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Defect physics of the kesterite thin-film solar cell absorber Cu_2ZnSnS_4

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Cu_2ZnSnS_4 is one of the most promising quaternary absorber materials for thin-film solar cells. Examination of the thermodynamic stability of this quaternary compound reveals that the stable chemical potential region for the formation of stoichiometric compound is small. Under these conditions, the dominant defect will be p-type Cu_{Zn} antisite, which has an acceptor level deeper than the Cu vacancy. The dominant self-compensated defect pair in this quaternary compound is $[Cu_{Zn}^{-}+Zn_{Cu}^{+}]^0$, which leads to the formation of various polytype structures of Cu_2ZnSnS_4. We propose that to maximize the solar cell performance, growth of Cu_2ZnSnS_4 under Cu-poor/Zn-rich conditions will be optimal, if the precipitation of ZnS can be avoided by kinetic barriers. © *2010 American Institute of Physics*. [doi:10.1063/1.3275796]

Distinct compound semiconductors can be formed by taking binary building blocks and cross-substituting to form ternary and quaternary systems.[1] This breeding process can be used to tune the physicochemical properties (e.g., band gap), while keeping many of the favorable parent traits (e.g., structure). Taking the transition from binary ZnS to ternary $CuGaS_2$, where two Zn(II) species are replaced by Cu(I) and Ga(III), one step further results in quaternary Cu_2ZnGeS_4 or Cu_2ZnSnS_4 (CZTS), where two Ga(III) are replaced by Zn(II) and Ge(IV) or Sn(IV). This evolutionary process can be employed to construct an entire class of quaternary semiconductor systems,[1,2] in which the tetrahedral networks maintain the octet rule (Fig. 1).

CZTS has become the subject of intense interest because it is an ideal candidate absorber material for thin-film solar cells with an optimal band gap (1.5 eV), high absorption coefficient ($>10^4$ cm^{-1}), abundant elemental components, and is adaptable to various growth techniques.[3–10] The energy conversion efficiency of CZTS based solar cells has increased from 0.66% in 1996 to close to 7% recently;[9] however, it is still well below the 32% single-junction limit determined by the detailed balance between the solar cell and the sun modeled as black bodies, as proposed by Shockley and Queisser.[11] To further improve the efficiency, it is crucial to understand the thermodynamic stability of this quaternary compound and the formation mechanism of the dominant intrinsic defects. However, in contrast to ternary compounds such as $CuInSe_2$,[12] no systematic studies have been carried out for the quaternary systems. In this letter, we have performed a series of first-principles electronic structure (density functional theory) calculations to help direct experimental optimization. Total energy calculations were performed in the VASP code,[13,14] using a plane wave cutoff of 300 eV and a $2\times2\times2$ k-point mesh for the 64-atom supercell. Forces were relaxed to below 0.01 eV/Å and defect corrections, including potential alignment for charged defects, were performed as described in Ref. 12.

Thermodynamic Stability of CZTS. The ground-state crystal structure of CZTS is kesterite ($I\bar{4}$), a $1\times1\times2$ expansion of the cubic binary zinc-blende lattice (Fig. 1). To be stable under equilibrium growth conditions, CZTS has to satisfy certain conditions. For example, to be in equilibrium with its elemental components, it should satisfy

$$2\mu_{Cu}+\mu_{Zn}+\mu_{Sn}+4\mu_{S}=\mu_{Cu_2ZnSnS_4}=-4.21\ \text{eV}, \qquad (1)$$

where μ_i is the chemical potential of element or compound i referenced to the most stable phases of the involved elements, as defined and explained in Refs. 12 and 15. Here $\mu_{Cu}=0$, $\mu_{Zn}=0$, $\mu_{Sn}=0$, and $\mu_S=0$ means these elements are so rich that their pure solid phase can form, and $\mu_{Cu_2ZnSnS_4}$ equals the formation enthalpy of CZTS, which can be calculated from the total energy of CZTS and its elemental standard states. It should also avoid the precipitation of secondary phases such as CuS, Cu_2S, ZnS, SnS, SnS_2, and

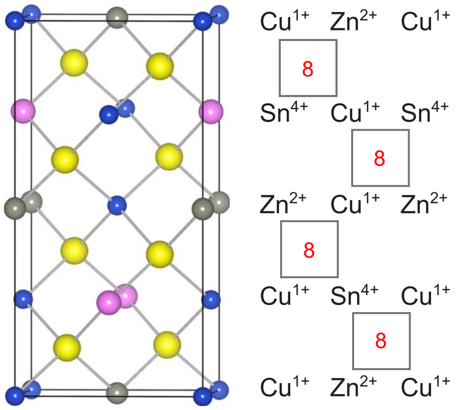

FIG. 1. (Color online) The tetragonal ($I\bar{4}$) kesterite crystal structure of CZTS (left) with the corresponding cation ordering (right). The formal cation charge states around each sulfur are shown, which obey the octet rule ($8/4+6=8$ electrons around each S atom).

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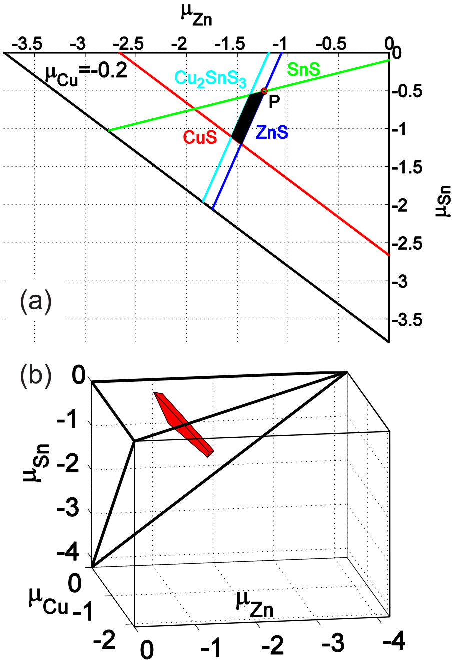

FIG. 2. (Color online) The calculated polyhedron (bottom panel) of the chemical potential region where CZTS is stable against formation of four elements and six competitive compounds. The plane at $\mu_{Cu}=-0.2$ eV is also shown (top panel), where the allowed chemical potential region (black) are bounded by SnS (green line), ZnS (blue line), CuS (red line), and Cu_2SnS_3 (navy line). All the energies are in electron volts. Point **P** shows the region near which all intrinsic defects have positive formation energies.

Cu_2SnS_3, as well as any states that deviate from the stoichiometry (2:1:1:4) of the CZTS compound,[12] i.e., the following relationships such as:

$$\mu_{Cu}+\mu_S<\mu_{CuS}=-0.49\ \text{eV}, \tag{2a}$$

$$\mu_{Zn}+\mu_S<\mu_{ZnS}=-1.75\ \text{eV}, \tag{2b}$$

$$\mu_{Sn}+\mu_S<\mu_{SnS}=-1.01\ \text{eV}, \tag{2c}$$

$$2\mu_{Cu}+\mu_{Sn}+3\mu_S<\mu_{Cu_2SnS_3}=-2.36\ \text{eV}, \tag{2d}$$

must be satisfied. Under these constraints, the chemical potential range of Cu, Zn, and Sn that stabilizes the CZTS compound is bound to a polyhedron in the three-dimensional (μ_{Cu}, μ_{Zn}, and μ_{Sn}) space, whereas the chemical potential of S is related to that of Cu, Zn, and Sn through Eq. (1); we find that this region is very small. The stable polyhedron is plotted in Fig. 2, together with a slice through the $\mu_{Cu}=-0.2$ eV plane, where, for competitive secondary phases, the four elements, five binary compounds, and one ternary compound mentioned above are considered. In this case, μ_{Cu} is restricted to between 0 and −0.5 eV and μ_{Zn} and μ_{Sn} are also limited to a small range depending on the value of μ_{Cu}. However, other ternary and quaternary compounds such as $Cu_4Sn_7S_{16}$ or $Cu_9Zn_3Sn_4S_{16}$ may also become limiting secondary phases under certain conditions, which are reflected by the spontaneous formation of intrinsic defects that have negative formation energies. To avoid this situation, the allowed chemical potential region becomes even smaller and is located around point **P** ($\mu_{Cu}=-0.20$ eV, $\mu_{Zn}=-1.23$ eV, and $\mu_{Sn}=-0.50$ eV), as shown in Fig. 2(a). We find that in this region μ_{Zn} is much lower than μ_{Cu}, indicating that Cu-rich/Zn-poor conditions are necessary for the growth of single-phase stoichiometric CZTS crystals. The small stability region in the chemical potential landscape indicates that although quaternary compounds exhibit more flexibility for tuning the physical properties than binary or ternary compounds, secondary phases also become more competitive, and thus it is more difficult to form the desired stoichiometric phase. In the following, we will focus our discussion only at stable CZTS region around point **P**.

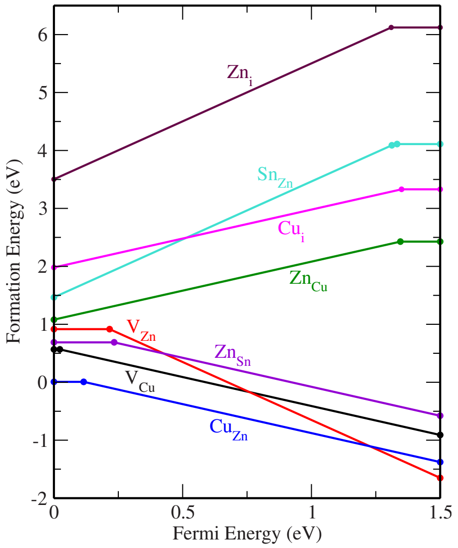

FIG. 3. (Color online) Formation energy of intrinsic defects as a function of the Fermi energy at point **P**. The defect charge state determines the slope of the line, and the turning points represent the transition energy levels between different charge states for a given defect.

Intrinsic defects in CZTS. For ternary compounds such as $CuInSe_2$, the dominant *p*-type acceptor is the Cu vacancy, because the formation of V_{Cu} with a nominal valence zero produces a minimal perturbation at the Cu(I) site, whereas other defects such as Cu(I) on In(III) result in a much larger perturbation.[12] It has been assumed that V_{Cu} is also the dominant acceptor defect in CZTS.[16] However, in the quaternary compound, the valence difference between Cu(I) and Zn(II) in Cu_{Zn} is equal to one, similar to V_{Cu}. Thus Cu_{Zn} could also be a strong candidate for the dominant acceptor. Indeed, our calculations find that at point **P**, the formation energy of neutral V_{Cu} is 0.57 eV, whereas the formation energy of neutral Cu_{Zn} is lower at 0.01 eV, as shown in Fig. 3. This is consistent with the fact that the chemical difference between Cu and Zn is smaller than that between Cu and a vacancy. All donor defects have higher formation energy, consistent with the experimental finding that most samples show *p*-type conductivity.[17,18] The calculated acceptor (0/−) transition energy level for V_{Cu} is at 0.02 eV above the valence band maximum (VBM), whereas the (0/−) level for Cu_{Zn} is at 0.10 eV above the VBM (Fig. 3), which can be explained by the fact that the $p-d$ coupling for Cu_{Zn} is enhanced, whereas it is reduced for V_{Cu}, thus the acceptor level of V_{Cu} is shallower.

Our results, therefore, predict that under the equilibrium growth conditions (Cu-rich/Zn-poor) required to form high quality CZTS samples, Cu_{Zn} will dominate over V_{Cu}. However, because of the relatively deep acceptor level of Cu_{Zn}, this situation may not be optimal for solar cell applications. Indeed, Cu-poor and Zn-rich conditions are sometimes used to improve solar cell efficiency,[7,9,19] which has the effect of enhancing the formation of V_{Cu} and suppressing the formation of Cu_{Zn}.

Compensating defect complex in CZTS. One omnipresent issue in the related chalcopyrite thin-film solar cell absorbers is the passivation of active point defects through formation of defect complexes. For example, the formation of $[2V_{Cu}^{-}+In_{Cu}^{2+}]^0$ in $CuInSe_2$ plays a key role in the use of $CuInSe_2$ as a high efficiency thin-film solar cell absorber.[12] It has been proposed that the facile formation of this defect complex leads to a locally Cu-poor β-phase domain that facilitates electron and hole separation, thus helping to improve the cell efficiency.[20]

The easy formation of the $[2V_{Cu}^{-}+In_{Cu}^{2+}]^0$ defect complex is attributed to the presence of two cations in the ternary compound.[12] In the quaternary system CZTS, there are three cations as follows: Cu, Zn, and Sn, from which the antisite defect pair $[Cu_{Zn}^{-}+Zn_{Cu}^{+}]^0$ should be even easier to form due to the smaller chemical and size disparities between the elements. Indeed, we find that neutral Zn_{Cu} has a formation energy of 2.43 eV at point **P** and its $(+/0)$ transition energy level is 0.15 eV below the conduction band minimum (CBM), however, when it forms a defect pair with Cu_{Zn}, it has a predicted binding energy of 2.22 eV, giving an overall formation energy of 0.21 eV, which is independent of the element chemical potentials and can be further lowered to several millielectron volts when arrays of $[Cu_{Zn}^{-}+Zn_{Cu}^{+}]^0$ antisite pairs are formed, leading to various polytype structures of CZTS. These pairs can be viewed as partial disorder in the Cu–Zn sublattice,[2] which has been observed in neutron scattering experiments.[21] Due to the small chemical perturbations, the corresponding isolated defect states are delocalized, because the Cu_{Zn} acceptor state follows the character of the VBM (antibonding Cu *d*-S *p*) while the Zn_{Cu} donor state follows CBM (Sn *s* and S *s*). In comparison, disorder in the Zn–Sn and Cu–Sn (formation energy of antisite pair; 0.86 and 1.99 eV, respectively) sublattices is less favorable because they have large chemical and size disparity.

It has been established that for the quaternary systems, the valence band offset between compounds with different degrees of antisite disorder is small,[2,22] which indicates that the carrier separation between different domains of site disorder will not be significant, especially for holes. Comparing with $[2V_{Cu}^{-}+In_{Cu}^{2+}]^0$ in $CuInSe_2$,[20] we suggest that formation of the $[V_{Cu}^{-}+Zn_{Cu}^{+}]^0$ pair under Zn-rich and Cu-poor conditions should be more beneficial for maximizing solar cell performance. According to our calculation, the formation energy of $[V_{Cu}^{-}+Zn_{Cu}^{+}]^0$ is 0.65 eV at point **P**, and decreases quickly when Cu becomes poorer and Zn becomes richer. However, in that case, one has to avoid the formation of Zn related precipitates such as ZnS by utilizing kinetic energy barriers.

Our calculations explain a number of unique features for CZTS, which are relevant to its use as a solar cell absorber; (i) the chemical potential region that CZTS can form stoichiometrically is very small. Therefore, it is very important to control the growth conditions for obtaining high quality CZTS samples; (ii) the dominant *p*-type acceptor in CZTS is Cu_{Zn}, however, the associated acceptor level is relatively high, suggesting that *p*-type doping in CZTS is more difficult than the ternary compounds such as $CuInSe_2$; (iii) the formation of the self-compensated defect pair $[Cu_{Zn}^{-}+Zn_{Cu}^{+}]^0$ will not lead to strong carrier separation, and thus will not provide the same beneficial effect observed in ternary chalcopyrite compounds; (iv) we predict that to avoid the aforementioned issues in (ii) and (iii), it will be optimal to grow the sample under Cu-poor/Zn-rich conditions, so V_{Cu} and Zn_{Cu} become the dominant defects in the system. However, in this case, nonequilibrium growth techniques may be required to avoid the formation of secondary phases such as ZnS. Further experimental investigation to test our predictions will be highly beneficial.

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