



The suppression of Cu-related charge localized defects in Cu₂ZnSnS₄ thin film solar cells



Xiaoli Zhang^a, Miaomiao Han^a, Xiaohong Zheng^a, Zhi Zeng^{a,b,*}

^a Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

^b University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

Cu₂ZnSnS₄ (CZTS) is a promising low cost thin-film solar cell material. However, the charge localized defects greatly hinder the improvement of the solar cell efficiency, thus the identification and knowledge of the possible charge localized defects in it are extremely important. Using hybrid functional calculation, we find that Cu_{Sn} and Cu_{Zn} are the main charge localized defects in CZTS. In detail, our results show that Cu_{Sn} is a deep level recombination center. Moreover, the growth condition of Sn determines the population of Cu_{Sn} because the stable chemical potential region of Δμ_{Sn} ([-1.74, 0] eV) is larger than that of Δμ_{Cu} ([-0.77, 0] eV). Thus Sn-rich growth condition is proposed to suppress the Cu_{Sn}. As for Cu_{Zn} antisites, part is deep acceptors which will be beneficial for the efficiency of solar cell, while part forms donor-acceptor pairs with Zn_{Cu}. The Cu_{Zn} + Zn_{Cu} donor-acceptor pairs will lead to large potential fluctuation in CZTS, which is a disadvantageous factor. Fortunately, such pairs can be greatly suppressed by Cd doping due to two reasons: one is that the Cd atoms prefer to substitute the Zn atomic sites leading to the reduction of the Cu_{Zn} concentration, and the other is that the Cd dopant in the CZTS makes it difficult for its neighboring Zn atom to be substituted by Cu atom.

1. Introduction

Kesterite Cu₂ZnSnS₄ (CZTS) thin film solar cells are currently promising candidates for large-area module production, utilizing more earth abundant elements compared to the two leading thin film solar cells Cu(In,Ga)Se₂ and CdTe. CZTS has many properties necessary for a high performance thin film solar cell, such as a direct and tunable band gap (1.0–1.5 eV) by cation or anion substitution [1,2] and high absorption coefficient (10⁴ cm⁻¹) [3]. Remarkable progress has been made in CZTS technology, with recent record power conversion efficiencies of 9.2% for CZTS solely [4] and 12.7% for those incorporating selenium [5]. However, the efficiency of CZTS-based solar cell is lower than that of Cu(In,Ga)Se₂, which is likely due primarily to the non-radiative recombination via deep level defects and the potential fluctuation (band tail) caused by high degree of compensated donor-acceptor pair (DAP) in CZTS [6–10]. The common feature of deep level defect and DAP which induces large potential fluctuation is charge localization [11,12]. Since the charge localized defects limit the solar cell efficiency greatly, it is necessary to identify and suppress them to further improve the CZTS solar cell efficiency.

The charge localized defects have been studied mainly by the formation energy and the charge transition level calculations. Results have

shown that Sn_{Zn}, Cu_{Sn} and uncompensated Sn_{Zn} + Cu_{Zn} complex are effective deep level recombination center [7,13–15]. The preferred Cu-poor and Zn-rich growth condition in high efficiency solar cells are also used to explain the suppression of these deep level defects [7]. In fact, in addition to Cu-poor and Zn-rich growth conditions, Sn-rich growth condition was found playing an important role in the enhancement of the solar cell efficiency experimentally [16]. Apparently, the Sn-rich growth condition inhibits Cu_{Sn}, but promotes the development of Sn_{Zn}-related defects. Therefore, the present theoretical results can not form a complete understanding of the deep level defects in CZTS. The theoretical studies also found that similar to the shallow acceptor defect V_{Cu}, the deeper acceptor defect Cu_{Zn} also produces carriers [7,14]. Moreover, although the Cu_{Zn} and Zn_{Cu} form compensated DAP Cu_{Zn} + Zn_{Cu} which is the main DAP in CZTS, this DAP hardly affects the electronic structure and the optical properties of CZTS [14]. However, these theoretical results are different from the experimental ones, which showed that the potential fluctuation is larger at higher DAP concentration [17]. Moreover, the potential fluctuation is largely due to the Cu_{Zn} in Cu_{Zn} + Zn_{Cu} [8]. Thus, the theoretical results of formation energy and charge transition level can not explain the role of the Cu_{Zn} in the CZTS. In addition, it is found that Cd doping can reduce the potential fluctuation, but the microscopic mechanism is not clear [1,12].

