Origin of off-stoichiometry and electrical benignity at the grain boundaries in CuInSe$_2$: A first-principles study

Guo-Jun Zhu, Ji-Hui Yang, and Xin-Gao Gong

ABSTRACT

Grain boundaries (GBs) in polycrystalline CuInSe$_2$ are of both fundamental interest and technological significance for photovoltaic applications. However, the atomic composition and the exact roles of the GBs in CuInSe$_2$ are still unclear despite a large off-stoichiometry around the GBs being reported. In this work, based on first-principles calculations and using $\Sigma 3$(114) GB as an example, we show that the GB acts as a sink of defects, leading to defect segregations and off-stoichiometry. Furthermore, depending on the chemical potential conditions, different point defects dominate the different segregations. Under common experimental conditions with In rich and Cu poor, we find that the most dominant defect at the GBs is the antisite defect In$_{Cu}$. Our studies show that the existence of In$_{Cu}$ can eliminate defect states in the bandgap and thus suppress recombination of photo-generated electron–hole pairs, making the GB electrically benign. To enhance the formation of In$_{Cu}$, we propose an optimal region of chemical potential to realize In segregation and Cu depletion at the GB. Our work thus provides useful insights and understandings for further improvement of CISe polycrystalline solar cells.

INTRODUCTION

Optoelectronic devices such as photovoltaic solar cells often necessitate monocrystalline active materials without grain boundaries (GBs) because monocrystalline solar cells usually exhibit better performance compared to their polycrystalline counterparts. For example, commercial panel solar cells based on monocrystalline silicon have reached an energy conversion efficiency of up to 26.3% compared to about 21.3% for those based on polycrystalline silicon. The relatively poor performance of polycrystalline solar cells is commonly explained by classical GB models, where chemical impurities and structural defects tend to segregate at GBs from the grain interior (GI) during growth and introduce deep in-gap states. These states often act as effective recombination centers for the optically generated electrons and holes, thus reducing photovoltaic energy conversion efficiency. Such GB models have successfully explained the low energy conversion efficiency in many solar cells.

Recently, multiple chalcogenides such as CuInSe$_2$ (CISe) and Cu$_2$ZnSnSe$_4$ (CZTSe) have shown great promise for the absorber layers in photovoltaic devices due to their low cost and high energy conversion efficiency. In contrast to classical GB models, GBs in CISe can benefit rather than reduce solar cell efficiencies. For example, polycrystalline CISe solar cells can achieve efficiencies of around 20% even without deliberate passivation, outperforming its best monocrystalline devices (~13%). To understand the mechanism of GB benignity in CISe polycrystalline films, researchers have made tremendous research efforts in the past and two main models have been proposed. In the first model, a potential barrier is created by GB, which repels majority carriers (holes) away from the GB area and benefits the photovoltaic effect. Experimentally, Hetzer et al. performed nanoscale electric characterization and found the local built-in potential near the GB of Cu(In,Ga)Se$_2$ (CIGS) thin films. They reported a work function decrease of up to 480 meV and massive (~50%) loss of Cu...
atoms at GB interfaces, leading to a valence band offset, which repels holes from the GB. Theoretically, calculations show that an energetic barrier arises from reduced p–d repulsion due to Cu-vacancy reconstruction, which repels holes into the GI from the GB. In the second model, GBs play a similar role as that in the classical models, where GBs act as the sinks of defects. However, large atomic relaxation induced by defects at GBs eliminates deep levels created by the GB interface and thus GBs become invalid recombination centers. Evidence is given by scanning tunneling spectroscopy that the density of deep level defects is reduced in the GB region more than in the GI region. Meanwhile, defects in the GB region are found electrically benign and not harmful to solar cell performance based on first-principles calculations.

To reveal the exact role of GBs, it is of great importance to know the atomic composition information at the GBs. According to experimental results, the chemical composition mismatch is very serious near GBs of CIGS. For example, a Cu deficient region near GBs was identified by several different experimental methods. Combination of techniques including atomic force microscopy (AFM), scanning tunneling microscopy (STM), and transmission electron microscopy (TEM) showed Cu decreasing and In increasing within a few nm region around the GBs. However, Lei et al. reported that the GB in a sample deposited at 400 °C was In deficient and Se sufficient. In general, different experiments with different growth conditions give different atomic compositions at GBs. Despite this, all experimental results have something in common; that is, off-stoichiometric composition at GBs in polycrystalline materials always exists, and if the Cu (In) signal is increased at the GBs, the In (Cu) signal will be reduced. Such a mismatch of components is quite similar to the defect properties in monocrystalline CIGS, in which the off-stoichiometry of In depletion and Cu depletion is mainly induced by the point defects \( V_\text{Cu} \) and \( \text{In}_{\text{Cu}} \) through forming ordered defects \( \text{In}_{\text{Cu}}^2 + 2V_\text{Cu} \). Such ordered defects are also helpful to suppress relatively deep in-gap levels of \( \text{In}_{\text{Cu}}^2 \) and improve solar cell efficiencies as revealed by several theoretical works. Apparently, the off-stoichiometry in the bulk is not fully in agreement with experimental results at the GBs, and how the chemical composition mismatch near GBs arises and affects photovoltaic conversion efficiency is still unclarified, which makes the debate on the roles of GBs in CIGS unsettled.

