**Abundance of Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ defect clusters in kesterite solar cells**

Shiyou Chen,$^{1,2}$ Lin-Wang Wang,$^2$ Aron Walsh,$^3$ X. G. Gong,$^4$ and Su-Huai Wei$^5$

$^1$Key Laboratory of Polar Materials and Devices (MOE), East China Normal University, Shanghai 200241, China
$^2$Joint Center for Artificial Photosynthesis (JCAP), Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
$^3$Key Laboratory for Computational Physical Sciences (MOE) and Surface Physics Laboratory, Fudan University, Shanghai 200433, China
$^4$Center for Sustainable Chemical Technologies and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
$^5$National Renewable Energy Laboratory, Golden, Colorado 80401, USA

(Received 25 August 2012; accepted 5 November 2012; published online 26 November 2012)

Kesterite solar cells show the highest efficiency when the absorber layers (Cu$_2$ZnSnS$_4$ [CZTS], Cu$_2$ZnSnSe$_4$ [CZTSSe] and their alloys) are non-stoichiometric with Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2. The fundamental cause is so far not understood. Using a first-principles theory, we show that passivated defect clusters such as Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ have high concentrations even in stoichiometric samples with Cu/(Zn+Sn) and Zn/Sn ratios near 1. The partially passivated Cu$_{Zn}$ + Sn$_{Zn}$ cluster produces a deep donor level in the band gap of CZTS, and the fully passivated 2Cu$_{Zn}$ + Sn$_{Zn}$ cluster causes a significant band gap decrease. Both effects are detrimental to photovoltaic performance, so Zn-rich and Cu, Sn-poor conditions are required to prevent their formation and increase the efficiency. The donor level is relatively shallower in CZTSSe than in CZTS, which gives an explanation to the higher efficiency obtained in Cu$_2$ZnSn(S, Se)$_4$ (CZTSSe) cells with high Se content. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768215]

The development of thin film solar cells using the earth-abundant kesterite Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSSe) semiconductors as the light-absorber layer has rapidly progressed over the past three years,$^1$ e.g., a 10.1% efficiency has been achieved by Barkhouse et al. in CZTSSe cells,$^4$ and 9.2% by Repins et al. in CZTSSe cells.$^6$ Despite the ideal electronic properties for visible light absorption (band gaps around 1.0 and 1.5 eV, respectively, and high optical absorption coefficients$^7$–9), the increased number of elements makes it challenging to synthesize high-quality single-crystal samples, i.e., non-stoichiometry and the coexistence of secondary compounds are frequently observed.$^{10}$–14

One unusual observation is that all the kesterite solar cells with reported efficiencies higher than 8% have the element ratios Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2,$^1$ which seriously deviating from the ideal value of 1. This has resulted in an empirical rule that the Cu poor and Zn rich growth condition gives the highest efficiency.$^{13}$ Typically, such a high level of non-stoichiometry indicates either the high population of intrinsic defects or the coexistence of secondary compounds (e.g., low Cu/(Zn+Sn) and high Zn/Sn ratios may be caused by ZnS coexistence), which can have detrimental influence and cause the photovoltaic performance worse than that of the stoichiometric cell. Why do then kesterites exhibit the opposite effect?

One possible explanation is that when Cu/(Zn + Sn) ≈ 1 and Zn/Sn ≈ 1, intrinsic defects that act as recombination centers (deep donors or acceptors) are formed, which can be eliminated when the environment becomes Zn-rich and Cu, Sn-poor. In the chalcopyrites CuGaSe$_2$ (CGSe) and CuInSe$_2$ (CISe), Ga$_{Zn}$ and In$_{Cu}$ antisite defects have been reported as deep donors, and are considered as the limiting factors of the Cu(In, Ga)$_2$Se$_2$ based solar cell efficiency.$^{19,20}$ Similarly, we may ask if such kind of antisite defects also produce deep donor levels in CZTS and CZTSSe. Previously, Sn$_{Cu}$ and Sn$_{Zn}$ donor levels are found to be deep,$^{21}$–23 but their formation energies are high, even when they are fully ionized in p-type samples,$^{21}$–22 so their population is rather low and their influence is weak.