* Corresponding author at: Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.
E-mail address: zzeng@theory.issp.ac.cn (Z. Zeng).

In this study, we identify the main harmful intrinsic defects in CZTS and propose new suppression schemes based on hybrid functional calculations, which may help improving the CZTS solar cells application. First, by comparing the defect induced gap states we identify V_{Sn} , Cu_{Zn} , Cu_{Sn} , S_i , Sn_{Zn} and Sn_{Cu} with certain charge states are harmful charge localized defects. Secondly, we calculate the charge transition levels and formation energies corresponding to the charge localized defects, which show that Cu_{Sn} and Cu_{Zn} are the main harmful defects with the former acting as a deep recombination center and the later inducing large potential fluctuation. Cu_{Sn} is found to be greatly suppressed by Sn-rich but rather Cu-poor growth condition because of the larger chemical potential region of Sn than that of Cu. Lastly, Cd-related defects in CZTS are studied, which reveal the underlying mechanism about the suppression of Cu_{Zn} in CZTS by Cd doping. That is, the Cd dopant prefers to substitute the Zn atomic site and makes more difficult for its neighboring Zn atom in the system to be substituted by Cu atom.

2. Methods

The following intrinsic point defects in kesterite CZTS are investigated: four vacancies (V_{Cu} , V_{Zn} , V_{Sn} and V_S), six antisites (Cu_{Zn} , Cu_{Sn} , Zn_{Cu} , Zn_{Sn} , Sn_{Cu} and Sn_{Zn}) and four interstitials (Cu_i , Zn_i , Sn_i and S_i). In addition a DAP $Cu_{Zn} + Zn_{Cu}$ is considered. The Cd-related defects include four antisites Cd_{Cu} , Cd_{Zn} , Cd_{Sn} , Cd_S and an intersite Cd_i with Cd occupying the cation octahedron site. Each defect is embedded into a 64-atom supercell.

The calculations are carried out using the density functional theory (DFT) as implemented in the plane wave VASP code [18]. In the structure optimization procedure, generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE-GGA) [19] exchange-correlation functional is used to obtain the ground state geometries. Screened Coulomb hybrid functional Heyd-Scuseria-Ernzerhof (HSE06) [20,21] is used to calculate the electronic structures and defect properties. The amount of Hartree-Fock exchange is set to 0.3 and the range-separation screening parameter μ is set to 0.2 \AA^{-1} in the HSE06 functional. The interaction between ions and electrons is described by the projector-augmented wave (PAW) method [22,23]. The cutoff energy for the plane-wave basis is set to 300 eV. These parameters ensure the calculated band gap (1.43 eV) close to the reported values (1.44–1.51 eV) for parent CZTS [24,25]. The Brillouin zone sampling is done using $2 \times 2 \times 2$ k -point mesh. The structure optimization calculations are deemed as converged when the Hellman-Feynman forces on each atom are less than 0.05 eV/\AA . A defect can attract or lose different number of electrons so as to present multiple charge states. The number of valence electrons is changed to mimic the various defect charge states. For example, the charge state of Cu_{Zn}^{1-} is defined by adding one more valence electron to the neutral Cu_{Zn} defect system. The additional electron will rearrange in the self-consistent procedure in the DFT calculation. But a reasonable electron distribution depends on a suitable functional. The HSE06 functional was proved to have good application in the study of defect properties in $CuInS_2$ [26,27], a sister compound of CZTS. These studies indicate that the HSE06 hybrid functional ensures a reasonable electron distribution in the Cu-based solar cell materials. Since the charge state greatly affects the crystal structure as well as the electronic structure, the structures of all the possible charge states of the considered defects are fully optimized.

We identify the charge localized defects by analyzing the defect-induced gap states in the local density of states (LDOS) and the band structure of defect system, as described in Ref. 11. Defects with larger LDOS peak heights of the gap states are more charge localized than those with lower LDOS peak heights [11]. For those charge localized defects, the electrons on them are strongly bounded to the defects and difficult to be ionized while for those charge delocalized defects, the electrons on them are loosely bounded to the defects and easy to be ionized. The ionization energy is equivalent to defect level of the two relevant charge states. Therefore, the transition levels of the charge

localized defects are much deeper than those of the charge delocalized defects.

