Reconstruction and Energetics of the Polar (112) and (112) Versus the Non-Polar (220) Surfaces of CuInSe$_2$

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Reconstruction and Energetics of the Polar (112) and ($\overline{11}2$) Versus the Non-Polar (220) Surfaces of CuInSe$_2$

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ABSTRACT

First-principles total-energy study for CuInSe2 reveals a number of (112) and ($\overline{11}2$) surface structures stable at different atomic chemical potentials. This structure richness raises the possibility for engineering CIS/CIGS properties by surface control during the growth.   The experimentally observed spontaneous decomposition of the (220)/(204) surfaces into (112) and ($\overline{11}2$) is also confirmed by calculating the absolute surface energies.

1. Introduction

CuInSe$_2$ (CIS) is an important thin-film solar cell material. Poly-crystalline CIS is exclusively used in the CIS solar cell technology. Either at the grain boundaries or at the interface of heterojunctions, the physical properties of the CIS surfaces are important.   For example, recent studies of CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells showed that certain surface orientations [e.g., (220)] of thin films might have superior properties than others. [1]   It is therefore essential to understand the effects of the various surfaces on the electronic properties of CIS. More interestingly, unlike the conventional semiconductors, some CIGS (220)/(204) surfaces are unstable against the decomposition into (112) and ($\overline{11}2$) facets. [2] Here, based on the general principles being developed for III-V, and to a lesser extent for II-VI surfaces, we have studied a number of self-compensated (112)/($\overline{11}2$) surfaces and compared their energies to the (220)/(204) surfaces.

2. Theoretical approaches

The calculation was carried out using the VASP code, [3] the Vanderbilt ultrasoft pseudopotential, the local density approximation, and a supercell approach.   The supercell contains 12 atomic layers + 4 equivalent vacuum layers. A 180-eV cutoff energy was used and tested up to 234 eV. Atoms at the back surface are fixed while the rest of them are relaxed until the forces are less than 0.1 eV/ Å. Absolute surface energies are calculated.   Details will be given elsewhere. [4] The calculation for the (220)/(204) surfaces is straightforward with 16/8 atomic layer + 4 equivalent vacuum layer supercells.

It is well known that surface energy is a sensitive function of the sample preparation/growth conditions. These translate into the dependence on the atomic chemical potentials. For ternary CIS, there are two quasi-independent chemical potentials: μ_{Cu} and μ_{In}, whereas the chemical potential of Se can be determined by the heat of formation ($\Delta H_{CIS} = 2.11$ eV) via $\mu_{Cu} + \mu_{In} + 2\mu_{Se} = -\Delta H_{CIS}$. [5] Figure 1 shows the triangle indicating the assessable region of the Cu and In chemical potentials. Given the constraints that binary compounds In$_2$Se$_3$ and Cu$_2$Se also may form from the Cu-In-Se mixture, the triangle in Fig. 1 is further divided into three
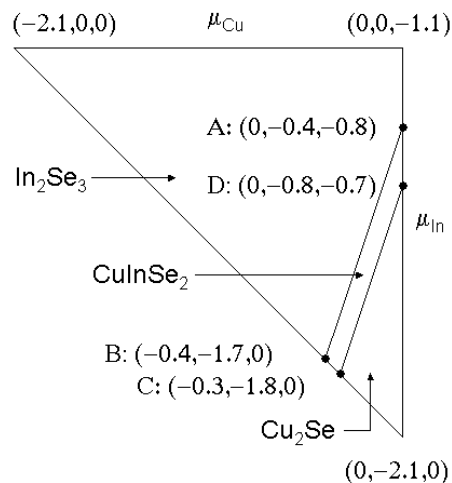

Figure 1. Region of Cu and In chemical potentials. CIS region is defined by the four corners (A-D) where (μ_{Cu}, μ_{In}, μ_{Se}) is given.

subregions.   CIS is only a narrow stripe with four corners defined by (A-D).   In principle, the CIS region in Fig. 1 is further narrowed [5] by the formation of ordered vacancy compounds, 1-3-5, 1-5-7, etc. but these will not be considered here.

3. Results

We will present the results using the convention for binary compounds. Thus, for the non-polar (220) surface, the primitive unit cell is c(2x2) whereas for the (204) surface, the primitive unit cell is 1x4.   Similar to the binary (110) counterpart, these surfaces are non-polar with equal (Cu+In) and Se coverage, as well as equal Cu and In coverage. The calculated surface energies are 1.08 eV/a$_0^2$ for (220), and 1.16 eV/a$_0^2$ for (204), respectively, where a$_0$ is the calculated bulk lattice constant = 5.72 Å. It is well known that charge transfer between cation and anion takes place in every (110)-derived surfaces. A 0.08 eV/a$_0^2$ increase of the surface energy thus reflects a decrease in the Coulomb binding between the positive and negative charges in the elongated 1x4 reconstruction over the more compact c(2x2) reconstruction.

For the nominally cation-terminated polar (112) surfaces, we considered 10 different structures of which 7 have c(4x2) and 3 have 4x2 reconstructions.   Note that c(4x2) is the smallest surface cell for CIS. The surface models include (i) Cu vacancies, (ii) Cu + In vacancies, (iii) Cu-on-In antisite, (iv) Se addimer, (v) Se adatom, (vi) Cu adatoms, and (vii) In adatoms + In-on-Cu antisite, on different lattice sites. Figure 2(a) shows the calculated absolute surface energy for low-energy structures. We see that the surface reconstruction and the underlying atomic structure are very sensitive to the atomic chemical potentials: From A to B, 2V$_{Cu}$ per c(4x2) (=

complete depletion of the Cu atoms from the surface layer) is the most stable. From C to D, Cu_{In} surface antisite is the most stable, instead. In Figure 1, we see that A-B line is more In-rich than the C-D line. This explains the change of the energy order between the two. The (Cu, In) vacancy pair also has reasonably low surface energy to within 0.04 eV/a_0^2 above the global minimum, and becomes true minimum in regions where transition between V_{Cu} and Cu_{In} is under the way. The energy of Se ad-dimer goes down quite significantly when approaching the Se-rich limit. However, it never gets low enough to dominate over others.

