Selenium Passivation of the CuInSe₂ for High-Efficiency Solar Cells

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Abstract. In this paper, selenium passivation of the CuInSe₂ for high-efficiency solar cells is studied through first-principles calculations. It is revealed that, the formation energy of Se-terminated surface and the surface with Se overlayer are different. The surface with Se overlayer are more stable, it guarantees an ideal growth that can efficiently limit the formation of point defects. It is further proved that the unique surfaces of CuInSe₂ play the critical roles on the high efficiency of the based thin film solar cell. It is the significant foundation for improving the growth of related solar cells and it is very important for the formation and control of related defects in the growth of CIS. Due to the different surface energy and property, the study of the growth of Selenium passivation of CIS is very important.

1. Introduction

The chalcopyrite CuInSe₂ (CIS) is a widely used absorber material in thin-film solar cells [1-6]. The optical and electronic properties of this compound can be tuned by varying the Gu:In ratio, but are also strongly affected by the presence of lattice defects [7]. An important factor to limit the conversion efficiency is the formation of various point defects [8-9]. In theory, there are many kinds of intrinsic defects existing in CIS, most of which have very low defect formation energies [10-11]. In other hand, these defects can affect the solar cell performance of CuInSe₂ -based solar cells [7-8]. However, the defects’ correlation with the material properties and growth conditions, and their impact over the device performances have not been all studied clear yet. Thus, a complete understanding of the defect physics is indispensable to achieve higher conversion efficiency [7]. Our previous study shows that Se-Se terminated surface are more stable, Se-related defects in CIS are also an important issue which needs to be investigated.

In this paper, using the first-principle calculations we studied selenium passivation of the CuInSe₂ for high-efficiency solar cells. Calculations show that, a Se overlayer guarantees an ideal growth that can efficiently limit the formation of point defects. It is further proved that the unique surfaces of CuInSe₂ play the critical roles on the high efficiency of the based thin film solar cell.
2. Computational method and computational model

The spin-polarized calculations were carried out based on density-functional theory in this work, as implemented in the Vienna Ab initio Simulation Package (VASP) code [12]. We use the projector-augmented-wave method and the PBE potential for the exchange-correlation functional [§3]. The cut-off energy is set to 400 eV. In this paper, the CIS (001) surface is considered, and the CIS (001) surface modeled by a slab with $2 \times 2$ 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 $2 \times 2 \times 1$, dense enough for good convergence of CuInSe$_2$ surfaces.

![Fig 1. The atomic structures of the (a)bulk CuInSe$_2$, and the point defects (b) Cu$_{\text{In}}$, (c) In$_{\text{Cu}}$, (d) V$_{\text{Cu}}$ and (e) V$_{\text{In}}$ in bulk CuInSe$_2$. The corresponding vacancies are indicated by dashed circles. The pink, blue and green balls show In, Cu and Se atoms in order, and the black lines show the range of the surface unit cells. The arrows denote the location of the point defects, and the dashed line means that one atom is removed from the site.](image)

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

$$E_f = E_{\text{tot}} - E_s + n \cdot (\mu_{\text{Cu}} + E_{\text{Cu}}^{\text{bulk}}) + m \cdot (\mu_{\text{In}} + E_{\text{In}}^{\text{bulk}}) + l \cdot (\mu_{\text{Se}} + E_{\text{Se}}^{\text{bulk}})$$  \hspace{1cm} (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 CuInSe$_2$ surface which acts as a reference; $\mu_{\text{Cu}} + E_{\text{Cu}}^{\text{bulk}}$ represents the energy of Cu in the chemical reservoir (similarly for In and Se). In the expression $\mu_{\text{Cu}} + E_{\text{Cu}}^{\text{bulk}}$, $\mu_{\text{Cu}}$ 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[14].

3. Results and discussion

Fig. 2(a) shows the relaxed all possible low energy configurations of the surface defects (a) Cu$_{\text{In}}$+2V$_{\text{In}}$, (b) 4Cu$_{\text{In}}$, and (c) 2V$_{\text{Cu}}$ +2V$_{\text{In}}$ in (2×2) surface supercells for the CuIn-terminated (001) surface.
Fig 2. All possible low energy configurations of the surface defects (a) CuIn+2VIn, (b) 4CuIn, and (c) 2VCu +2VIn in (2×2) surface supercells for the CuIn-terminated (001) surface after relaxation.

Generally, for the cation-terminated (001) surface, there are one Cu and one In dangling bonds on each (1×1) surface unit cell, each dangling bond has 2/4 and 6/4 electron, respectively, which usually leads to unstable surface. So two extra electrons each (1×1) surface unit cell should be removed to satisfy the ECR. This can be achieved through the formation of acceptor-like surface defects. Various point defects are possible be formed in the surface to satisfy charge balance. 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.

Due to the unstable surface, various point defects are possible be formed in the surface, which is likely to affect the solar cell performance of CuInSe2-based solar cells. We studied selenium passivation of the CuInSe2 and the impact over the formation of these various point defects.

Fig 3. Surface energies of the ideal Se-terminated, plus the all possible low energy configurations of the surface defects in (2×2) surface supercells for the cation-terminated and Se-terminated (001) surface reconstructions. These 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.

The properties of CuInSe2 are depended on the growing conditions, the growing conditions are depended on the chemical potential of different atoms. CuInSe2 has one unique properties, it is that the achievable chemical potential range for stable stoichiometric CuInSe2 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 CuIn₅Se₈, the value of $\mu_{Cu}$, $\mu_{In}$ and $\mu_{Se}$ are limited in a certain range, which is similar to previous results from the calculation in reference [**], where $\Delta H_f (CuInSe_2) = -1.78$ eV is the calculated formation energy of solid CIS, and The formation of the secondary compounds, such as CuSe, Cu₂Se, InSe, and CuIn₅Se₈ for CIS should be avoided, as described by the following relations:

$$u_{Cu} < 0, u_{In} < 0, u_{Se} < 0;$$
$$u_{Cu} + u_{Se} < \Delta H_f (CuSe) = -0.26 \text{ eV};$$
$$u_{In} + u_{Se} < \Delta H_f (InSe) = -1.07 \text{ eV};$$
$$u_{Cu} + 5u_{In} + 8u_{Se} < \Delta H_f (CuIn₅Se₈) = -7.14 \text{ eV};$$

We plotted these formation energies versus $u_{Cu} - u_{In}$ along the Se-rich stability line $u_{Se} = 0$; noting that along this line $u_{Cu} + u_{In}$ is constrained to equal the CIS heat of formation since $u_{Cu} + u_{In} + 2u_{Se}$ 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 1 is the number of Se atoms at the surface [15-16].

Fig. 3 shows the surface energies of the ideal Se-terminated, plus all possible low energy configurations of the surface defects in (2×2) surface supercells for the cation-terminated and Se-terminated (001) surface. These surface energies are plotted as a function of the chemical potentials of Cu, In and Se. Under Se-poor condition, the surface is featured by CuIn+₂VIn or ₂VCu+₂VIn complexes. The (2×2) Se-termination is more stable than the surface with defects under most environmental conditions. The structures with a full Se layer plus dimerized Se adatoms are favored and at Se-rich conditions, it has the lowest surface energy of all reconstructions. That is to say, the Se-rich growing condition is benefit.

4. Conclusion
In conclusion, we studied the Selenium passivation of the CuInSe₂ for high-efficiency solar cells. The study shows that overlayer guarantees an ideal growth that can efficiently limit the formation of point defects. It is further proved that the unique surfaces of CuInSe₂ play the critical roles on the high efficiency of the based thin film solar cell.

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