Defect formation energetics at the grain boundary in CuInSe₂ using first-principles calculations

Hiroyuki YAMAGUCHI and Teruyasu MIZOGUCHI[†]

Institute of Industrial Science, University of Tokyo, 4–6–1 Komaba, Meguro, Tokyo 153–8505, Japan

We investigated defect formation energetics at the grain boundary (GB) in CuInSe₂ (CIS) using first-principles calculations. We focused on the (112)[110] Σ 3 twin GB in CIS because this GB is known to be easily formed in CIS. Formation energies and accompanied atomic relaxation of neutral Cu, In, and Se vacancies (V_{Cu}^0 , V_{In}^0 , and V_{Se}^0), the In antisite defect (In_{Cu}^0), and the Schottky defect ($\text{In}_{\text{Cu}}^{2+} + 2V_{\text{Cu}}^-$) were investigated in the bulk and GB. We found that CIS shows characteristic atomic relaxation after vacancy formation, and V_{Cu}^0 is the most energetically favorable defect in both the bulk and the GB. Furthermore, we found that (112)[110] Σ 3 twin GB does not promote the formation of the Cu vacancy under all conditions, whereas it relatively promotes the formation of the Se vacancy under metal-rich conditions.

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1. Introduction

CuInSe₂ (CIS) has attracted great interest as a material for the photo-absorption layer in thin-film photovoltaic devices because it has a direct band gap and the band gap is tunable by making a solid solution.¹⁾ CIS and its solid solutions have been extensively studied, and the solar ray conversion efficiency recently reached 20% by making a solid solution with CuGaSe₂ [Cu(In,Ga)-Se₂].^{2),3)} Through the previous studies, it was revealed that the vacancy formation behavior of these materials is crucial for the photo-absorption property because extra bands are formed in the band gap by the vacancies. Thus, the vacancy formation behavior of CIS-type materials has been studied theoretically and experimentally,^{4)–8)} and it has been reported that neutral Cu vacancy (V_{Cu}^0) and defects pair ($\text{In}_{\text{Cu}}^{2+} + 2V_{\text{Cu}}^-$) are preferably formed in CIS.^{4),7)}

However, most of previous studies focused on the vacancy formation inside the CIS bulk, despite the fact that CIS used in the photovoltaic devices is a polycrystalline material. That is, many grain boundaries (GB) are present in the photo-absorption layers.⁹⁾ Although it is expected that the GB influences the vacancy formation behavior,^{10)–12)} the details of the vacancy formation behavior at the GBs in CIS have not been clarified.

Here, we investigated the defect formation energies of intrinsic defects at the GB of CIS using a first-principles projector augmented wave (PAW) method based on density functional theory (DFT). We focused on a (112)[110] Σ 3 twin GB of CIS, because this twin GB is known to be easily formed in CIS and related materials.¹³⁾ In this study, we have calculated the vacancy formation energies of neutral Cu, In, and Se vacancies (V_{Cu}^0 , V_{In}^0 , V_{Se}^0), antisite In on the Cu site (In_{Cu}^0), and a Schottky type defect ($\text{In}_{\text{Cu}}^{2+} + 2V_{\text{Cu}}^-$). In addition, the site dependence of the vacancy formation at the GB is discussed.

2. Methods

Figure 1(a) shows the unit cell of the chalcopyrite CIS structure.¹⁴⁾ Viewing this from the [110] axis, the dumbbell structure consists of Cu/In and Se columns. The stable atomic structure of the (112)[110] Σ 3 twin GB was determined in previous work using high resolution transmission electron microscopy and first-principles calculations.¹⁵⁾ The lattice vectors of each direction and the dimensions of the supercell were $X = [221]$ (40.82 Å), $Y = [11\bar{1}]$ (7.22 Å) and $Z = [1\bar{1}0]$ (8.37 Å). This supercell included 96 atoms. To introduce the vacancy, this supercell was repeated $1 \times 2 \times 2$ in the [221], $[11\bar{1}]$ and $[1\bar{1}0]$ directions, and a 384 atom supercell was constructed.

In the calculations, we used the first-principles projector augmented-wave (PAW) method based on density functional

Fig. 1. (a) Atomic structure of the CuInSe₂ unit cell and the calculated and experimental lattice constants. (b) Schematic view of the (112)[110] Σ 3 twin GB. V(GB,1) and V(GB,2) denote the first and second nearest neighbor sites to GB, and V(Bulk) denotes the bulk interior site.

