The Atomic Structure of the Se-Passivated CuInSe2

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Abstract. Through the first-principles calculations, we studied the atomic structure of Se-passivated CuInSe2. It is revealed that, the CuInSe2 can be passivated by selenium, under Se-rich condition, the structures with a full Se layer plus dimerized Se adatoms are favored. The formation energy of Se-terminated surface and the surface with Se overlayer are different, the formation energy of the surface with Se overlayer is more lower than the pure Se-terminated surface, that is to say, the surface with Se overlayer is more stable. On the other hand, the atomic structure of the Se-passivated CuInSe2 are also different from the atomic structure of the pure Se-terminated surface. Studying the structure of the Se-passivated CuInSe2 is very helpful for the high-efficiency solar cells.

1. Introduction

Many studies shows that, the CuInSe2 (CIS) thin film solar cell has exhibited prominent performance with efficiency as high as 22.6% [1,2], which is one of the most competitive candidates in the photovoltaic industry, approaching the efficiency of the crystalline Si cells [3-6]. In previous papers, Na or K has played a significant role during the development of the CIGS solar cells, on the other hand, Na or K improves the photovoltaic performance as a dopant [7]. There are little study about how to improve the performance of CuInSe2 solar cells without any dopant. For example, little is known for instance on the properties and the surface structures of the CuInSe2 (001) polar surface passivated by Se, which might be an important information towards growth and interface optimization. Although the CIS based solar cells have achieved an energy efficiency higher than 20% [8,9], the current knowledge about the Se-passivated surface properties is limited. In order to deeply explore the surface and interface of semiconductor materials, theoretical calculation is the efficient path.

In this paper, we studied the atomic structure of se-passivated the CuInSe2. We propose that, under Se-rich condition, the structures with a full Se layer plus dimerized Se adatoms are favored.

2. Computational method

We use the spin-polarized calculations based on density-functional theory, which is implemented by the Vienna Ab initio Simulation Package (VASP) [10] software package. We use the PAW method and the PBE potential for the exchange-correlation functional [11]. The CuInSe2 (001) surface is modeled by a slab with 2x2 surface cell and 10 atoms layers as shown in Fig 1. 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 12Å. 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 cut-off energy is set to 400 eV, the M-P k-point mesh is 2×2×1, dense enough for good convergence of CuInSe₂ surfaces [7].

Fig 1. The atomic structures of the top and side views of the fully-relaxed Se-terminated (001) surface reconstruction. The pink, blue and green balls show In, Cu and Se atoms in order.

3. Results and discussion

3.1. The Se-passivated atomic structure with Se coverage is around 0.5 monolayers.
Fig.1 shows the top and side views of the fully-relaxed Se-terminated (001) surface reconstruction. The black rectangle represents the (2×2) unit cell and the dashed one represents the (4×1) surface unit cells. The atomic positions of Se in the top layer are numbered from 1 to 8, atom 1 and ⪫, atom 2 and ⪬, atom 7 and ⪫, atom 8 and ⪬ are equivalent, respectively. All of the top view of the surface reconstruction, we just show the top layer of Se atoms, the others are described as light circles.

Fig 2. The atomic structures of Se-passivated CIS with Se coverage is around 0.5 monolayers.

Fig.2 shows the top and side views of the atomic structures of Se-passivated CIS with Se coverage is around 0.5 monolayers. For the (001) surface terminated with the Se anions (as shown in Fig. 1, two electrons should be added per (1×1) surface unit cell to satisfy the ECR. This can be achieved through the formation of donorlike surface defects. The atomic structures of Se-passivated CIS with Se coverage is around 0.5 monolayers is one of the structures which satisfy the ECR.

3.2. The Se-passivated atomic structure with Se coverage is around 0.75 monolayers.
Fig.3 shows the top and side views of the atomic structures of Se-passivated CIS with Se coverage is around 0.75 monolayers. It is the other one of the structures which satisfy the ECR.
3.3. The Se-passivated atomic structure with Se coverage is around 1 monolayers.

Fig. 3 shows the top and side views of the atomic structures of Se-passivated CIS with Se coverage is around 0.75 monolayers. It is the other one of the structures which satisfy the ECR. From the top views of the atomic structures of Se-passivated CIS with Se coverage is around 1 monolayers, the Se atoms in the topest layer are dimers.

Fig. 4 shows the top and side views of the atomic structures of Se-passivated CIS with Se coverage is around 1 monolayers. 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.
Fig. 5 shows the surface energies of the ideal Se-terminated, and Se-passivated CIS with Se coverage is around 0.5, 0.75 and 1 monolayers. From Fig. 5, we can see that the CuInSe$_2$ can be passivated by selenium, under Se-rich condition, the structures with a full Se layer plus dimerized Se adatoms are favored.

The achievable chemical potential range for stable stoichiometric CuInSe$_2$ in Fig. 5 is very narrow. The properties of CuInSe$_2$ are depended on the growing conditions, the growing conditions are depended on the chemical potential of different atoms. As our former work, we synthesis the single-phase CIS samples without the coexistence of bulk Cu, In and Se, and secondary compounds such as CuSe, InSe, and CuIn$_n$Se$_m$, the value of $\mu_{\text{Cu}}$, $\mu_{\text{In}}$, and $\mu_{\text{Se}}$ are limited in a certain range, which is similar to previous results from the calculation in reference [1], 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$_n$Se$_m$ for CIS should be avoided. We plotted these formation energies 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 [15,16].

4. Conclusion

As we all know, the (001) surface is also a polar surface, which needs a strong reconstruction to provide surface charges. Understanding the surface differences is helpful for us to find the key to increasing the efficiency of the solar cells. Due to the ability of the surface Se to eliminate dangling bonds, the structures with a full Se layer plus dimerized Se adatoms are favored.

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