For the nominally anion-terminated polar ($\overline{112}$) surfaces, we considered 5 different structures all in primitive c(4x2) reconstruction. These include (i) In-on-Cu subsurface antisite, (ii) Se vacancy, (iii), Se addimer, (iv) Se adatom, and (v) Cu adatoms. Different from the (112) surface, the ($\overline{112}$) surface has two distinct features: (a) the Se addimer at the Se-rich limit. Being 0.7 eV/a_0^2, it is by far the most stable surface structure for CIS. (b) The lack of top layer modification away from the Se-rich limit. The lower-energy In-on-Cu structure has the antisite in the *subsurface* layer, instead. Because the A-B line is more In-rich than the C-D line, the In-on-Cu antisite is more stable in the A-B region than in the C-D region.
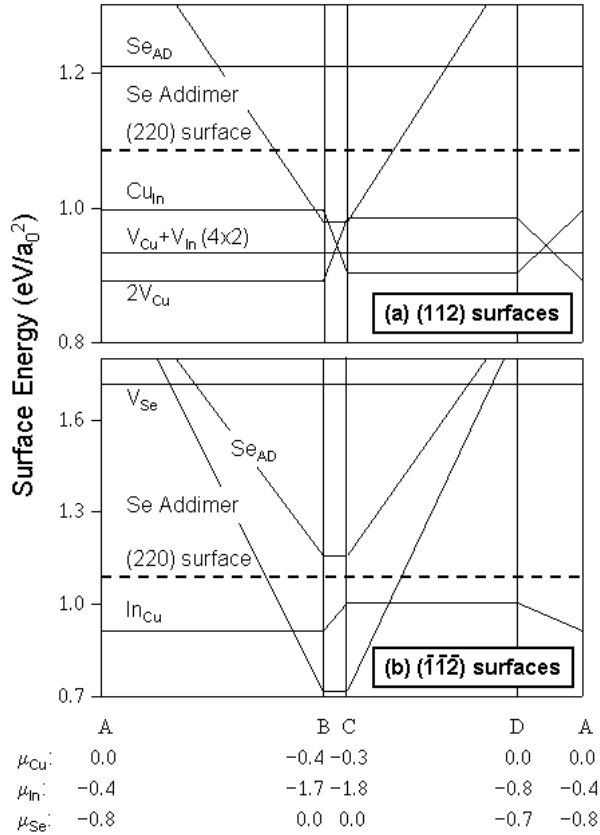

Figure 2. Absolute surface energy for (a) (112) and (b) ($\overline{112}$) surfaces. Energy for (220) surface is also shown. Chemical potential ranges are indicated at the bottom.

4. Discussions

(i)   Even though in the literature [2] one often does not make the distinction between the (220) and (204) surfaces, we found that their energy difference can be significant due to an intrinsic difference in the surface Coulomb attraction.

(ii)   The (112) and ($\overline{112}$) surfaces possess complex surface-structure "phase diagrams". Such complexity raises the possibility for tailoring the physical properties of CIS films by imposing desired structures during the growth. For example for the (112) surface, growth along the A-B line would result in a Cu-vacancy rich environment. Even if a fraction of the surface vacancies can be buried to become bulk vacancies, it would naturally lead to p-type films. The same is true for the C-D line, which, however, provides a much deeper Cu_{In} double acceptor. This could be undesirable if achieving good p-typeness is the purpose, but could be desirable if semi-insulating is the purpose. For the ($\overline{112}$) surface, the formation of the Se addimers will lead to a Se double layer that could interrupt the growth sequence, thereby causing surface roughness. [2] Finally, we note that self-compensation at the (112) surface is always achieved by intrinsic defects that are p-type in the bulk (V_{Cu}, Cu_{In} and V_{In}), whereas for the ($\overline{112}$) surface, it is always achieved by intrinsic defects that are n-type in the bulk (In_{Cu}, Se antisites), instead.

(iii)   Recently, Liao and Rockett [2] reported AFM observation of the spontaneous decomposition of the (220)/(204) surfaces into (112) and ($\overline{112}$) facets. Figure 2 shows the calculated surface energy: the (220) [and (204) not shown but nonetheless has slightly higher energy] surface is less stable, on the absolute energy scale, against either (112) or ($\overline{112}$), not only against the average of the two. Interestingly for the (112) surface, not only the structures involving CIS-specific defects such as Cu vacancy and Cu-on-In antisite have lower energies, but also the (Cu, In) vacancy pair. In comparison with the binary counterpart, ZnSe, the latter result suggests that even the cation-terminated (111) surface of ZnSe may have lower energy than (110) by the cation vacancy formation. On the other hand, the low energy of the ($\overline{112}$) surface at least in the Se-poor condition is due entirely to the CIS-specific In-on-Cu antisites. Thus, spontaneous decomposition may not occur in ZnSe. Moreover, the In-on-Cu antisite is in the subsurface layer with larger diffusion barrier as it has four nearest neighbors, instead of three being typical for surface defects. One has the opportunity to kinetically suppress the In_{Cu} formation during the growth. This will force the ($\overline{112}$) surface to be either Se vacancy or addimer terminated, preventing decomposition of the (220) surface in the Se-poor condition: at point A of Fig. 2, [E(2V_{Cu}) + E(V_{Se})]/2 is 0.22 eV/a_0^2 higher, instead of lower, than E(220).

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