In order to settle the debate on the roles of GBs and study the influence of the off-stoichiometric composition, we report the first-principles total-energy calculations are based on the density-functional theory using the Vienna \textit{ab initio} simulation package (VASP). We use the standard frozen-core projector augmented-wave (PAW) method with 17, 13, and 6 valence electrons for Cu, In, and Se, respectively, to describe the interaction between valence electrons and ionic cores. A kinetic energy cutoff of 400 eV is used for plane-wave basis expansion. The general gradient approximation (GGA) prescribed by Perdew–Burke–Ernzerhof (PBE) is used for the exchange-correlation potential. To correct the well-known bandgap errors, the commonly used plus U method is adopted. In this study, we use \( U = 6 \) eV on the cation orbital.

To construct an accurate GB model without built-in electric fields, we build a slab model with a vacuum thickness of 20 Å, which contains only one GB. For the Brillouin zone sampling, the reciprocal space is presented by the Monkhorst–Pack special \((6 \times 5 \times 1)\) meshes for static calculations. The convergence criteria are set to \( 1 \times 10^{-6} \) eV and \( 0.01 \) eV/Å for total energies and Hellmann–Feynman forces on atoms, respectively.

The point defect formation energy \( \Delta H_f \) in polycrystalline CIGS is defined as

\[
\Delta H_f = \Delta E + n_{\text{Cu}} \mu_{\text{Cu}} + n_{\text{In}} \mu_{\text{In}} + n_{\text{Se}} \mu_{\text{Se}} + n_{\text{O}} \mu_{\text{O}},
\]

where

\[
\Delta E = E(\text{defect}) - E(\text{Host}) + n_{\text{Cu}} \mu_{\text{Cu}}^D + n_{\text{In}} \mu_{\text{In}}^D + n_{\text{Se}} \mu_{\text{Se}}^D + n_{\text{O}} \mu_{\text{O}}^D.
\]

Here, \( E(\text{Host}) \) is the total energy of polycrystalline CIGS without point defects, which is set as the reference; \( E(\text{defect}) \) is the total energy of the defective polycrystalline CIGS; \( n_{\text{Cu}}, n_{\text{In}}, n_{\text{Se}}, \) and \( n_{\text{O}} \) are the number changes of Cu, In, Se, and O atoms when forming defective GBs; and \( \mu_{\text{Cu}}, \mu_{\text{In}}, \mu_{\text{Se}}, \) and \( \mu_{\text{O}} \) are the chemical potentials of Cu, In, Se, and O, respectively, which are referenced to the total energies of stable elemental phases, \( \mu_{\text{Cu}}^D, \mu_{\text{In}}^D, \mu_{\text{Se}}^D, \) and \( \mu_{\text{O}}^D \), respectively. Here, we choose face-centered cubic copper, body-centered cubic indium, Se\(_{64}\), and oxygen molecules as the stable reference phases for Cu, In, Se, and O, respectively.
RESULTS AND DISCUSSIONS

Figure 1(a) shows our structural model for the $\Sigma 3$ (114) GB where we have adopted a slab model with only one GB core. To avoid interactions between periodic cells, a lattice with $a = 8.30$ Å, $b = 11.01$ Å, $c = 90$ Å, and $\gamma = 67.83^\circ$ is used, which contains 57 Cu atoms, 57 In atoms, 114 Se atoms, and 16 pseudo-hydrogen atoms. The upper and bottom four atomic layers in Fig. 1(a) are fixed to atoms, 57 In atoms, 114 Se atoms, and 16 pseudo-hydrogen atoms. 

While the formation energies of point defects in the GI (far from the GB interface) are very close to those in the bulk,22 we find that the point defects near the GB interface have much smaller formation energies. Our calculations thus indicate that the point defects at different distances from the GB are shown in Fig. 2. While the formation energies of point defects in the GI (far from the GB interface) are very close to those in the bulk,22 we find that the point defects near the GB interface have much smaller formation energies. Our calculations thus indicate that the point defects at different distances from the GB are shown in Fig. 2. 

