Stability of CIS (001) Surface: First-Principles Study

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Abstract. In this paper, the stability of CIS (001) surface is studied through first-principles calculations. It is revealed that, different atom-terminated surface models have different formation energy. For many possible structural patterns, the stability of CIS (001) surface are also become more complicated.

1. Introduction
CIS are promising materials for photoelectronic devices such as solar cells and has been inspired more and more scientists’ studies over the past few years. Recently, the conversion efficiency is approaching more than 20% [1] [2]. Unfortunately, the stability of the CIS (001) surface are still have not yet been studied, whose properties have important influence on their performance.

Besides, in contrast to other usual compound semiconductors, stable reconstructions for the (001) surfaces are not known so far [3]. All these issues highlight the necessity of a computational study on the stability of CIS (001) surface.

In this paper, using the first-principle calculations we studied the energetic stability of the CIS (001) surface. Calculations show that, under most condition, the structures with Se-terminated surface are favored.

2. Computational method and computational model
In this work, the spin-polarized calculations were carried out based on density-functional theory, as implemented in the Vienna Ab initio Simulation Package (VASP) code [4]. The cut-off energy is set to 400 eV. We use the projector-augmented-wave method and the PBE potential for the exchange-correlation functional [5]. The CIS (001) surface is modeled by a slab with 2×2 surface cell and 10 atoms layers. The bottom of the slab is fully passivated by hydrogen atoms with different electron, and the slabs are separated by a vacuum layer of more than 12 Å. During relaxation, the atoms in the three bottom layers are fixed, and all the other atoms are allowed to relax until the forces are smaller than 0.05 eV/Å. The M-P k-point mesh is 2×2×1, dense enough for good convergence of CuInSe2 surfaces.

In our calculations, the formation energy of a defect formed at the surface is defined as:

$$ E_f = E_{\text{tot}} - E_s + n \cdot (\mu_{\text{Cu}} + E_{\text{Cu bulk}}) + m \cdot (\mu_{\text{In}} + E_{\text{In bulk}}) + l \cdot (\mu_{\text{Se}} + E_{\text{Se bulk}}) $$

(1)

where $E_{\text{tot}}$ is the total energy of the surface supercell with the defect; $E_s$ is the total energy of the fully hydrogenated CuInSe2 surface which acts as a reference; $\mu_{\text{Cu}} + E_{\text{Cu bulk}}$ represents the energy of Cu in the chemical reservoir (similarly for In and Se). In the expression $\mu_{\text{Cu}} + E_{\text{Cu bulk}}$, $\mu_{\text{Cu}}$ is the chemical
potential of Cu referenced to bulk Cu and $E_{\text{Cu}}^{\text{bulk}}$ is calculated as in bulk Cu, so in the figures in this paper the $\mu_{\text{Cu}}$ value of 0 eV represents Cu is as rich as in the growth environment that the bulk Cu will start to form.

One of the unique properties for CuInSe$_2$ is that the achievable chemical potential range for stable stoichiometric CuInSe$_2$ is very narrow. To synthesize the single-phase CIS samples without the coexistence of bulk Cu, In and Se, and secondary compounds such as CuSe, InSe, and CuIn$_5$Se$_8$, the value of $\mu_{\text{Cu}}$, $\mu_{\text{In}}$ and $\mu_{\text{Se}}$ are limited in a certain range shown in Fig. 1, which is similar to previous results from the calculation in reference [6], where $\Delta H_f (\text{CuInSe}_2) = -1.78$ eV is the calculated formation energy of solid CIS, and the formation of the secondary compounds, such as CuSe, Cu$_2$Se, InSe, and CuIn$_5$Se$_8$ for CIS should be avoided, as described by the following relations:

$$u_{\text{Cu}} < 0, \quad u_{\text{In}} < 0, \quad u_{\text{Se}} < 0;$$
$$u_{\text{Cu}} + u_{\text{Se}} < \Delta H_f (\text{CuSe}) = -0.26 \text{ eV};$$
$$u_{\text{In}} + u_{\text{Se}} < \Delta H_f (\text{InSe}) = -1.07 \text{ eV};$$
$$u_{\text{Cu}} + 5u_{\text{In}} + 8u_{\text{Se}} < \Delta H_f (\text{CuIn}_5\text{Se}_8) = -7.14 \text{ eV};$$

We plotted these formation energies in Fig. 1 versus $u_{\text{Cu}} - u_{\text{In}}$ along the Se-rich stability line $u_{\text{Se}} = 0$; noting that along this line $u_{\text{Cu}} + u_{\text{In}}$ is constrained to equal the CIS heat of formation since $u_{\text{Cu}} + u_{\text{In}} +2u_{\text{Se}}$ must always equal that quantity in chemical equilibrium. The symbol n (m) is the number of Cu (In) atoms removed from the reference surface in order to form the defect, and l is the number of Se atoms at the surface.

3. Results and discussion

Fig. 2(a) shows the relaxed, CuIn-terminated (001) surface as a reference. Besides this, the side views of CuSe—terminated, Se-terminated reconstructions are shown in Fig 2(b) - 2(e). Calculations show that, the energy of reconstructions in Fig 2(d) - 2(e) are higher than Fig 2(c), that is to say, the reconstructions in Fig 2(d) - 2(e) are not favored.
Generally, surfaces terminated with a cation layer and an anion layer exhibit charge imbalance, which usually leads to unstable surface. The CIS (001) surface is just belong to this kind of situation. The polar surfaces can be stabilized when the surface reconstructs, such as Se-Se dimer that can compensate the charge imbalance. An empirical electron counting rule (ECR) was proposed [7] [8] [9], which states that a surface is stable when the cation dangling bonds at the surface are unoccupied and the anion dangling bonds at the surface are fully occupied.

Fig. 3 shows the surface energies of the ideal Se-terminated, CuIn-terminated and CuSe-terminated (2×2) surfaces. These surface energies are plotted as a function of the chemical potentials of Se, Cu and In, which are constrained to vary along the border of the stability region set up in Fig. 1.
Se. These variables have been constrained to vary along the border of the stability region set up in Fig. 1. In this figure, point A represents the Cu and in rich regions, and segment B-C represents the Se rich region. 0 eV represents the energy of CuIn-terminated surface. The ideal (2x2) CuIn-terminated surface is unstable under most environmental conditions and has the highest surface energy among the surfaces modelled. The (2x2) CuSe-termination in Fig 2(b) and Se-termination is more stable than the (1x1) CuIn-termination under most environmental conditions.

4. Conclusion
In conclusion, we studied the the stability of polar CIS (001) surface and its critical effect on the high efficiency of CuInSe2-based thin film solar cell. It is revealed that the formation of Se-terminated surface is easier than CuIn-terminated or CuSe-terminated surface. It is likely because that the Se-terminated surface reconstruction and form Se-Se dimer.

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