The examination of stable charge states of vacancies in Cu₂ZnSnS₄

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The stable charge states of vacancies in the solar cell absorber material Cu₂ZnSnS₄ are investigated using Kohn-Sham (KS) defect-induced single particle levels analysis by concerning the screened Coulomb hybrid functional. We find out that the Cu, Zn and S vacancies (denoted by V_{Cu}, V_{Zn}, V_{S}) do not induce single particle defect levels in the vicinity of the band gap thus each of them has only one stable charge state corresponding to the fully occupied valence band V_{Cu}^{1−}, V_{Zn}^{2−} and V_{S}^{3−}, respectively (and therefore cannot account for any defect transition energy levels). The Sn vacancy (V_{Sn}) has three stable charge states V_{Sn}^{2−}, V_{Sn}^{3−} and V_{Sn}^{4−}, which may account for two charge transition energy levels. By comparing with previous charge transition energy levels studies, our results indicate that the examination of stable charge states is a necessary and important step which should be done before charge transition energy levels calculations.
I. INTRODUCTION

Cu(In,Ga)Se$_2$ (CIGS) possesses the highest energy conversion efficiency up to 20.3% among the thin film solar cells$^4$. Researchers are still making their efforts on improving the CIGS solar cell efficiency$^{2,3}$. CIGS solar cells compete today as successors of the dominating silicon technology. Nevertheless, there are concerns about their large scale production due to the price and the availability of In. By replacing In and Ga elements in CIGS with Zn and Sn elements it formulates Cu$_2$ZnSnSe$_4$ (CZTSe)$^4$, which is very similar to Cu$_2$ZnSnS$_4$ (CZTS) in structure and physical properties$^{5,6}$. CZTS and CZTSe quaternary compounds overcome the disadvantages in CIGS owing to their earth-abundant and low-toxicity constituents. Moreover, the kesterite CZTS possesses the $I4$ space group$^7$, characteristic optimal band gap of about 1.5 eV$^8$ (bandgap of CZTSe is 1.0 eV) and large absorption coefficient of more than $10^4$ cm$^{-1}$$^{10}$. The energy conversion efficiency of CZTS-based solar cell has achieved a world record of 12.6% in November 2013$^{11}$. The relatively high energy conversion efficiency is partly due to the $p$-type conductivity via inducing the intrinsic point defects in the parent CZTS. Point defects significantly influence the efficiency of the $pn$-junction-based solar cells. Therefore, much attention has been paid to the point defects in CZTS to understand the relationship between defects and solar cell efficiency$^{12-17}$.

Previous theoretical researches mainly focus on the formation energies and defect transition energy levels of the intrinsic defects in CZTS using the first-principles total energy calculations$^{14-17}$ based on density functional theory$^{18,19}$. Formation energies define the formation ability of defects in samples. The defects with low formation energies can exist in large amount in the samples while those with high formation energies can exist in relatively small amount which will not affect the properties of the CZTS. Defect transition energy levels are directly related to the defect (donor or acceptor) levels in the band gap. Deep defect levels mainly act as recombination centers, while shallow defect levels allow the transformation from one charge state to another easily which will increase carrier concentration in the sample. The theoretical value of a defect transition energy level is closely related to the total energy difference of two charge states of the defect, which was always taken in previous studies$^{14-17}$. However, the way of inspecting total energy difference is not able to examine the stability of the considered charge states, which may lead to theoretically unphysical defect transition energy levels$^{20-23}$. Taking Cu vacancy ($V_{Cu}$) as an example,
first, the neutral \( V^0_{Cu} \) was simulated by removing an Cu atom in the supercell, and the \( V^1_{Cu} \) charge states was simulated by adding an additional electron to the jellium background of \( V^0_{Cu} \). Next, the two models were fully relaxed to get the total energy difference and the value of defect transition energy level \( \epsilon(-/0) \). In this procedure one ignored the examination of whether the 0 and 1- charge states are stable, which should be done before defect transition energy level calculation\(^{20-23}\). Therefore, in this paper, we are motivated to go a prior step to identify the possible stable charge states of defects in CZTS using band structures and defect-induced single particle levels (Kohn-Sham eigenvalues) analysis\(^{20,21,23}\).