To identify which defects are easily attracted to the GB, we first consider the formation energies of intrinsic defects by placing them at different distances from the GB. We consider four kinds of possible point defects including $V_{\text{Cu}}$, $V_{\text{In}}$, $\text{Cu}_{\text{In}}$, and $\text{In}_{\text{Cu}}$,22 where $V_{\alpha}$ denotes a vacancy of atom $\alpha$ and $\alpha_\beta$ denotes an antisite of atom $\alpha$ on site $\beta$. The relative formation energies of these point defects at different distances from the GB are given in Fig. 1(b). While the formation energies of point defects in the GI (far from the GB interface) are very close to those in the bulk,22 we find that the point defects near the GB interface have much smaller formation energies. Our calculations thus indicate that the point defects in polycrystalline CISE tend to segregate at the GB, in agreement with many experimental results.22,23 In this situation, the defects in the GI will move to the GB interface during the synthesis process, resulting in a purer grain structure, which is beneficial for improving the photovoltaic conversion efficiency.

Next, we consider the effects of the atomic chemical potentials on the defect formation energies and identify what defects are most possibly formed at the GB. To make sure CISE stabilize under equilibrium growth conditions, the atomic chemical potentials need to satisfy certain conditions. For example, to be in equilibrium with the elemental components, they should satisfy

$$\mu_{\text{Cu}} + \mu_{\text{In}} + 2\mu_{\text{Se}} = \Delta H_f(\text{CuInSe}_2) = -2.192 \text{ eV},$$

where $\Delta H_f(\text{CuInSe}_2)$ is the formation enthalpy of the CISE. To avoid the formation of the secondary phases such as CuS, Cu$_2$S, InS, In$_2$S, and In$_3$Se$_5$, the following relations must be satisfied:

$$\Delta H_f(\text{CuS}) = -0.378 \text{ eV},$$
$$\Delta H_f(\text{Cu}_2\text{Se}) = -0.678 \text{ eV},$$
$$\Delta H_f(\text{In}_2\text{Se}) = -1.167 \text{ eV},$$
$$\Delta H_f(\text{In}_3\text{Se}_5) = -0.830 \text{ eV},$$

$$2\mu_{\text{In}} + 3\mu_{\text{Se}} < \Delta H_f(\text{In}_3\text{Se}_5) = -2.902 \text{ eV},$$
$$\mu_{\text{Cu}} + 5\mu_{\text{In}} + 8\mu_{\text{Se}} < \Delta H_f(\text{CuIn}_3\text{Se}_5) = -9.086 \text{ eV},$$

where $\Delta H_f(\text{CuS})$, $\Delta H_f(\text{Cu}_2\text{Se})$, $\Delta H_f(\text{In}_2\text{Se})$, $\Delta H_f(\text{In}_3\text{Se}_5)$, and $\Delta H_f(\text{CuIn}_3\text{Se}_5)$ are the calculated formation enthalpies of binary and ternary compounds. Under these constraints, the chemical potentials of Cu and In that can stabilize CISE are bound to a polygon in the two-dimensional ($\mu_{\text{Cu}}$ and $\mu_{\text{In}}$) space, as shown in Fig. 3. We find that the region is not very large with the
chemical potentials of Cu and In being limited within 0.000 to −0.625 eV and −0.306 to 1.815 eV, respectively. Within this region, we chose five sidelines of the polygon in Fig. 3 to calculate the point defect formation energy dependence on the chemical potentials. The five vertices of the polygon represent different chemical potential conditions as the followings: point A represents Cu rich and In rich; points B, C, and D represent Cu and In relatively poor; and point E represents Cu rich and In poor. Different from the case in monocrystalline CISe that the formation energies of VCu and CuIn are lower than that of InCu, InCu near the GB will have a lower formation energy in a certain chemical potential region. It can be seen that the dominant defects change from InCu to CuIn and back to InCu along A–B–C–D–E–A lines. Accordingly, the atomic composition at the GB gradually changes from Cu depletion and In abundance to Cu abundance and In depletion, thus explaining diverse experimental measurements.

