Behavior of $\Sigma 3$ grain boundaries in CuInSe$_2$ and CuGaSe$_2$ photovoltaic absorbers as revealed by first-principles hybrid functional calculations

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The inconclusive results of the previous first-principles studies on the $\Sigma 3$ grain boundaries (GBs) in CuInSe$_2$ reveal the importance of employing a method that can correctly describe the electronic structure of this solar-cell material. We have employed hybrid functional calculations to study the $\Sigma 3(112)$ and $\Sigma 3(114)$ GBs in CuInSe$_2$ and CuGaSe$_2$. The electronic structure changes introduced by the formation of GBs are threefold: creation of gap states, shift in band edges, and alteration of bandgap sizes. Gap states commonly behave as recombination centers, but the band alignment and the change in the bandgap size induced by GBs mitigate the destructive effect of these states in CuInSe$_2$. That means, $\Sigma 3$ GBs are not detrimental for the carrier transport in devices based on CuInSe$_2$. Conversely, these GBs are destructive for the carrier transport in CuGaSe$_2$. The different behaviors of the $\Sigma 3$ GBs in CISE and CGSe might be considered by experimentalists to optimize the device fabrication to achieve high-performance solar cells.

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INTRODUCTION

Thin-film solar cells based on Cu(In,Ga)Se$_2$ (CIGSe) are fabricated and deployed worldwide on an industrial scale due to their outstanding price/performance ratio [1, 2]. In contrast to silicon-based solar cells [3], the efficiency of CIGSe cells with polycrystalline light absorber exceeds the efficiency of their monocrystalline counterpart [4]. This is remarkable, because typically the performance of optoelectronic devices is considered to be worse for polycrystalline semiconductors due to the presence of grain boundaries (GBs). GBs are expected to create deep gap levels that act as recombination centers and are commonly regarded detrimental for the solar-cell performance. While the existence of GBs is experimentally identified in CuInSe$_2$ and CuGaSe$_2$ [6], its semiconducting nature of CuInSe$_2$ is in contrast to the results of Yan et al. [6]. Other authors employed different flavors of (local) LDA and (semi-local) GGA to study the cation-terminated (112) surface of CuInSe$_2$ to explain the anomalous characteristics of the symmetric GBs. They proposed that the valence band maximum (VBM) of the surface is lower than the bulk VBM therefore the GBs act as a hole barrier. The Cu vacancy reconstruction at the surface, which lowers the surface VBM with respect to the bulk VBM, is in contrast to the results of Yan et al. [6]. Other authors employed different methods to study the atomic composition near the cation-terminated (112) plane GBs. This discrepancy could be due to different methods employed to study the atomic composition [7, 8]. Another type of $\Sigma 3$ GB, namely $\Sigma 3(114)$, has been studied in CuInSe$_2$ and CuGaSe$_2$ [9–12]. Although this type of GB is not experimentally identified in CuInSe$_2$ and CuGaSe$_2$, its structure is adopted from GBs in CdTe. A common feature of the $\Sigma 3$ GBs is that high percentage of these GBs in CuInSe$_2$ and CuGaSe$_2$ are charge neutral [13–15].

Due to the complex nature of thin-film devices, it would be highly desirable to achieve new insights from theoretical calculations. Such results can serve as common ground between experimentalists and theoreticians leading to a better understanding of the properties of devices. Taking advantage of the calculated results makes experimentalists able to improve the cells in the laboratory scale. Consequently these knowledge can be transferred to the industrial scale.

