

First principles calculations of defect formation in In-free photovoltaic semiconductors $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$

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1. Introduction

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) solar cells are among the most promising materials for thin film solar cells. Recently, wide and narrow band gap absorber materials have been studied for thin film full spectrum solar cells. New materials are required that have wide band gap ($E_g > 1.7$ eV) and narrow ($E_g < 1.0$ eV) band gap. Finding a substitute for indium in CIS has also become an important issue because indium is scarce and expensive. $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) are anticipated as indium-free absorber materials. Katagiri *et al.* reported CZTS-based solar cells with an efficiency of 6.7% by the sputtering method [1]. Most recently, Todorov *et al.* fabricated $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells with an efficiency of 9.6% by the hybrid liquid process [2]. For the $\text{Cu}(I)_2\text{-Zn}(II)\text{-IV-VI}_4$ compounds, three kinds of crystal structures have been reported: kesterite-, stannite- and wurtz-stannite-types. We studied the phase stability of the kesterite-, stannite- and wurtz-stannite-type CZTSe by first-principles calculation [3]. Formation enthalpy of kesterite-type CZTSe was smaller than those of stannite- and wurtz-stannite-type CZTSe. Then, we identified the kesterite-type CZTSe by neutron powder diffraction. We also reported the electronic structure of CZTSe and CZTS by first principles calculations [4]. The VBM of kesterite-type CZTSe is the antibonding state of ($\text{Cu } 3d + \text{Se } 4p$), while CBM is the antibonding state of ($\text{Sn } 5s + \text{Se } 4p$).

The basic sciences group at the National Renewable Energy Laboratory (NREL) has studied the electronic structure and defect formation energy of CIS and the related compounds since the 1980s. In a previous study, we reported that the formation energy of Cu vacancy is smaller than those of In and Se vacancies in CIS [5]. Recently, Chen *et al.* calculated formation energies of the defects in CZTS [6]. They reported that Cu vacancy and ($V_{\text{Cu}} + \text{Zn}_{\text{Cu}}$) are easily formed in the Cu-poor and Zn-rich condition. However, defect formation in CZTSe and the related compounds has not been reported.

In this study, we calculate the vacancy formation energy in CZTSe, and CZTS. We compare the defect formation in In-free photovoltaic semiconductors CZTSe and CZTS with that of CIS. We discuss the defect formation of Cu and the other cationic elements on the basis of their chemical bonds.

2. Computational Procedures

We performed first-principles calculations within a density functional theory using a plane-wave pseudopotential

method. First, we optimized lattice parameters a and c , and the u -parameter of the Se atom, $u(\text{Se})$, through the minimization of total energy. Structural optimization was performed using the primitive cells of the kesterite-type unit cell.

The formation energy of point defects was calculated from the difference of total energy between perfect crystal and imperfect crystal with defect. The total energy of the perfect crystal was calculated using the kesterite-type unit cell 14 with 16 atoms. Calculations for imperfect crystal with vacancy were performed using the supercell with 64 atoms. Since we used a neutral supercell, the result corresponded to quantities for a neutral vacancy. Since we dealt with the imperfect crystal with infinitely dilute defect concentration, lattice constants were fixed at the optimized values of the perfect crystal. Atomic arrangements around a vacancy were optimized allowing relaxation of the first- and second-nearest neighbor atoms. The relaxation procedures were truncated when all the residual forces for the relaxed atoms were less than 0.01 eV/Å. To calculate the chemical potentials of constituent elements, we also performed calculations of many reference materials, i.e., Cu_2Se , ZnSe , SnSe_2 , Cu , Zn , Sn , and Se . The total energies of the reference materials were obtained after the structure was optimized by the same computational method for consistency.

3. Results and discussion

The formation energy of a neutral vacancy in a compound depends on the atomic chemical potentials in the system. The formation energies of Cu, Zn, Sn, and Se vacancies can be respectively presented by

$$\begin{aligned} E_F(V_{\text{Cu}}) &= E^V_t[\text{Cu}_{2n-1}\text{Zn}_n\text{Sn}_n\text{Se}_{4n}] - E_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_n\text{Se}_{4n}] + \mu_{\text{Cu}}, \\ E_F(V_{\text{Zn}}) &= E^V_t[\text{Cu}_{2n}\text{Zn}_{n-1}\text{Sn}_n\text{Se}_{4n}] - E_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_n\text{Se}_{4n}] + \mu_{\text{Zn}}, \\ E_F(V_{\text{Sn}}) &= E^V_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_{n-1}\text{Se}_{4n}] - E_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_n\text{Se}_{4n}] + \mu_{\text{Sn}}, \\ E_F(V_{\text{Se}}) &= E^V_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_n\text{Se}_{4n-1}] - E_t[\text{Cu}_{2n}\text{Zn}_n\text{Sn}_n\text{Se}_{4n}] + \mu_{\text{Se}}, \end{aligned}$$

where E^V_t is the total energy of the supercell with a vacancy and E_t is the total energy of the perfect crystal of kesterite-type CZTSe.