To identify the possible stable charge states of all the intrinsic defect completely, one would better investigate all vacancies, antisites, intersites and defect complexes in the CZTS. Due to the bigger defect number in CZTS than in CuInSe\(_2\), in this paper, only the vacancies are considered as a first step to explore the possible stable charge states of defects in CZTS.

Our results show that all the enforced charge states of Cu vacancy \( V^0_{Cu} \) and Zn vacancy \( V^0_{Zn} \) and S vacancy \( V^0_{S} \) cannot produce localized defect-induced single particle levels in the vicinity of band gap as well as defect transition energy levels within the band gap, for that each of them only has one stable charge state corresponding to the fully occupied valence band \( V^1_{Cu} \), \( V^2_{Zn} \) and \( V^0_{S} \), respectively. The exception is that \( V_{Sn} \) (Sn vacancy) in its 2-, 3-, 4- charge states are stable due to that the defect-induced single particle levels are located at the top of the valence band maximum (VBM). Consequently, Cu, Zn and S vacancies can not while Sn vacancy can induce charge transition energy levels in the band gap, which is partly at odd with previous charge transition energy levels studies. Our results indicate that the examination of stable charge states is a necessary and important step which should be done before charge transition energy levels calculations.

**II. THEORETICAL APPROACHES**

The electronic structure calculations are carried out using the density functional theory as implemented in the plane wave VASP code\(^{24}\). For the exchange-correlation functional, both generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)\(^{25,26}\) and screened Coulomb hybrid functional Heyd-Scuseria-Ernzerhof (HSE06) are used\(^{27,28}\). PBE-GGA is used to obtain an initial structures and HSE06 is used to calculate the electronic structures, since GGA often under estimates the band gap of Cu-based semiconduc-
tor compounds and HSE06 functional describes the localized orbitals more correctly than (semi)local-density functionals by substituting part of short range PBE-GGA exchange energy with the short range Hartree-Fock (HF) exchange energy. HSE06 functional is verified to improve the description of the band gap of CZTS as well as the defect properties. The parameter controlling the amount of HF exchange in the HSE06 functional is set to 0.3 and the range-separation screening parameter $\mu$ is set to 0.20 Å$^{-1}$. The interaction between ions and electrons is described by the projector-augmented wave (PAW) method. The cutoff energy for the plane-wave basis is set to 300 eV. Using these setup our calculated band gap of 1.43 eV is close to the reported 1.44 - 1.51 eV for CZTS. The vacancy models are constructed by removing an atom from a 64-atom $2\times2\times1$ supercell. The Brillouin zone sampling is done using $2\times2\times2$ k-point mesh. The ground state geometries of all the defect systems are obtained by minimizing the Hellman-Feynman forces on each atom to become less than 0.02 eV/Å.

A defect often has multiple possible charge states. Taking $V_{Sn}$ as an example, $V_{Sn}$ has five possible charge states from -4 to 0. The stability of these possible charge states is strongly related to the positions of the defect-induced single particle levels relative to the band gap. On one hand, if a defect with a certain charge state induces single particle levels in the vicinity of the band gap, the corresponding charge state is stable because the defect-induced single particle levels may form a stable bound state bounding electrons or holes. On the other hand, if a defect with a certain charge state induces single particle levels in the valence band or conduction band, the corresponding charge state is unstable because the defect-induced single particle levels are always occupied or unoccupied and the electrons or holes on them are communized. A defect with multiple stable charge states is a necessary though not a sufficient condition for transitions among the stable charge states to take place. Such transitions produce defect transition energy levels as others investigations by DFT calculations. Additionally, a defect with all the charge states produce none single particle levels in the vicinity of the band gap will stable at one charge state corresponding to the fully occupied valence band. Other charge states are physically unstable because the existence of either holes at the VBM or electrons at the conduction band maximum (CBM). This kind of defects will not have charge transition energy level in the gap. Therefore, we conclude that the examination of possible stable charge states must be done before charge transition energy levels calculations. To pick out the defect-induced single
levels, we examine the local density of states (LDOS) of vacancy systems which corresponds to the DOS of the four nearest neighbor atoms around the vacant site. The additional sharp peaks in density of states (LDOS) of a vacancy system compared with that of parent compound are defect-induced single particle levels.