The outcomes of the previous first-principles studies on GBs, however, are not conclusive [6, 9–12, 16]. In their pioneering work, Persson and Zunger [16] employed LDA and PBE+U method to study the cation-terminated (112) surface of CuInSe$_2$ to explain the anomalous characteristics of the symmetric GBs. They proposed that the valence band maximum (VBM) of the surface is lower than the bulk VBM therefore the GBs act as a hole barrier. The Cu vacancy reconstruction at the surface, which lowers the surface VBM with respect to the bulk VBM, is in contrast to the results of Yan et al. [6]. Other authors employed different flavors of (local) LDA and (semi-local) GGA to study the $\Sigma 3(114)$ GBs in CuInSe$_2$ and CuGaSe$_2$. While some studies [9, 10] suggested that these GBs do not create any gap state, the other studies predicted the formation of deep gap states in the bandgap of the systems with GBs [11, 12].

The results achieved by (semi-)local methods remain doubtful, even if they are in agreement with experimental findings. This is because of the employed methods in the aforementioned studies that do not describe the semiconducting nature of CuInSe$_2$ and CuGaSe$_2$ adequately [17, 18]. Namely, for the defect-free CuInSe$_2$ and CuGaSe$_2$ bulk, the bandgaps predicted by PBE and PBE+U are severely underestimated [19]. This failure is partly due to the shortcomings of (semi-)local methods and partly due to underestimation of the anion displacement (u) of CuInSe$_2$ [20]. The size of the bandgap is of particular importance when the defect states, which
Hybrid functionals are known as a rather accurate method to study the electronic structure of semiconductors. In this approach a portion of the exact exchange calculated by Hartree-Fock method is incorporated into the exchange-correlation functional calculated by density functional theory (DFT). In the present work, we used HSE06 functional [21] with the fraction of the exact exchange set to 30% [17, 22, 23]. Using this setup, the value of the anion displacement is calculated with an error smaller than 0.3% and the computed bandgaps are 1.0 eV and 1.6 eV for CuInSe$_2$ and CuGaSe$_2$, respectively, in agreement with experimental values [24].

All calculations have been performed within the framework of DFT as implemented in Vienna Ab-initio Simulation Package (VASP) [25]. We used the projector augmented wave (PAW) [26, 27] method together with a plane-wave cutoff energy of 300 eV and a mesh of (3 × 3 × 1) k-points. For density of states (DOS) calculations a denser k-mesh has been used. The supercells consist of 128 and 180 atoms for the Σ3(112) and Σ3(114) GBs, respectively. To construct the supercells, the optimized lattice constants and atomic positions of the bulk have been used. The distance between periodic supercells separated by vacuum is about 30 Å.

Slab calculations, which are generally employed to represent a material with GBs, might suffer from the charge transfer through the slabs due to dangling bonds at the surfaces of the slabs. To quench the dipole moment of the slabs and prevent charge transfer, the surface dangling bonds were passivated with hydrogen-like pseudoatoms with partial charges. The valency of these hydrogen-like pseudoatoms are chosen in such a way that they provide the amount of missing electrons for the surface atoms, so they fulfill the octet rule. The position of atoms in the outer four atomic layers were fixed to their bulk position to mimic the underlying bulk material. Other atoms were fully relaxed until the forces on each atom were below 0.01 eV/Å. Using the same methodology, a defect-free supercell with {112}-plane termination was constructed and considered as the reference.

To evaluate the relative shift of the VBM and conduction band minimum (CBM) with respect to the bulk, the macroscopic average of the electrostatic potentials are calculated [28–31]. The VBM shift can be expressed as

\[ \Delta E_v = \Delta \varepsilon_1 - \Delta \varepsilon_2, \]  

where \( \Delta \varepsilon_1 \) is the energy difference from the VBM to the reference level of system ‘1’ and \( \Delta \varepsilon_2 \) is the energy difference from the VBM to the reference level of system ‘2’, see FIG. 1. The energy difference \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) are calculated in the region far from the GBs and are very close the values calculated for the perfect periodic bulk. By knowing the size of the bandgap, the CBM shift calculation is straightforward.

