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Passivation for Cu_2ZnSnS_4/WZ-ZnO interface states: From the first principles calculations

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ABSTRACT

We employed the first-principles calculations to investigate F, Cl and H's passivation effects for Cu_2ZnSnS_4 (102)/WZ-ZnO (110) interface, in which the interface states mainly originate from Sn atoms. The interface states peaks can be reduced more or less by introducing F, Cl and H around Sn atom. H and F have a more efficient passivation effect than Cl atoms. The charge density difference and Bader atomic charge analysis suggests that F, Cl and H can get part of the electrons leading to interface states and that the interface states can be passivated by F, Cl or H atoms.

1. Introduction

Recent years, Cu_2ZnSnS_4 (CZTS) as a potential absorber material for thin film solar cells has been intensely studied. Researchers have studied CZTS solar cells propperties to give a detailed structural about solar cells. Teixeira et al. [1] investigated the optical and structural of CZTS based solar cells by photoluminescence. Xiao et al. [2] studied the structural and electronic properties of CZTS cells from a density theory. From another aspect, researchers have tried to improve the preparation of CZTS to increase the conversion efficiency. Gong et al. [3] have success-fully synthesized CZTS nanocrystals via a facile solvothermal method. Patil [4] have success-fully deposited on glass substrates Cu_2ZnSnS_4 (CZTS) thin films by using a spray pyrolysis method.

It was reported that the conversion efficiency of CdS/CZTS solar cells has reached to 8.4% [5], still lower than that of CIGS (Cu(In, Ga)Se_2) solar cells. Whereas Cd is a highly toxic element, and then a friendlier environmental buffer layer to replace CdS is needed. ZnO is a wide-gap (the band gap is 3.30 eV) n-type semiconductor material [6], consisting earth abundant and nontoxic elements. So it is considered as a good substitute for CdS [7]. Previous reports found that CZTS/ZnO heterojunction solar cells had efficiencies about 5% [8], lower than those of the solar cells with CdS as the buffer layer. During past years, experimental and theoretical attempts [7,9–13] have been made to study the reason for the low conversion efficiency of ZnO/CZTS heterojunction solar cells, including interface band offsets, CZTS surface treatments and surface passivation.

We previously studied the CZTS (102), wurtzite-ZnO (WZ-ZnO) (110) and their interface [14]. The interface binding energy is $-0.21\,J/m^2$ and the lattice mismatch is less than 3.2%. CZTS/WZ-ZnO interface is different from our findings of $CuInS_2/MoS_2$ [15] and WZ-ZnO/CdS [16] interfaces. The binding energy of $CuInS_2/MoS_2$ and WZ-ZnO/CdS is $-0.65\,J/m^2$ and $-0.61\,J/m^2$, respectively. The interface space of $CuInS_2/MoS_2$ and WZ-ZnO/CdS interfaces is 1.87 Å and 1.824 Å, respectively, while CZTS/WZ-ZnO has a larger interface space 2.044 Å. Obviously, this interface is a weak interface that has a smaller interface binding energy and a larger interface space. This may be the reason that CZTS/WZ-ZnO has higher interface states. And we found that CZTS (102)/WZ-ZnO (110) interface states (at about 0.1–1.0 eV above the Fermi level) mainly derived from Sn atom. The F, H and Cl are the common passivation elements for they easily get eletrons from others elements when they formed compound with others elements, and researchers have studied F and H [17], Cl [18] passivation for SiC/SiO_2, HfO_2/GaAs interfaces by the first principles calcuations. Their results showed that the interface states can be reduced by F, H and Cl atoms. In this letter, we employed the first-principles calculations to study F, Cl and H's passivation effect on CZTS/WZ-ZnO interface. By analyzing the density of states (DOS), charge density difference and Bader charge, we find that F, Cl and H can reduce the interface states. The results also show that F, H can be more efficient than Cl atom to passivate the interface states of CZTS/WZ-ZnO.

2. Computational details

All of the calculations work was done within the Vienna *ab initio* simulation package (VASP) [19–21] based on first principles density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) [22] version of the generalized gradient approximation (GGA). The projector augmented wave (PAW) [23,24] method was applied to describe the pseudopotential. The electronic configurations are $[Ar]3d^{10}4s^1$, $[Ar]3d^{10}4s^2$, $[Kr]4d^{10}5s^25p^2$, $[Ne]3s^23p^4$, $2s^22p^4$, $1s^1$ for Copper, Zinc, Tin, Sulfur, Oxygen, Hydrogen, respectively. The energy cutoff is 450 eV and *k*-point gamma-centered meshes of $4 \times 10 \times 1$ were used to calculate CZTS(102)/WZ-ZnO(110) interface. For CZTS (102) surface and WZ-ZnO (110) surface, three top

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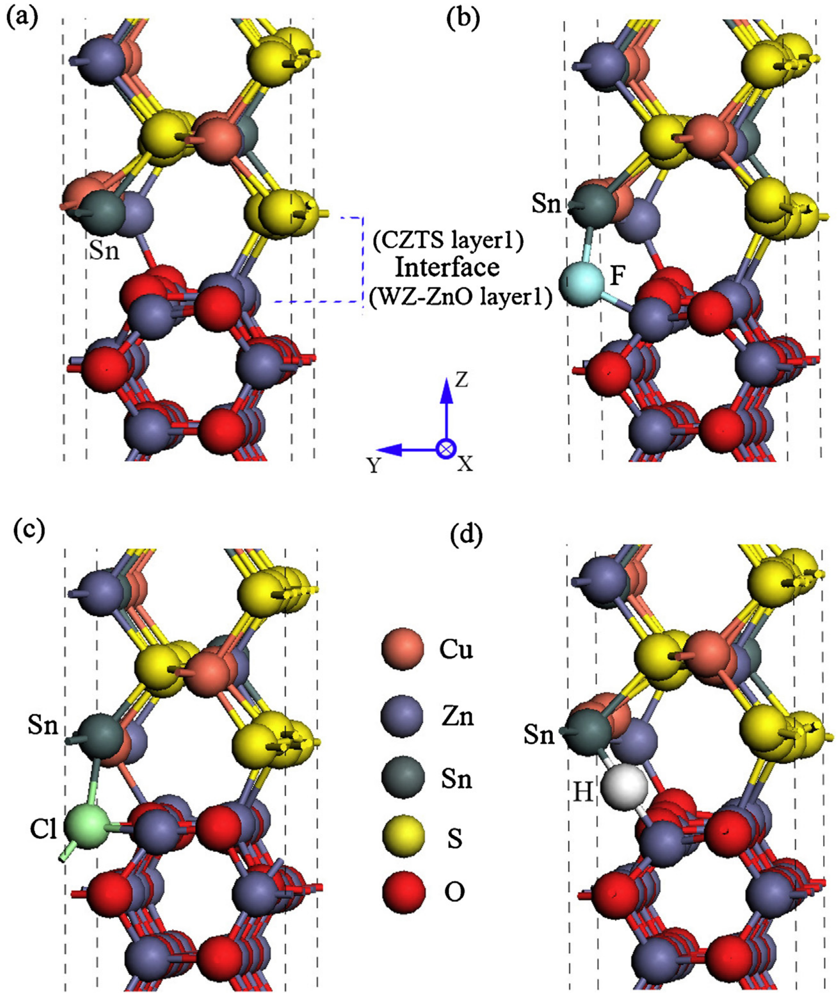

Fig. 1. The interface configuration after relaxation without passivation (a) and with F (b), Cl (c) and H (d) passivation.

layers are relaxed to mimic the surface and three bottom layers are fixed to mimic the bulk. We add eight pseudohydrogen atoms on the top of CZTS atomic layer and twelve pseudohydrogen atoms on the bottom of WZ-ZnO atomic layer to eliminate the influence of dangling bonds on the surfaces (see Ref 12 for more details about this interface model).

3. Results and discussion

On the CZTS first layer, there are 2 Cu atoms, 1 Zn atom, 1 Sn atom, 4 Satoms. On the WZ-ZnO first layer there are 6 Zn atoms, 6 O atoms. As we analyzed in our previous work [12], the eight atoms in the first CZTS layer may have not enough chance to bind with the twelve atoms in the first WZ-ZnO layer. As a consequence, the interface states are introduced. And possibly this may be one of the reasons that CZTS/WZ-ZnO solar cells have a lower conversion efficiency. Our work shows that Sn, S atoms on the CZTS first layer and O atoms on the WZ-ZnO first layer contribute interface states to CZTS (102)/WZ-ZnO (110), especially Sn atom (labeled as Sn in Fig. 1(a)). To study the passivation effect of H, F and Cl atom to CZTS/WZ-ZnO interface, we added them near Sn, respectively, to ensure new bonding to Sn. When an atom on the interface is added near Sn, it may lead to some deformation in the interface. In this work, we relaxed the local lattice of the interface after adding the passivating atom and then discuss the electronic properties of the interface slab.

Fig. 1(a)–(d) show the interface configuration after relaxation without passivation and with F, Cl and H passivation, respectively. From Fig. 1(a), we can see that on the CZTS first layer, the distance of $d_{\text{Zn-S}}$ is 2.516 Å, and on the WZ-ZnO first layer, the $d_{\text{Zn-O}}$ is 1.923 Å. As shown in Fig. 1(b), when we use F atom for passivation, $d_{\text{Sn-F}}$ is 2.073 Å and $d_{\text{Zn-F}}$ is 1.990 Å. When a Cl atom is near the Sn atom, $d_{\text{Sn-Cl}}$ is 2.294 Å and $d_{\text{Zn-Cl}}$ is 2.150 Å (Fig. 1(c)). When a H atom bonds to Sn and Zn atom, the bond length $d_{\text{Sn-H}}$ is 1.743 Å and $d_{\text{Zn-H}}$ is 1.720 Å (Fig. 1(d)). Thus, F, Cl and H atoms can bond to Sn atom on the interface.

Fig. 2(a) is the total density of states (TDOS) of CZTS/WZ-ZnO interface. At the interface, there are four interfacial peaks at about 0.1-1.0 eV, labeled as P1, P2, P3 and P4. These four peaks are mainly derived from Sn, and a few from O and S atoms on the CZTS first layer. The biggest peak P2 is derived from 5*s*-orbital of Sn atom and 3*p*-orbital of S atom. Fig. 2(b) is the TDOS after F passivation Sn atom on CZTS first layer. It is found that P1 and P3 is removed, and P2 is reduced. However, P4 becomes stronger than that without F passivation. For Cl passivation, it is found that just P2 become lower than that without Cl passivation, while P1, P3 and P4 have almost no change (in Fig. 2(c)). When H atom passivates the interface, P1 and P3 peaks are eliminated, and P2 and P4 peaks are also reduced (in Fig. 2(d)). Our first-principles calculations results suggest that interfacial density state peaks can be reduced by F, Cl and H atom passivation. Compared Fig. 2(b) and (d) with Fig. 2(c), we know that the P1 and P3 peaks are removed, the P2 peak is reduced by F and H atoms passivation. While the P1 and P3 peaks have almost no