It should be emphasized that this work provides a qualitative view of the basic nature of defect in CZTS, which is also a precondition of the quantitative view from defect transition energy levels calculations. The qualitative investigation of CuInSe$_2$ was previously done by Oikkonen et. al, which lead to new insight about the defect physics in CuInSe$_2$. Unlike total energy difference investigations which emphasize the importance of V$_{Cu}$, they found out that only Se related defects can induce charge transition energy levels in the gap. Hopefully, our work may improve the understanding of the defect physics in CZTS.

III. RESULTS AND DISCUSSION

The movements of atoms of CZTS induced by the vacancy under the relaxation are qualitatively similar for Cu, Zn and Sn vacancy (denoted as V$_{Cu}$, V$_{Zn}$ and V$_{Sn}$) as shown in Fig. 1, which can be understood by the similar surroundings of Cu, Zn and Sn vacancies (four nearest-neighbor S atoms). The four nearest-neighbor S atoms move toward the Cu (Zn and Sn) vacancy, and therefore decrease the V$_{Cu}$-S (V$_{Zn}$-S and V$_{0}^{S_n}$-S) bond with 0.04 Å (0.005 Å and 0.14 Å) compared with the parent compound. The relaxation difference of the nearest S atoms around the vacancies is determined by the size mismatch between Cu, Zn and Sn ions. It is obvious that the displacements of four nearest-neighbor S atoms around V$_{Sn}$ are decreasing with increasing electronegativity, which can be explained by the increasing Coulomb repulsion among the four nearest-neighbor S atoms. In the kesterite CZTS, the S atom has four nearest neighbors: two Cu, one Zn and one Sn atoms. With the creation of a S vacancy, the nearest neighbor Cu and Zn atoms move away from the S vacancy site, whereas the Sn atoms relax toward the vacancy site.

To figure out the defect-induced single particle levels of the V$_{Cu}$ and V$_{Zn}$, we look into the LDOS of the four nearest neighbor S atoms around the V$_{Cu}$ and V$_{Zn}$ vacancy, respectively. Our KS band structure analysis shows that all the charge states of V$_{Cu}$ and V$_{Zn}$ can not produce defect-induced single particle levels in the vicinity of the band gap. Consequently, each Cu or Zn vacancy has only one stable charge state corresponding to the fully occupied
valence bands $V_{Cu}^{1-}$ or $V_{Zn}^{2-}$, seeing Fig. 2, where the defect-induced single particle levels are marked in the band structures with red lines. The defect-induced single particle levels introduced by $V_{Cu}^{1-}$ and $V_{Zn}^{2-}$ locate deep at about 2.7 eV below the VBM, as shown in Fig. 2. For $V_{Zn}^{2-}$, additional two defect-induced single particle levels lying right below the VBM. Such defect-induced single particle levels lying in the valence band are always occupied, and will not influence the electric behavior of CZTS, which could be seen from the almost unchanged band gap of $V_{Cu}^{1-}$ and 0.1 eV band gap decrease of $V_{Zn}^{2-}$ in comparing to the parent material in Fig. 2.

