 0.03 eV/Å, respectively.

The key quantity to be calculated in this work is the formation energy, which follows that [13]

\[ E_{\text{form}}(q) = E_{\text{def}}^{\text{tot}}(q) - E_{\text{ideal}}^{\text{tot}} - \sum_{i} n_{i} \mu_{i} + q \left( E_{F} + E_{V} \right) \]  (1)
where $E_{\text{tot}}^0(q)$ and $E_{\text{tot}}^\text{def}$ are total energies of the supercell with and without the defect in charge state $q$; $n_i$ is the number of atoms of type $i$ (host atom or impurity atom) that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell; $\mu_i$ are the corresponding chemical potentials of these species; $E_i$ is the valence-band maximum of the supercell containing defect; $E_r$ is the Fermi level referenced to $E_i$.

The activation energy of a diffusion process $E_a$ is the sum of the formation energy for the diffusing species $E_{\text{form}}$ and the migration barrier $E_m$, i.e., $E_a = E_{\text{form}} + E_m$ [13]. To obtain the migration barrier for a diffusion process, we employed synchronous transit methods to find the transition state when reasonable structures for the reactant and product exist; the difference in the energy between reactant and transition state is migration barrier.

### 3. Results and Discussion

To validate the foregoing computational methods, we optimized the lattice parameter and calculated the formation enthalpy of GaSb, as shown in Table 1. Our PBESOL results are in good agreement with experimental [20] and theoretical results [17] previously reported. We also calculated the formation energies of Ga vacancies in different charge states under Ga rich condition. Our results has the same trend as that of Hakala [17].

<table>
<thead>
<tr>
<th>Lattice parameter $a$ (Å)</th>
<th>PBESOL</th>
<th>Other theoretical results</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation enthalpy $\Delta H_f$ (eV)</td>
<td>6.14</td>
<td>6.01[17]</td>
<td>6.09[20]</td>
</tr>
<tr>
<td></td>
<td>-0.36</td>
<td>-0.32[21]</td>
<td>—</td>
</tr>
</tbody>
</table>

The initial interstitial Zn ($Zn_i^0$) comes from diffusion sources and becomes substitutional ($Zn_{cT}^+$) via dissociative mechanism or kick out mechanism. $Zn_i$ may occupy two tetrahedral sites, cation-surrounded tetrahedral site (labelled $T_c$) and anion-surrounded tetrahedral site (labelled $T_a$). We calculated the formation energies of $Zn_i$ under ZnGa condition and complex $Zn_i V_{Ga}$ under pure Zn condition, as shown in Fig. 1 and Fig. 2, respectively. Lines of solid, dash and dash dot represent $Zn_i$ in charge states 0, +1 and +2, respectively. The experimental band gap value is used as the upper limit of the Fermi Level. Fig. 1 shows that, irrespective of the site of $Zn_i$, $Zn_i^{+}$ is favoured over a wide Fermi level range until the Fermi level is near the bottom of the conduct band where $Zn_i^0$ forms. By comparing Fig. 1(a) and (b), it is seen that $Zn_i$ at $T_c$ site has a lower formation energy than at $T_a$ site, indicating that $Zn_i$ is more stable at $T_c$ site under ZnGa condition. Fig. 2 shows that $Zn_i^{+}$ forms when the Fermi level is near the top of the valence band and $Zn_i^0$ forms with increasing Fermi level. By comparing Fig. 2(a) and (b), it is observed that $Zn_i$ at $T_c$ site has a lower formation energy than at $T_a$ site, indicating $Zn_i$ is more stable at $T_c$ sites under pure Zn condition.

It is necessary to determine the configurations of reactant and product when computing migration barrier. For kick out process, we studied a diffusion process where initial $Zn_i$ at $T_c$ or $T_a$ site occupies Ga site to be $Zn_i^{+}$ and then interstitial Ga ($Ga_i$) at $T_c$ or $T_a$ site forms. In calculation, both the charge states of $Zn_i$ and $Ga_i$ may be 0, +1 and +2. Our results reveals that, irrespective of the site of initial $Zn_i$, the final $Ga_i$ at $T_c$ site has a lower migration barrier, indicating that the kicked-out $Ga_i$ is more stable at $T_c$ site. Thus the migration barrier of kick out process only depends on the site of initial $Zn_i$. For dissociative process, we studied a diffusion process where initial $Zn_i$ at $T_c$ or $T_a$ site occupies a Ga vacancy to be $Zn_i^{+}$. The migration barrier of dissociative process also depends on the site of initial $Zn_i$.
Adding the calculated formation energies and migration barriers together, the diffusion activation energies can be obtained. Since the formation energy depends on the Fermi level, the activation energy will also depend on the Fermi level. Fig. 3 depicts the diffusion activation energies of dissociative process and kick out process under ZnGa alloy and pure Zn conditions. From Fig. 3(a) it is observed that kick out process has a lower activation energy than dissociative process over the whole Fermi level range, implying that kick out mechanism is the dominant mechanism for Zn diffusion in n-GaSb under ZnGa alloy condition. It is seen from Fig. 3(b) that kick out process has a lower activation energy only when
Fermi level is near the top of the valence band, while dissociative process has a lower activation energy when Fermi level is near the bottom of the conduct band. This result indicates that under pure Zn condition, dissociative mechanism dominates at the beginning of the diffusion process and afterwards kick out mechanism becomes dominant due to the decrease of Fermi level caused by Zn doping. Our previous work [16] has revealed that kink and tail profiles obtained under pure Zn condition were formed via dissociative mechanism in the surface region and kick out mechanism in the tail region, and that box profiles obtained under ZnGa condition were formed via kick out mechanism. The results in this work are consistent with those in our previous work and could microscopically explain why Zn diffusion with different sources is mediated by two different diffusion mechanisms.

![Graph showing Fermi Level vs Activation Energy](image)

**Fig. 3.** The diffusion activation energies of dissociative process and kick out process under (a) ZnGa condition and (b) pure Zn condition.

### 4. Conclusion

First-principles method was employed to study Zn diffusion in n-GaSb under pure Zn and ZnGa alloy conditions. We calculated formation energies and migration barriers for interstitial Zn (in all possible charge states) at two tetrahedral sites. The results indicated that diffusion sources affect the diffusion mechanism by affecting the site of interstitial Zn. Initial interstitial Zn is stable at anion-surrounded tetrahedral site under pure Zn condition while stable at cation-surrounded tetrahedral site under ZnGa alloy condition. The difference in the site of interstitial Zn will lead to the difference in the diffusion activation energy. The calculated diffusion activation energies demonstrated that kick out mechanism plays a dominant role under ZnGa condition, and that dissociative mechanism plays a dominant role at the beginning of the diffusion process then kick out mechanism becomes dominant with the decrease of Fermi level due to Zn doping under pure Zn condition.

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References


Biography

Dr. Hong Ye is an associate professor in Department of thermal science and energy engineering, University of Science and Technology of China. Dr. Ye’s research interests are in the areas of heat transfer, application of solar energy, building efficiency, measurement of thermal properties and thermophotovoltaic (TPV) system.