In this letter, we show using the first-principles calculations that the compensation between the dominant acceptor defect Cu$_{Zn}$ and the donor defect Sn$_{Zn}$ can decrease the formation energies of the defect clusters (Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$) significantly, so they have high concentration in stoichiometric samples with Cu/(Zn + Sn) ≈ 1 and Zn/Sn ≈ 1. In CZTS, the partially compensated Cu$_{Zn}$ + Sn$_{Zn}$ cluster produces deep donor levels and the fully compensated 2Cu$_{Zn}$ + Sn$_{Zn}$ induces a significant band gap decrease. Both effects can contribute to the low efficiency of stoichiometric CZTS and CZTSSe solar cells. These states are relatively shallow in CZTSSe compared to CZTS, which explains the higher efficiency of the CZTSSe solar cells when the Se composition is higher.$^{1,3,15}$

In kesterite CZTS (CZTSe), each anion is tetrahedrally coordinated by four cations (two Cu in the nominal valence +1, one Zn in +2, and one Sn in +4). When Cu replaces Zn (Cu$_{Zn}$ antisite), an acceptor level is produced above the valence band maximum (VBM), and when Sn replaces Zn (Sn$_{Zn}$ antisite), two electrons occupy a donor level below the conduction band minimum (CBM), as shown in Fig. 1. Aggregation of these defects results in electronic compensation and Coulombic attraction: electron transfer from the donor to acceptor state (see Fig. 1) decreases the formation energy of the Cu$_{Zn}$ + Sn$_{Zn}$ cluster. Since Sn$_{Zn}$ is a double...
donor defect, Cu$_{Zn}$ + Sn$_{Zn}$ still has one donor electron that can compensate another Cu$_{Zn}$ acceptor, forming the 2Cu$_{Zn}$ + Sn$_{Zn}$ tri-cluster. Due to the strength of the attractive interactions, these compensated defect clusters can have high populations in the synthesized samples. This is similar to the case that high-population 2V$_{Cu}$ + In$_{Cu}$ and 2V$_{Cu}$ + Ga$_{Cu}$ clusters have been observed in the chalcogenides.

In our study, the populations of Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ clusters in CZTS and CZTSe can be predicted through calculation of the defect formation energies and statistical models.

The defect formation energy is calculated following the standard approach, i.e., a defect \( x \) with a charge state \( q \) is created in a 128-atom supercell. The resulting formation energy is explicitly dependent on the chemical environment (elemental chemical potentials \( \mu_i \), where \( i = \text{Cu, Zn, Sn, S} \)) and the Fermi energy (electron chemical potential, \( E_F \)). The total energy calculations were performed using the VASP code with the PW91 exchange correlation functional, a plane wave cutoff energy of 300 eV, and a \( 2 \times 2 \times 1 \) k-point mesh. Band gap corrections (\( \Delta E_{BM} = 0.40 \) and 0.39 eV for CZTS and CZTSe, respectively) were determined using the procedure as given for CGSe and CISe in Ref. 29, and further technical details can be found in Ref. 22.

In Fig. 2, the formation energies of several low-energy defects and defect clusters in (a) CZTS and (b) CZTSe are plotted as a function of the elemental chemical potentials shown in (c). Because the Cu$_{Zn}$ antisite is the dominant acceptor defect in both CZTS and CZTSe under these conditions, the samples are inherently p-type, so \( E_F \) will be close to the VBM (equal to 0 eV), which makes the donor defects such as Sn$_{Zn}^{-1}$, [Cu$_{Zn}$ + Sn$_{Zn}$]$^+$, and Zn$_{Cu}^{-1}$ ionized with a lower formation energy than in the neutral state. The element chemical potentials (\( \mu_{Cu}, \mu_{Zn}, \) and \( \mu_{Sn} \)) describe the richness of the elements, and are limited to a certain range to avoid the formation of the competitive compounds, which has been discussed in detail previously for CZTS.

In Fig. 2(c), the chemical potential range that stabilizes CZTSe is shown by the black region surrounded by the points P-Q-M-N. Due to the competitive secondary phases ZnSe and Cu$_2$SnSe$_3$, Zn$_{Cu}$ is limited to a very narrow range, i.e., too much Zn (higher \( \mu_{Zn} \)) leads to ZnSe formation while too little Zn (lower \( \mu_{Zn} \)) leads to Cu$_2$SnSe$_3$ formation.

**Population of defect clusters in CZTS.** It is clear in Fig. 2(a) that the Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ have low formation energies in the stable chemical potential range, corresponding to a population of the order of \( 10^{-10} \) to \( 10^{-15} \) and \( 10^{-10} \) to \( 10^{-18} \) cm$^{-3}$ in CZTS, respectively. When the chemical potentials are near the M-N line, their population can be as high as \( 10^{15} \) and \( 10^{14} \) cm$^{-3}$, respectively, which is easy to understand since Cu$_2$SnS$_3$ is stabilized if \( \mu_{Zn} \) is on the left side of the M-N line (Zn poor) and the formation of 2Cu$_{Zn}$ + Sn$_{Zn}$ can convert CZTS towards Cu$_2$SnS$_3$. In the stable chemical potential region, all defects (including the dominant Cu$_{Zn}$) have populations lower than \( 10^{10} \) cm$^{-3}$, which corresponds to deviation in Cu/(Zn+Sn) and Zn/Sn ratios by less than 0.01. CZTS samples under these conditions have Cu/Zn+Sn) and Zn/Sn ratios around one, which indicates that even in stoichiometric samples a high population of Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ defect clusters can still exist.
On the other hand, defect formation with populations lower than $10^{20}$ cm$^{-3}$ cannot cause a large deviation of the element ratios as in the high-efficiency solar cells (Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2). These materials must be synthesized under conditions beyond the stable chemical potential region of CZTS, e.g., on the right hand side of P-Q line. When $\mu_{Zn}$ is higher than P-Q line (Zn rich), the high population of defects such as V$_{Cu}$ + Zn$_{Cu}$ and Zn$_{Sn}$ + $2Zn_{Cu}$ as well as the coexistence of ZnS can cause Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2, but the population of Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ can be decreased dramatically, so their detrimental influence on photovoltaic performance can be reduced.

Electronic state of defect clusters. The charge density of the Cu$_{Zn}$ + Sn$_{Zn}$ donor state is shown in Fig. 3, which is localized around the Sn$_{Zn}$ antisite with almost no distribution around Cu$_{Zn}$. The combination of Sn 5$s$ and S 3$p$ orbitals is the characteristic of Sn$_{Zn}$ related donor defects. When Sn replaces Zn in the CZTS lattice, two Sn 5$p$ electrons are transferred to S, while the 5$s$ orbital forms a localized donor state. The Sn 5$s$ orbital is much lower in energy than the 5$p$ orbital (see Table II of Ref. 31), which is also why Sn is stable in two oxidation states. Using a hybrid density functional (HSE06), which performs well for CZTS, we predict the localized donor state (eigenvalue) to be 1.03 eV below the CBM (for one Sn$_{Zn}$ antisite in the 128-atom CZTS supercell).

Binding of Sn$_{Zn}$ and Cu$_{Zn}$ leads to level repulsion between the donor and acceptor states, thus pushes the energy of the donor state to 0.63 eV below the CBM, which can be seen in the calculated density of states (DOS) plotted in Fig. 4 (top panel). A small peak (~0.6 eV below the CBM) is located in the middle of the CZTS band gap, which is mainly composed of Sn 5$s$ states (as shown by the projected DOS). To describe the ionization of this donor defect more accurately, we have also calculated the optical and thermal transition energy levels, and found the values for the (0/+1) transition are 0.85 and 0.33 eV below the CBM, respectively. In contrast, the 2Cu$_{Zn}$ + Sn$_{Zn}$ complex is fully compensated, so there is no occupied donor state. The change in potential does, however, cause a CBM red-shift by 0.2 eV (a total band gap decrease by 0.35 eV due to an additional VBM upshift of 0.15 eV). It should be noted that for Sn$_{Zn}$, Cu$_{Zn}$ + Sn$_{Zn}$, and 2Cu$_{Zn}$ + Sn$_{Zn}$, the localization of the Sn 5$s$ state on the defect site is always kept (see Fig. 3), which indicates that a high population of these defects will either produce deep recombination centers for electron-hole pairs, or cause strong electron trapping, both detrimental to the photovoltaic efficiency. Considering the high population of both defect clusters even in the stoichiometric CZTS samples, we can understand the limited efficiency of stoichiometric kesterite solar cells. In contrast, when Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2, high $\mu_{Zn}$, low $\mu_{Cu}$ and $\mu_{Sn}$ conditions are required, so the populations of both defect clusters are decreased and a higher efficiency is expected.

Defect clusters in CZTSe. Since solar cells based on the CZTSSe alloy are found to show higher efficiency when the Se composition is high, now we will try to reveal if this is also related to Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$. In Fig. 2(b), the calculated formation energies in CZTSe are plotted. Comparing the values in CZTSe and in CZTS, it can be found that: (i) the population of Cu$_{Zn}$ + Sn$_{Zn}$, which produces deep donor levels, is between 10$^5$ and 10$^6$ cm$^{-3}$ in CZTSe, lower than the corresponding value in CZTS; (ii) the population of 2Cu$_{Zn}$ + Sn$_{Zn}$ is always high, between 10$^5$ and 10$^6$ cm$^{-3}$, even higher than that in CZTS. However, the Sn$_{Zn}$ induced donor levels (eigenvalues) are 0.35, 0.23, and 0.12 eV below the CBM for isolated Sn$_{Zn}$, Cu$_{Zn}$ + Sn$_{Zn}$ (see the calculated DOS in Fig. 4, bottom panel), and 2Cu$_{Zn}$ + Sn$_{Zn}$ clusters, respectively, consistently shallower than in CZTS (1.03, 0.63, 0.20 eV, respectively). Thus, high population of 2Cu$_{Zn}$ + Sn$_{Zn}$ in CZTSe is not too harmful. The results above show that the effects of both Cu$_{Zn}$ + Sn$_{Zn}$ and 2Cu$_{Zn}$ + Sn$_{Zn}$ clusters are therefore weaker in CZTSe. This gives an explanation to the higher efficiency observed when

FIG. 3. Electron density isosurface of the Cu$_{Zn}$ + Sn$_{Zn}$ donor state (isovalue 25% of the maximum value). The green, blue, gray, and yellow filled circles show Cu, Zn, Sn, and S atoms, respectively, and the black circles show the defect sites of Cu$_{Zn}$ and Sn$_{Zn}$.

FIG. 4. Calculated DOS of CZTS (top) and CZTSe (bottom) with a Cu$_{Zn}$ + Sn$_{Zn}$ defect cluster in a 128-atom supercell. The blue lines show the total DOS and the red lines show the projected DOS on Sn 5$s$ orbital at the Sn$_{Zn}$ site (multiplied by 128 for clarity). The energy is relative to the VBM of CZTS and CZTSe.
Se composition is high. It also suggests that the more negative influence of these defect clusters in CZTS imposes a limit to the efficiency of CZTSSe alloys, i.e., although increasing the S composition can increase the band gap of the absorber layer closer to the optimal value (1.4–1.5 eV according to the Shockley-Queisser model), the efficiency may be decreased when S composition is high due to the formation of the deep trap states that limit carrier lifetime.

In conclusion, we reveal that Cu$_{2}$Zn + Sn$_{2}$Zn and 2Cu$_{2}$Zn + Sn$_{2}$Zn clusters can be formed in high-populations even in stoichiometric CZTS and CZTSe samples with Cu/ (Zn + Sn) $\approx$ 1 and Zn/Sn $\approx$ 1. Zn rich and Cu, Sn poor conditions are required to decrease their population. In CZTS, Cu$_{2}$Zn + Sn$_{2}$Zn produces a deep donor level, with a localized Sn 5s component, and 2Cu$_{2}$Zn + Sn$_{2}$Zn causes a significant band gap decrease, which are both detrimental to the solar cell efficiency. However, in CZTSe, the detrimental effects of both clusters are weaker. Based on these results, we provide an explanation for the experimental observation that: (i) kesterite solar cells with the highest efficiencies are fabricated under a Zn rich and Cu, Sn poor conditions, with Cu/ (Zn + Sn) $\approx$ 0.8 and Zn/Sn $\approx$ 1.2; (ii) CZTSSe alloy solar cells have higher efficiencies when the Se composition is high. Experimental identification of the Cu$_{2}$Zn + Sn$_{2}$Zn and 2Cu$_{2}$Zn + Sn$_{2}$Zn defect clusters is called for.

The work in China was supported by NSF of China (Nos. 61106087 and 10934002), the Special Funds for Major State Basic Research Program (No. 2012CB921401), the Research Program of Shanghai municipality and MOE, PCSIRT and CC of ECNU. The work (manuscript preparation) performed in JCAP, a DOE Energy Innovation Hub, was supported through the Office of Science of the U.S. DOE under Award No. DE-SC0004993. A.W. acknowledges support from the Royal Society for a University Research Fellowship and EPSRC Grant No. EP/I01330X/1. The work at NREL was funded by the U.S. DOE, under Contract No. DE-AC36-08GO28308.