Contrary to the $V_{Cu}$ and $V_{Zn}$ vacancies, the $V_{Sn}$ with multiple charge states create defect-induced single particle levels at the VBM as shown in Fig. 2. The neutral $V_{Sn}^{0}$ creates two defect levels lying at about 0.5 eV below the VBM, but the addition of 2 to 4 electrons forming 2- to 4- charge states shift one level up to the top of the valence band, which can be explained by the increasing levels Coulomb repulsion. The shifting of the defect states is accompanied by the reduced lattice relaxation around the vacant sites. As shown in Fig. 1, the four nearest neighbor S atoms move towards the vacant sites for $V_{Sn}^{1-}$, $V_{Sn}^{2-}$ and $V_{Sn}^{3-}$ with decreasing displacement, and move away from the vacant site for $V_{Sn}^{4-}$. The shallow defect-induced single particle levels of $V_{Sn}$ significantly change the electronic structure of CZTS. It is obvious that the band gaps decrease of 0.23, 0.36, 0.48, 0.61 and 0.76 eV for charge states from 0 to 4-, respectively, compared with parent CZTS. The defect levels at the top of the VBM may behave as an acceptor level if holes can be thermally excited to the VBM at room temperature, thereby introducing a shallow acceptor level in the CZTS gap. However, previous theoretical studies show that the $V_{Sn}$ has high formation energy and high charge transition levels and will not be a effective $p$-type acceptor.

Unlike cation vacancies, all the enforced charge states for anion S vacancy do not induce defect levels in the interested energy region. This is in consistent with HSE06 findings by D. Han et al., who found out that there is no defect transition level for $V_{S}$ in the band gap. If one charging two additional electrons into the neutral charge state $V_{S}^{0}$, the excess charge does not fully localize on the defect but fills the conduction band. The band structure and LDOS of $V_{S}^{2+}$ charge state is also examined, which show VBM up shift crossing the Fermi level. Therefore, the neutral $V_{S}^{0}$ is the only stable charge state for $V_{S}$, which corresponds to the fully occupied valence band. The characteristic of anion S vacancy in CZTS is also very different from that of Se vacancy in CuInSe$_2$. Se vacancies can produce defect-induced
single particle levels near the band gap region in CuInSe$_2$. We guess it might be caused by the difference of intrinsic characteristics between Se and S atoms, for example, lower $p$ orbital energy level and larger atomic size of Se than that of S atom. To verify our conjecture, we investigate the Se vacancies in the CZTSe. However, no single particle levels appear near the band gap region. Therefore, the difference of vacancies electron structures between CZTS and CuInSe$_2$ is caused by the different cations. This in turn implies that the Sn atoms significantly affect the electron structure of CZTS.

In summary, our results conclude that Cu, Zn and S vacancies have only one stable charge states and therefore can not induce charge transition levels in the band gap. Moreover, Sn vacancy with 2-, 3-, and 4- charge states are stable which indicates that two charge transition energy levels corresponding to $\epsilon(3-/4-)$ and $\epsilon(3-/2-)$ might be induced in the band gap. Our results are very different from previous charge transition energy level investigations which show that each Cu, Zn and S vacancy has one charge transition energy level, while Sn vacancy has three charge transition energy levels. We think that the more charge transition energy levels obtained from previous charge transition energy level study compared with our results are caused by the consideration of the unstable charge states. Therefore, our conclusion in turn indicate that the examination of stable charge states is a necessary and important step which should be done before charge transition energy levels calculations.

IV. CONCLUSIONS

In this work, we investigated the band structures of the four vacancy defects in CZTS by employing screened Coulomb hybrid functional Heyd-Scuseria-Ernzerhof (HSE06). Our results reveal that the Sn vacancy with 2-, 3-, and 4- charge states can provide Kohn-Sham (KS) defect levels in the vicinity of band gap while Cu, Zn and S vacancies can not. Thus Cu, Zn and S vacancies have only one stable charge states corresponding to $V_{Cu}$, $V_{Zn}$ and $V_{S}$, respectively, which can not induce charge transition energy level in the band gap. Our results are partly at odd with previous charge transition energy levels studies, however, indicate that the examination of stable charge states is a necessary and important step which should be done before charge transition energy levels calculations.
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FIG. 1. (color online). Schematic representation of atomic relaxation (expressed in Å) around each vacancy.

FIG. 2. (color online). The band structure of parent CZTS, $V_{Cu}^{1-}$, $V_{Zn}^{2-}$, $V_{S}^{0}$ and Sn vacancy with 0, 1-, 2-, 3-, 4- four different charge states calculated in a 64-atom supercell. The dashed lines illustrate the defect levels induced by the vacancy compared to the parent band structure in each case.
Fig.1 Zhang.ep
Fig. 2 Zhang.ep