[†] Corresponding author: T. Mizoguchi; E-mail: teru@iis.u-tokyo.ac.jp

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Table 1. Chemical potentials of the three elements at the equilibrium points in Fig. 2

	μ_{Cu}	μ_{In}	μ_{Se}
A	$\frac{1}{2}(\mu_{\text{Cu}_2\text{Se}} - \mu_{\text{Se}})$	$\mu_{\text{CuInSe}_2} - \frac{1}{2}(\mu_{\text{Cu}_2\text{Se}} + 3\mu_{\text{Se}})$	μ_{Se}
B	$\mu_{\text{CuInSe}_2} - \frac{1}{2}(\mu_{\text{In}_2\text{Se}_3} + \mu_{\text{Se}})$	$\frac{1}{2}(\mu_{\text{In}_2\text{Se}_3} - 3\mu_{\text{Se}})$	μ_{Se}
C	$\mu_{\text{CuInSe}_2} - \frac{1}{3}(2\mu_{\text{In}_2\text{Se}_3} - \mu_{\text{In}})$	μ_{In}	$\frac{1}{3}(\mu_{\text{In}_2\text{Se}_3} - 2\mu_{\text{In}})$
D	μ_{Cu}	μ_{In}	$\frac{1}{2}(\mu_{\text{CuInSe}_2} - \mu_{\text{Cu}} - \mu_{\text{In}})$
E	μ_{Cu}	$\mu_{\text{CuInSe}_2} - 2\mu_{\text{Cu}_2\text{Se}} + 3\mu_{\text{Cu}}$	$\mu_{\text{Cu}_2\text{Se}} - 2\mu_{\text{Cu}}$

theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation using the Hubbard U correction (GGA+ U) with the VASP code.¹⁶⁾ As the U parameter, we used $U - J = 5$ eV on the Cu d orbitals.¹⁷⁾ The cutoff energy of the plane wave was set to 400 eV, and the calculated numerical integrations over the Brillouin zone were performed at the Γ point. The calculated band gap of CIS using these calculation conditions was 0.98 eV, which is in good agreement with the experimental value of 1.04 eV.¹⁸⁾

To introduce a Cu, In or Se vacancy, an atom was removed from the supercell. It is known that the formation energies depend on the atomic sites at the GBs, so the calculated defect formation energies were a Cu, In, or Se vacancy at the first nearest neighbor site to the GB, at the second nearest neighbor site to the GB, and in the bulk interior site, which are denoted as V(GB,1), V(GB,2), and V(Bulk), respectively in Fig. 1(b). To take account of atomic relaxation around a vacancy, all the atoms in the supercell were allowed to relax with the volume fixed. The atomic relaxation was performed until the residual forces of the relaxed atoms were less than 0.1 eV/Å.

The defect formation energies were calculated from the total energies of the supercells based on the standard formalism introduced by Zhang and Northrup.¹⁹⁾ In this case, the defect formation energies depend on the atomic chemical potentials of Cu, In, and Se. The formation energy of a defect is given by

$$E_f = E_T(\text{defect}; q) - \{E_T(\text{perfect}) - n_{\text{Cu}}\mu_{\text{Cu}} - n_{\text{In}}\mu_{\text{In}} - n_{\text{Se}}\mu_{\text{Se}}\} + q(\varepsilon_F + E_{\text{VBM}}). \quad (1)$$

Here, $E_T(\text{defect}; q)$ and $E_T(\text{perfect})$ are the total energies of the supercell containing a defect in a charged state q and the supercell without any defects, respectively. n_{Cu} , n_{In} , and n_{Se} are the number of Cu, In, and Se atoms removed from the GB supercell to introduce a vacancy. μ_{Cu} , μ_{In} , and μ_{Se} are the atomic chemical potentials, and ε_F is the Fermi energy measured from the valence band maximum (VBM). In previous studies, band gap correction was performed in the neutral anion vacancy because DFT-GGA calculations usually underestimate the band gap.^{20)–23)} In this study, however, we did not perform the band gap correction because the present calculation reproduces the band gap well, as mentioned above. To determine the atomic chemical potentials in the above equilibrium states, the total energies of the bulk systems of Cu (*fcc*), In (*F4/mmm*), Se (*P3₁21*), Cu₂Se (*Fm $\bar{3}$ m*), and In₂Se₃ (*P6₁*) were calculated.

The chemical potentials were determined from the equilibrium conditions of the related phases. **Figure 2** shows a schematic phase diagram of the ternary Cu–In–Se system, and the vertices of the three phase regions are denoted A–E. Under the assumption that CIS is always stable, the chemical potentials of the three elements were obtained from combinations of the chemical

Fig. 2. Schematic phase diagram of the ternary Cu–In–Se system. The vertex at the center corresponds to CIS.

potentials of Cu, Cu₂Se, In, In₂Se₃, and Se, and the chemical potentials satisfy the following correlation:

$$\mu_{\text{Cu}} + \mu_{\text{In}} + 2\mu_{\text{Se}} = \mu_{\text{CIS(bulk)}}, \quad (2)$$

where $\mu_{\text{CIS(bulk)}}$ is the total energy per formula unit of the perfect CIS crystal. At each point A–E in the phase diagram of Fig. 2, CIS is the equilibrium with the constitute elements, so the chemical potentials are constrained by the equations in **Table 1**. According to the phase diagram in Fig. 2, points A and B correspond to Se-rich conditions because the system is in equilibrium with selenium, while point D corresponds to metallic conditions because the system is in equilibrium with the Cu and In metals.