The crystal structure of Cu(In,Ga)Se$_2$ and CdTe has the same fundamental characteristics and the GBs in CuInSe$_2$ and CuGaSe$_2$ can be modeled based on the observed GB structures in CdTe. In the present work, Σ3(112) and Σ3(114) correspond to lamellar and double-positioning twins in CdTe [32, 33]. In the Σ3(112) GBs, either a cation-containing plane is next to a Se-containing plane (Σ3(112)-I) or Se-containing planes are facing each other (Σ3(112)-II). In the Σ3(114) GBs, either Se atoms have dangling bonds (Σ3(114)-I) or cations have dangling bonds (Σ3(114)-II). The atomic structure of the Σ3(112) and Σ3(114) GBs are very different: while the Σ3(114) GBs contain dangling, wrong, and extra bonds the atomic structure of Σ3(112)-I is very similar to the bulk and the Σ3(112)-II GB contains Se dangling and Se-Se wrong bonds.

**RESULTS AND DISCUSSION**

The atomic structures of GBs in CuInSe$_2$ after geometry optimization are presented in FIG. 2. While Σ3(112)-I shows little changes in its structure, Σ3(112)-II undergoes dramatic structural relaxation. Compared to the bulk, Se atoms at the Σ3(112)-II GB are not surrounded...
by four cations. After optimization, the minimum distance between Se atoms increases from 3.11 Å to 3.52 Å. In contrast to CuInSe₂, Se atoms at the Σ3(112)-II GB of CuGaSe₂ (not shown here) are not located at the outermost layer of the GB: on one side of the GB Se atoms migrate into the bulk and instead of Se-Se wrong bonds at the GBs, Se-cation bonds are formed. In a qualitative agreement with the previous studies [9, 11], in the FIG. 2. (Color online) Atomic structure of the (a) cation-Se-terminated (type I) and (b) Se-Se-terminated (type II) Σ3(112) GB. (c) and (d) depict the atomic structure of the type I and type II of the Σ3(114) GB. The Cu, In, and Se atoms are shown as brown, large-light gray, and small-dark gray spheres, respectively.

Σ3(114) GBs the atoms with dangling bonds show larger relaxation compared to the other atoms. It has been discussed that dangling and wrong bonds in CdTe can create defect levels [34]. Since the Σ3(114) and Σ3(112)-II GBs contain these defects, one expects to see defect levels in the bandgap of the systems with these GBs as well. To study the effects of the GBs on the electronic structure, we calculated atom-projected partial DOS for the systems with GBs. The projected partial DOS for the Σ3(112) and Σ3(114) GBs in CuInSe₂ are shown in FIG. 3. All GBs (except Σ3(112)-I that creates no gap state) create unoccupied gap states close to the CBM which are in resonance with the conduction band states in agreement with the \( \frac{dI}{dU} \) simulations [35]. From the total energy of the charged (+1 and −1) GBs we have computed the thermodynamic charge transition levels. In CuInSe₂ and CuGaSe₂, the positively-charged GBs are not stable but the defect states can trap electrons to make the GBs negatively charged.

Our data show that the existence of GBs shifts the VBM and CBM with respect to the bulk VBM and CBM. This can lead to ‘electron-free’/‘hole-free’ zone near the GBs where the concentration of electrons/holes is less than in the grain interior (GI). It has been discussed that the creation of such a barrier at the GBs for one type of the carrier (electron or hole) impedes electron-hole recombination at the GBs [16, 36, 37]. FIG. 4 schematically presents the computed band offsets between the GB and GI for CuInSe₂ and CuGaSe₂.

The other effect of the GBs on the electronic structure is to change the size of the bandgap. In the case of CuInSe₂, the systems containing Σ3(112)-I, Σ3(112)-II, Σ3(114)-I, and Σ3(114)-II have the bandgap size of 1.0 eV, 1.4 eV, 1.3 eV, and 1.3 eV, respectively. For the corresponding GBs in CuGaSe₂, the bandgaps are 1.6 eV, 1.8 eV, 1.8 eV, and 1.8 eV, respectively. In the following paragraphs, we give a detailed discussion of our findings for different types of GBs.