The defect formation energy and charge transition level calculations are based on the supercell approach in which a defect α with charge state q is embedded. The formation energy is given by: [28]

$$\Delta H_{\alpha,q}(E_F, \mu_i) = (E_{\alpha,q} - E_h) + \sum_i n_i \mu_i + q(\varepsilon_{VBM} + E_F), \quad (1)$$

where $E_{\alpha,q} - E_h$ is the energy difference between the defect system and host material. μ_i is the corresponding chemical potential of element i in CZTS. ε_{VBM} is the energy of the valence band maximum (VBM) of the host, and E_F is the Fermi energy, which varies from the VBM to the conduction band minimum (CBM). The charge-image interaction and the potential alignment error for charged defect are corrected using Lany and Zunger electrostatic correction method [29] and the alignment of the core-averaged electrostatic potentials far from the defect, respectively, as described in Ref.11 and 30 [11,30].

3. Results and discussion

We will classify the strongly charge localized defects in CZTS first and then calculate their charge transition levels to understand in depth of the defect properties [29]. We list the LDOS peak positions and heights within the band gap region in Table 1. Our previous studies have shown that all the charge states of V_{Cu} are charge delocalized with its gap states strongly hybridized with the valence band. [31] Thus the band structure of VBM of V_{Cu}^{1-} are very similar to that of the host material [31]. On the other hand, the Cu_{Zn} shows stronger charge localization feature than the V_{Cu} [9]. Our LDOS results exhibit that the peak heights for all the charge states of Cu_{Zn} are larger than 4 states/eV and also larger than that of V_{Cu} . Hence, it is reasonable to set a value of 4 states/eV to classify those strongly charge localized defects. With this criterion, from Table 1 we can see the charge localized defects include V_{Sn} (with 2-, 3-, 4- charge states), Cu_{Zn} (with 0, 1- charge states), Cu_{Sn} (with 2- and 3- charge states), S_i (with 0, 1-, 2- charge states), Sn_{Zn} (with 0, 1 + charge states) and Sn_{Cu} (with 1 +, 2 + charge states). For these charge localized defects, the defect-induced single particle levels (Kohn-Sham eigenvalues) within the band gap are obviously presented, as shown in Fig. 1 the dashed red lines. The defects with LDOS peaks smaller than 4 states/eV are more charge delocalized, for which the

Table 1

The locations and heights of the peaks of local density of states (LDOS corresponds to the defect and the nearest neighbor atoms) of all the considered defect charge states. E (eV) denotes the location of the LDOS peak at the band gap region and H (states/eV) denotes the height of the peak.

defect	charge	E	H	defect	charge	E	H
V_{Sn}	0	-0.07	2.73	Zn_{Sn}	0	0.17	1.08
	1-	0.21	3.33		1-	-0.07	2.65
	2-	-0.12	6.15		2-	0.15	3.28
	3-	-0.09	7.09		0	0.19	1.21
Cu_{Zn}	4-	-0.15	10.06	V_{Zn}	1-	-0.13	2.61
	0	-0.13	4.38		2-	-0.26	2.72
	1-	-0.25	8.10		0	-0.08	0.94
	0	0.02	3.20		1-	-0.25	1.55
Cu_{Sn}	1-	0.34	3.58	Zn_{Cu}	0	0.06	0.88
	2-	-0.29	7.95		1+	1.31	0.75
	3-	-0.27	21.17		0	0.09	1.16
S_i	0	0.91	5.35	Cu_i	1+	1.15	1.23
	1-	0.08	5.78		0	-0.11	1.13
	2-	-0.13	5.34		1+	0.03	1.71
Sn_{Zn}	0	-0.25	7.03	Zn_i	2+	1.15	1.67
	1+	0.09	5.82		0	-0.25	3.52
	2+	1.06	2.78		1+	0.10	2.48
Sn_{Cu}	0	0.00	0.39	2+	-0.25	1.41	
	1+	-0.36	8.00	3+	0.07	0.84	
	2+	0.10	5.61	4+	0.24	1.12	
	3+	0.70	3.17				

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