In an actual process of the CIS layer in photovoltaic devices, Cu and In metals are deposited on a substrate and selenization of the metallic layer is performed.^{1),24),25)} That is, the manufacture of CIS is performed under Se-rich conditions. Thus, points A and B correspond to the actual process conditions.

3. Results and discussion

First, we investigated the atomic relaxation accompanied with vacancy formation. Similar to the previous study, the magnitude of the atomic relaxation was estimated from the distance between the vacancy site and the first nearest neighbor atoms.^{10),21),22)} We averaged the value when there was more than one nearest neighbor bond. The magnitude of the atomic relaxation was calculated by following equation;

$$\text{Magnitude of the atomic relaxation} = (L_{\text{vacancy}} - L_{\text{perfect}}) / L_{\text{perfect}}. \quad (3)$$

L_{vacancy} is distance from vacancy site to neighboring atoms and L_{perfect} is distance between atoms in perfect bulk. The values were represented by percentage. **Table 2** lists the magnitude of the atomic relaxation of the vacancies. In addition to CIS, the results in the reference compounds Si, GaAs, and BaTiO₃ are also given for comparison. The negative and positive values indicate atomic relaxation towards and away from the vacancy site, respectively.

Table 2. Structural relaxations from each vacancy site (Bulk, GB,1, and GB,2) to the neighboring ions of CIS, Si, GaAs, and BaTiO₃ in %

	(%)	Bulk	GB,1	GB,2
CIS	V _{Cu} ⁰ – Se	–4.2	–4.8	–4.4
	V _{In} ⁰ – Se	–9.6	–10.3	–8.7
	V _{Se} ⁰ – Cu	21.8	26.9	21.3
	V _{Se} ⁰ – In	–17.7	–19.1	–18.0
Si	V _{Si} ⁰ – Si	–4.3		
GaAs	V _{Ga} ⁰ – As	–6.6		
	V _{As} ⁰ – Ga	–7.2		
BaTiO ₃ (Ref.[22])	V _{Ba} ⁰ – O	1.7		
	V _{Ti} ⁰ – O	8.6		
	V _O ⁰ – Ba	2.4		
	V _O ⁰ – Ti	10.4		

In the bulk interior, the magnitude of the relaxation for V_{Cu}⁰ is small (–4.2%) and that for V_{In}⁰ is approximately twice that of V_{Cu}⁰ (–9.6%). On the other hand, relatively large distortions are present for V_{Se}⁰ (21.8% or –17.7%). The differences in the magnitude of the relaxation can be explained by the ionic size of each element, that is, Cu is smaller than In, and Se is much larger than the other ions. Furthermore, it is notable that the direction of the relaxation is also dependent on the vacancy species. In the cases of V_{Cu}⁰ and V_{In}⁰, the neighboring Se ions move towards the vacancy, whereas in the case of V_{Se}⁰ the neighboring Cu ions move away from the vacancy and the neighboring In ions move towards the vacancy. We also investigated the atomic relaxation of charged vacancies and confirmed that the trend of relaxation is not dependent on the charge state of the vacancy. Comparing with the reference materials listed in Table 2, the atomic relaxation in CIS resembles that of a covalent materials, such as Si and GaAs, rather than ionic materials, such as BaTiO₃. Actually, a Mulliken population analysis using a first principles plane wave pseudopotential calculation (CASTEP code) indicated that chemical bonding in CIS, especially the Cu–Se bonding, has strong covalent character.^{26),27)}

In the vicinity of the GB, the atomic relaxation for Cu and In vacancies are basically the same as that in the bulk interior. That is, the relaxation for V_{Cu}⁰ and V_{In}⁰ are approximately –4 to –5% and –8 to –10%, respectively. However, we found that the V_{Se}⁰ at the GB shows larger relaxation than that in the bulk (21.8% in the bulk and 26.9% in the GB). This difference can be attributed to the electronic structure of CIS. Because the valence band of CIS, which is responsible for chemical bonding, is mainly composed of Se components, the electronic structure of Se can be more sensitive to the local atomic coordination than the electronic structures of Cu and In.

Figure 3 shows the formation energies of Cu, In, and Se vacancies, antisite In on the Cu site, and a Schottky defect (In_{Cu}²⁺ + 2V_{Cu}[–]) in bulk CIS at each point in the phase diagram shown in Fig. 2. In the Schottky-type defect, charged defects were calculated and the formation energy per defect was calculated for comparison. From Fig. 3, the formation energies of V_{Cu}⁰ and V_{In}⁰ decrease under Se-rich conditions (points A and B), whereas they increase under metal-rich conditions (point D). On the other hand, the vacancy formation energy of Se is high under Se-rich conditions (points A and B), and it decreases under metal-rich conditions (point D). At point D, the formation energy of V_{Se}⁰ is comparable to that of V_{Cu}⁰. The antisite In_{Cu}⁰ defect shows a similar tendency to the V_{Se}⁰: it is more preferable under metal-rich than Se-rich conditions. Furthermore, it was found that a defect pair (In_{Cu}²⁺ + 2V_{Cu}[–]) shows relatively low formation

Fig. 3. Calculated formation energies of V_{Cu}⁰, V_{In}⁰, V_{Se}⁰, In_{Cu}⁰, and In_{Cu}²⁺ + 2V_{Cu}[–] at each equilibrium point indicated in Fig. 2.Table 3. Differences of formation energy (ΔE_f) between the bulk interior and the GB

(eV)	$\Delta E_f(\text{GB,1-Bulk})$	$\Delta E_f(\text{GB,2-Bulk})$
V _{Cu} ⁰	0.00	–0.08
V _{In} ⁰	–0.02	–0.09
V _{Se} ⁰	–0.21	0.00
In _{Cu} ⁰	–0.15	–0.17
In _{Cu} ²⁺ + 2V _{Cu} [–]	–0.06	0.08

energy under both Se-rich and metal-rich conditions, and it is preferable under In-rich conditions (points C and D). From Fig. 3, we concluded that V_{Cu}⁰ is the preferable vacancy under all conditions, and V_{Se}⁰ and the In_{Cu}²⁺ + 2V_{Cu}[–] Schottky defect can be present under metal-rich conditions. The tendency that the formation of V_{Cu}⁰ is lower than other vacancies in our calculations, especially under Se-rich conditions, is identical to the conclusions of previous reports.^{4),27),28)}

Next, the defect formation energies in the vicinity of the GB and in the bulk were compared. To confirm the site dependence of vacancy formation at the GB, the difference in the vacancy formation energy between the bulk and the GB were calculated.¹⁰⁾ Hereafter, this value is denoted ΔE_f . Since ΔE_f represents a relative value, it does not depend on the atmospheres. **Table 3** lists ΔE_f for V_{Cu}⁰, V_{In}⁰, V_{Se}⁰, In_{Cu}⁰, and In_{Cu}²⁺ + 2V_{Cu}[–] Schottky defects. We found that the ΔE_f values were very small in most cases, but that for V_{Se}⁰ and In_{Cu}⁰ were –0.21 and –0.15 eV, respectively. Those ΔE_f are comparable to that in high angle GB in oxides materials,¹⁰⁾ indicating that the formation of V_{Se}⁰ and In_{Cu}⁰ would be promoted at the GB. However, the concentration of In_{Cu}⁰ should be small both at GB and bulk because the absolute formation energy of In_{Cu}⁰ is relatively high (Fig. 3).

As mentioned above, the V_{Cu}⁰ is preferably formed over the other vacancies under all conditions, and V_{Se}⁰ and the In_{Cu}²⁺ + 2V_{Cu}[–] Schottky defect can be formed under metal-rich conditions (Fig. 3). Based on those results, we can conclude that the (112)[110] Σ 3 twin GB does not promote the formation of the Cu vacancy irrespective of the atmospheres, whereas it promotes the formation of the Se vacancy in metal-rich conditions.

As mentioned above, the CIS films are fabricated under Se-rich condition. We revealed that V_{Cu}⁰ is energetically favorable under the Se-rich condition and this V_{Cu}⁰ does not segregate to the (112)[110] Σ 3 twin GB. Our conclusion is consistent to an experimental study that significant V_{Cu} segregation was not observed in (112)[110] Σ 3 twin GB of CIS.⁸⁾

4. Conclusions

We performed first-principles calculations to understand the defect formation behavior at the (112)[1 $\bar{1}$ 0] Σ 3 twin GB in CuInSe₂ (CIS). We found that atomic relaxation around the vacancy in CIS resembles covalent materials rather than ionic materials. Furthermore, we revealed that the trend of the vacancy formation at the GB is similar to that in the bulk, that is, V_{Cu}^0 is the most preferable defect in all conditions. Through this study, we concluded that the (112)[1 $\bar{1}$ 0] Σ 3 twin GB does not promote the formation of Cu vacancies, whereas it promotes the formation of Se vacancies.

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