The symbol μ is the chemical potential of the constituent elements (Cu, Zn, Sn and Se) and $n = 8$. The chemical potential, μ , changes depending on the chemical environment of the system. Figure 1 shows the schematic phase diagram of quaternary Cu-Zn-Sn-Se system (a) and pseudo-ternary Cu-($\text{Zn}_{1/2}\text{Sn}_{1/2}$)-Se system (b). The chemical potentials of Cu, Zn, Sn, and Se should be correlated to

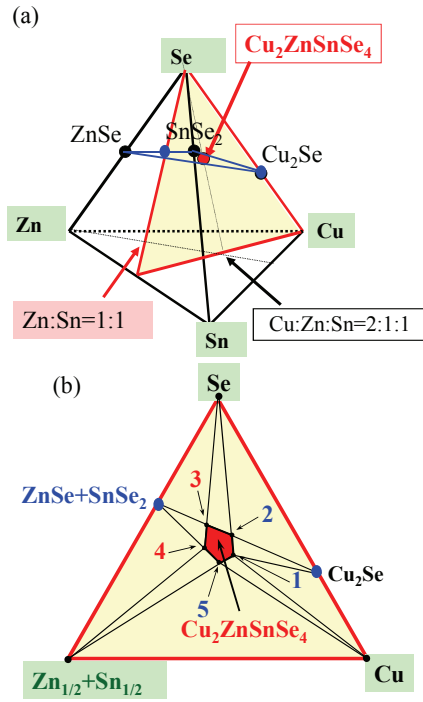


Fig. 1. Schematic phase diagram of quaternary Cu-Zn-Sn-Se system (a) and pseudo-ternary Cu-(Zn_{1/2}Sn_{1/2})-Se system (b)

satisfy the following equation:

$$2\mu_{\text{Cu}} + \mu_{\text{Zn}} + \mu_{\text{Sn}} + 4\mu_{\text{Se}} = \mu_{\text{Cu}_2\text{ZnSnSe}_4(\text{bulk})}$$

Five points in the pseudo-ternary Cu-(Zn_{1/2}Sn_{1/2})-Se phase diagram shown in Fig. 1(b) correspond to the vertices of the three-phase regions. For example, at point 1, CZTSe is in equilibrium with Cu₂Se and Cu metal. At point 3, CZTSe is in equilibrium with (ZnSe+SnSe₂) and Se. Points 1, 2 and 5 correspond to the Cu-rich condition and points 3 and 4 correspond to the Cu-poor condition. Chemical potentials for the bulk substances were obtained as the total energies per unit formula by separate calculations in this study, i.e., $\mu_X(\text{bulk}) = E_t(X)$.

Theoretical formation energies of Cu, Zn, Sn, and Se vacancies are plotted in Fig. 2 at five points as indicated in Fig. 1. Under the Cu-poor and Zn-rich condition such as point 4, the formation energy of Cu vacancy is smaller than those of Zn, Sn and Se vacancies, as well as the result reported by Chen *et al.* Under the Zn-poor and Se-rich conditions such as points 1 and 2, the formation energy of Zn vacancy is much smaller than that of Cu vacancy.

Furthermore, to investigate the difference in formation energy of Cu vacancy among CZTSe, CZTS and CIS, the formation energies of Cu vacancy in CZTSe and CZTS are plotted in Fig. 3 in comparison with CIS. Formation energy of Cu vacancy in CZTSe is much larger than that of Cu vacancy in CIS under the Cu-poor and Cu-rich conditions. Formation energy of Cu vacancy in CZTSe is slightly smaller than that in CZTS. Therefore, Cu vacancy in CZTS is not easily formed in comparison with Cu vacancy in CIS. We will discuss formation energies of Cu vacancy and the other vacancies (i.e., Zn, Sn and Se vacancies) in the related In-free photovoltaic semiconductors.

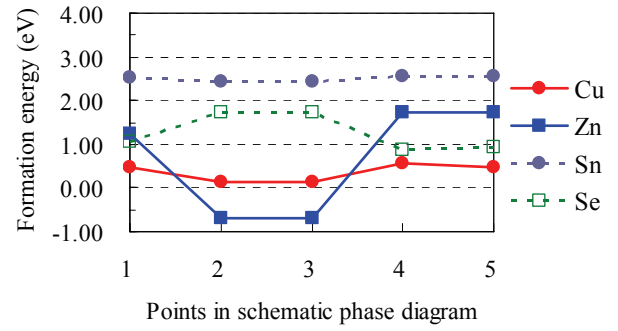


Fig. 2. Formation energy of Cu/ Zn/Sn/Se vacancy in CZTSe in pseudo-ternary phase diagram of Cu-(Zn_{1/2}Sn_{1/2})-Se.

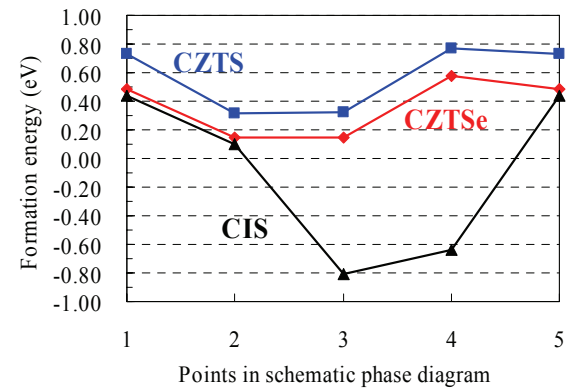


Fig. 3. Formation energy of Cu vacancy in CZTSe and CIS.

4. Conclusions

The formation energy of Cu vacancy in CZTSe is greater than that of Cu vacancy in CIS. Therefore, Cu vacancy in CZTSe is not easily formed in comparison with Cu vacancy in CIS.

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