Σ3(112)-I: in CuInSe₂ and CuGaSe₂, the Σ3(112)-I GBs do not create gap states but shift the VBM and CBM with respect to the bulk (FIG. 4). This band alignment draws electrons to the GB region but reflects holes away. The electron-hole recombination remains low because of insufficient holes at the GB. This GB forms easily in Cu(In,Ga)Se₂ due to its highly symmetric structure [38] and is harmless for the carrier transport.

Σ3(112)-II: the Σ3(112)-II GB in CuInSe₂ creates three gap states: one occupied state which is 0.1 eV above the VBM and two unoccupied states which are 0.3 eV and 0.4 eV below the CBM. The \( \varepsilon(+/0) \) level is not in the bandgap, therefore holes are not trapped in the defect states. The \( \varepsilon(0/-) \) level is in the bandgap, positioned 0.2 eV below the CBM. This defect level can be occupied by electrons only if CuInSe₂ is n-type. Our results are in agreement with the experimentally-observed charge-neutral Σ3(112) GBs in p-type CuInSe₂ [13].
the system containing this type of GB, the VBM and CBM are 0.2 eV lower and higher than the bulk VBM and CBM, respectively (see FIG. 4, top panel). This band alignment expels electrons and holes from the GB region. These electronic properties of the \( \Sigma 3(112) \)-II GBs in \( \text{CuInSe}_2 \) explain why this type of GB is harmless for the carrier transport in p-type \( \text{CuInSe}_2 \).

In the case of \( \text{CuGaSe}_2 \), the \( \varepsilon(+/0) \) level is not in the bandgap but \( \varepsilon(0/-) \) is 1.5 eV below the CBM. Hence, electrons from the conduction band can be trapped in this level. Considering the band alignment (FIG. 4, bottom panel), both the VBM and CBM of this system are 0.2 eV lower than the VBM and CBM of the bulk. That is, while this GB creates an electrostatic barrier for holes, concentration of electrons close to this GB is higher than in the GI. The valence band offset, however, is not large enough to suppress the holes concentration at the GB [37]; therefore the carrier lifetime is reduced if this type of the GB is formed in \( \text{CuGaSe}_2 \).

\( \Sigma 3(114) \)-I: as it is shown in FIG. 3 (c), the dangling and wrong bonds of the \( \Sigma 3(114) \)-I GB in \( \text{CuInSe}_2 \) cause unoccupied gap states to form. The deepest unoccupied state is 0.5 eV below the CBM. The \( \varepsilon(0/-) \) and \( \varepsilon(+/0) \) charge transition levels are 0.7 eV and 0.5 eV below the CBM and VBM, respectively. Thus, the positively-charged gap states are not stable but the defect levels can trap electrons and become negatively charged. The band offset of this system, however, screens this GB from bulk carriers and results in low probability of recombination.

Formation of the \( \Sigma 3(114) \)-I GBs in \( \text{CuGaSe}_2 \) creates three unoccupied gap states. The \( \varepsilon(0/-) \) level is 1.2 eV below the CBM, therefore the defect levels can trap electrons even for a p-type \( \text{CuGaSe}_2 \). Holes, on the other hand, cannot be trapped in the defect levels. The conduction band offset (FIG. 4, bottom panel) makes the region close to this GB electron rich. The motion of holes into the GB region, on the other hand, is impeded due to the valence band offset. The size of the valence band offset, however, is not large enough to mitigate the effect of the presence of this GB in the system [37].

\( \Sigma 3(114) \)-II: the cation dangling bonds create both occupied and unoccupied states in the bandgap of \( \text{CuInSe}_2 \) and \( \text{CuGaSe}_2 \). For \( \text{CuInSe}_2 \) (see FIG. 3 (d)), the occupied gap states are close to the VBM and the deepest state is 0.2 eV above the VBM. The deepest unoccupied

![FIG. 3. (Color online) Partial DOS calculated for GBs in \( \text{CuInSe}_2 \). Black and red line show the projected DOS for the bulk atoms and the atoms close to the GBs, respectively. The zero of the energy is set at the bulk VBM. Vertical dashed lines show the VBM and CBM.](image-url)

![FIG. 4. Schematic band offset and gap states of GBs for \( \text{CuInSe}_2 \) (top panel) and \( \text{CuGaSe}_2 \) (bottom panel). The occupied and unoccupied single particle levels are represented as black and white rectangles. Horizontal dashed lines show the bandgap of the bulk \( \text{CuInSe}_2 \) (\( E_g = 1.0 \text{ eV} \)) and \( \text{CuGaSe}_2 \) (\( E_g = 1.6 \text{ eV} \)), respectively. The distance between tics is 0.2 eV.](image-url)
gap state is 0.1 eV below the CBM. The $\varepsilon(+/0)$ level is not in the gap and $\varepsilon(0-/)$ is 0.5 eV below the CBM. This means, positively-charged gap states are not stable but if the chemical potential of the electrons is high, i.e. n-type CuInSe$_2$, then electrons can be trapped in the defect levels. Still, the electron- and hole-free zone near this GB make the probability of recombination low.

The VBM and CBM of this GB in CuGaSe$_2$ are 0.3 eV and 0.1 eV below the bulk VBM and CBM, respectively. The transition level $\varepsilon(+/0)$ is not in the gap and $\varepsilon(0-/)$ is 0.9 eV below the CBM. This GB remains neutral for p-type CuGaSe$_2$ but for high chemical potential of the electrons, the gap states can become negatively charged. The conduction band offset for this GB (FIG. 4, bottom panel) also leads to a high concentration of electrons close to the GB, meaning that the chance of electrons to be trapped in the gap state is high. Although the valence band offset repels holes from the GB, it cannot effectively screen the GB from holes and this GB is prone to recombination [37].

We note that in our study the electronic-structure changes are merely due to the existence of the GBs. To look into the influence of changing the chemical potential of the constituent atoms, we have studied the effect of the formation of a charge-neutral defect pair ($2V_{Cu}^- + In_{Cu}^{++}$) on the electronic structure of $\Sigma$3(112)-II in CuInSe$_2$. In agreement with previous results [16], the VBM is lower than the bulk VBM. In this system, the occupied gap state is removed from the bandgap but the unoccupied gap states are still present.

**SUMMARY**

In summary, our results are the following: (i) to study GBs in Cu(In,Ga)Se$_2$, employing a method that can correctly describe the electronic structure of this material, hybrid functional for example, is essential. (ii) The formation of GBs can alter the electronic structure of their systems in three different ways: a) GB creates gap states, b) GB shifts the VBM and CBM with respect to the bulk, and c) GB changes the bandgap size. (iii) Although gap states can be detrimental for the carrier transport, the band offsets and the change in the bandgap sizes mitigate this destructive effect in CuInSe$_2$. (iv) The behavior of the $\Sigma$3 GBs in CuGaSe$_2$ is different from CuInSe$_2$. The conduction band offset drives electrons to the GB region and the valence band offset is not large enough to suppress the concentration of holes. This band offset makes the presence of the symmetric GBs in CuGaSe$_2$ destructive, except for the $\Sigma$3(112)-I GB.

The electrically benign behavior of the $\Sigma$3 GBs in CuInSe$_2$ suggests that the $\Sigma$3 GBs in this material do not need passivation. The detrimental behavior GBs in CuGaSe$_2$, on the other hand, shows the necessity of the GBs passivation. Our findings could be of interest to the research groups seeking to optimize the device fabrication and to improve the efficiency of the solar cells based on Cu(In,Ga)Se$_2$.

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