Besides the intrinsic defects, we also consider O-related defects as O is introduced in the experiments. Apparently, O is most likely to substitute Se sites. Here, we consider two cases. First, we consider the case with a low O concentration by replacing one Se atom at the GB area with one O atom (denoted as OSe–GB). The most stable substitutional site is found to be Se3 with an energy gain of 2.801 eV referenced to the clean GB. In this case, the relative stabilities of intrinsic defects do not change, as shown in Fig. 4(b). The only difference is that the formation energies of all the intrinsic defects are slightly increased. This can be understood as follows. The OSe3 defect breaks the inversion symmetry of ∑3 GB and induces a large atomic distortion; i.e., the original distances of dSe3–Cu3 (dSe3–Cu3) and dSe3–In3 (dSe3–In3) are changed from 2.44 Å and 2.54 Å to 2.00 Å (dO–Cu3) and 2.04 Å (dO–In3), respectively. For the case of a high O concentration, we replace the Se3, Se30, Se4, and Se40 atoms by four O atoms (denoted as 4OSe–GB), and we find that the energy gain is 1.361 eV/defect in this case. Because the electronegativity of O is larger than Se, the length of O-metal bonds becomes shorter than that of Se-metal bonds. The consequence of O introduction is that the weak bonds of Se3–Se30 and Se4–Se40 will be broken, which means that the new GB with 4OSe defects would like to attract more defects that can donate electrons and repel defects that are electron-deficient. Among our considered defects, InCu, In3, and Cu, can provide electrons; thus, their formation energies are expected to decrease, while other defects that cannot provide electrons are expected to have larger formation energies. Indeed, comparing with defect-free GB, our
calculations show that the formation energies of In\textsubscript{Cu}, Cu\textsubscript{i}, and In\textsubscript{i} are reduced by more than 1 eV, while the formation energies of V\textsubscript{In}, V\textsubscript{Cu}, and C\textsubscript{Cu} are increased by nearly 1 eV in the 4O\textsubscript{Se}-GB, as shown in Fig. 4(c). Moreover, under this situation, the most dominant intrinsic defect is always In\textsubscript{Cu} throughout all the considered chemical potential intervals. This is because that In\textsubscript{i} and Cu\textsubscript{i} are expected to have larger defect formation energies than In\textsubscript{Cu} as they will introduce large atomic distortions due to their large atomic sizes.

Based on the above discussion and considering the fact that CISe is usually synthesized under In-rich and Cu-poor conditions, we can conclude that the most possible defect that can be formed at the GB is likely to be In\textsubscript{Cu}, no matter whether O-related extrinsic defects are present or not. Our calculations thus provide a reasonable explanation of the Cu depletion and In segregation near the GB and demonstrate that the dangling bonds of Se\textsubscript{3} and Se\textsubscript{3}' play the key roles in the defect formation process.

Now, we turn our focus to study how In\textsubscript{Cu} at the GB affects the electronic properties of CISe. It is clearly in Fig. 5(a) that the host GB has three in-gap states, which correspond to three unsaturated bonds including In\textsubscript{1}–Cu\textsubscript{1}, Se\textsubscript{3}–Se\textsubscript{3}' and Se\textsubscript{4}–Se\textsubscript{4}' as shown in Fig. 1. When In\textsubscript{Cu} presents, the incipient In\textsubscript{1}–Cu\textsubscript{1} wrong bond is broken, which eliminates one in-gap state and opens a bandgap, as shown in Fig. 5(b). Note that In\textsubscript{Cu} in monocrystalline CISe can induce a relatively deep level and thus is harmful. However, at the GB, In\textsubscript{Cu} is actually helpful. When O\textsubscript{Se} presents at the GB in addition to In\textsubscript{Cu}, the Se\textsubscript{3}–Se\textsubscript{3}' wrong bond is replaced by the Se\textsubscript{3}–O wrong bond. Since the electronegativity of O is much stronger than Se, the Se\textsubscript{3}–O will be much weaker than Se\textsubscript{3}–Se\textsubscript{3}'. When this happens, the wrong bond introduced by
Se$_3$ and Se$_3^-$ will be broken, and the GB will become more electrically benign, as seen in Fig. 5(c). Furthermore, when 4OSe and In$_{Cu}$ are present at the GB, all the in-gap states are eliminated, as shown in Fig. 5(d). This can be understood as that due to the large electronegative of O, 4OSe attracts more electrons from metallic atoms to O atoms and eliminate two in-gap states caused by dangling bonds of Se atoms. Moreover, the weak bond between In and Cu is broken with the distance increased from 2.65 Å to 4.00 Å. Consequently, all the three unsaturated bonds in the host GB are removed, and a relatively wide bandgap is opened. As In$_{Cu}$ at the GB is of great importance to eliminate in-gap states and make the GB electrically benign, a high concentration of In$_{Cu}$ is expected to help enhance photovoltaic energy conversion efficiency. To realize this, we give the optimal chemical potential conditions by considering the formation energies of In$_{Cu}$. As shown in Fig. 3, the red grid area indicates the chemical potential region that the formation energy of In$_{Cu}$ is lower than that of Cu$_{In}$.

CONCLUSION

In conclusion, based on the first-principles density-functional theory, we have studied the defects at the $\sum 3$ (114) GB using the slab model in polycrystalline CISE. By providing the point defect formation energies, we show that the GB acts as a sink of defects because defects always have lower defect formation energies near GBs in our calculations. By considering the point defect formation energy dependence on the chemical potential conditions, we have explained the diverse experimental findings of elemental segregation and Cu depletion at the GB. Our work is expected to help achieve higher photovoltaic energy conversion efficiency of CISE solar cells.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES