Band Alignment of the CuGaS$_2$ Chalcopyrite Interfaces Studied by First-Principles Calculations

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**ABSTRACT:** The valence and conduction band offsets for both polar and nonpolar CuGaS$_2$/CuAlSe$_2$ and CuGaS$_2$/ZnSe interfaces were studied here by the state-of-the-art first-principles calculations. Using the hybrid functional calculations, we show that the CuGaS$_2$/CuAlSe$_2$ and CuGaS$_2$/ZnSe heterostructures in all interfaces form type II band alignment. The difference of valence and conduction band offsets is mainly due to lattice mismatch, generating stress in the interface and affecting the electronic properties of each material; meanwhile, the polarity configuration does not play an important role in these values. From the local density of states and the charge density, we can determine how the nature of the band alignments changes when the semiconductor conforms to each interface. This allows us to localize the electrons and holes at different sites of the interface.

**INTRODUCTION**

The most important aspect of CuGaS$_2$ solar cells is the interface between CuGaS$_2$ and the buffer layer, where the essential physics of photovoltaics takes place with the intrinsic band alignment as the dominant factor. Since the band alignment between the compounds will always act as the boundary conditions imposed on a particular interface, its understanding is fundamental to comprise the driving force of the kinetics of the electronic charge carriers and the recombination mechanism. In the case of semiconductor heterojunctions, the correct description of the relative alignment of the energy bands is critical for the improvement of the design of high-performance electronic devices. In a previous report, we studied the band alignment of the interfaces between CuGaS$_2$ and several contact materials, and we found that the CuAlSe$_2$/CuGaS$_2$ and CuGaS$_2$/ZnSe interfaces show the desirable characteristics for the design and development of thin-film solar cells. The results suggest that the interfaces between them would affect the conversion efficiency in such devices.

However, theoretical complications arising from complex interfacial bonding interactions and the lattice mismatch between the compounds have hindered the development of general analytic models capable of accurately predicting fundamental interfacial quantities. The large lattice mismatch between CuGaS$_2$ and the contact material (CuAlSe$_2$ $\approx$ 6% and ZnSe $\approx$ 5%) and the type II band alignment of the two interfaces have motivated intensive studies on CuGaS$_2$ heterostructures because the type of alignment is always accompanied by natural charge carrier separation, which is advantageous for promising solar cells.

The band offsets are well defined when the materials are in contact with the interface, requiring a so-called pseudomorphic interface, in which at least one of the materials is strained to match the in-plane lattice constant across the interface. Also, according to an experimental report, epilayers of ternary chalcopyrite semiconductors grown on GaAs(111) or GaAs (110) exhibit several epitaxial orientations. It is for this reason that it is important to study how the polarity configuration of the interfaces can affect the band alignment.

In this work, we used calculations based on density functional (DFT) theory and the hybrid functional with the modified fraction of screened short-range Hartree–Fock exchange (HSE06) to deeply understand how the band alignment occurs at the interfaces of CuGaS$_2$ (a light absorber candidate) and the semiconductors CuAlSe$_2$ and ZnSe, proposed as contact materials in applications as solar cells, taking into account different polarity configurations such as polar directions (001) and (112) and nonpolar directions (110) and (102). According to our results, CuGaS$_2$ can act as a donor material and, at the same time, as an acceptor semiconductor depending on the material it is interacting with. This behavior is confirmed from our ab initio calculations.
based on the analysis of the local density of states (LDOS) and the charge density distribution of the heterostructures.

MODEL AND COMPUTATIONAL TECHNIQUE

We performed first-principles calculations based on the framework of the generalized Kohn–Sham scheme\(^6,7\) using the projector augmented-wave (PAW) method\(^8\) and either the Perdew–Burke–Ernzerhof (PBE)\(^9,10\) or the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional\(^11–13\) as implemented in the Vienna ab initio simulation package (VASP).\(^14–16\)

In particular, we showed that the hybrid functional HSE06 with the modified fraction of screened short-range Hartree–Fock exchange gives accurate band gaps for the semiconductors considered in this study.\(^7\) The electronic wavefunctions were expanded in a plane wave basis set to a kinetic energy cutoff of 450 eV, and the atomic positions were optimized using the conjugate gradient method until the force on each atom was less than 0.01 eV Å\(^{-1}\). The valence electron configurations used in our calculations are Cu 3d\(^{10}\)4p\(^1\), Ga 4s\(^2\)4p\(^3\), S 3s\(^2\)3p\(^4\), Al 3s\(^2\)3p\(^1\), Se 4s\(^2\)4p\(^4\), and Zn 3d\(^{10}\)4p\(^2\). Brillouin zone sampling was performed with the Monkhorst–Pack special k-point mesh.\(^17\)

To compute the interface between CuGaS\(_2\) and CuAlSe\(_2\) and the ZnSe semiconductors, the supercell slab model was used here, employing an 8 \times 8 \times 1 mesh for the (001), (112), and (110) interfaces; meanwhile, for the (102) surface, a 6 \times 2 \times 1 mesh was used. The valence band maximum (VBM) and conduction band minimum (CBM) energies were calculated at the center of the Brillouin zone. We constructed a supercell that includes one slab of each semiconductor and has one interface between them at the center of the supercell. Four specific polarity configurations are considered to construct the heterostructures: two polar interfaces, (001) and (112), and two nonpolar interfaces, (110) and (102) (Figure 1). For the polar interfaces, each slab contains 12 atomic layers, while for the nonpolar interfaces, each slab contains eight atomic layers of each semiconductor. All surfaces of contact are able to form cation–anion bonds across the interface, minimizing any charge accumulation.

To obtain the valence and conduction band offsets, we used an electrostatic potential-based alignment method.\(^8,19\) The goal of this method is to model a real epitaxial interface where the band gap of the materials forming the interface can be different from that of the bulk, while the electrostatic potential is used to connect the macroscopic band energy levels for the bulk systems and the interfaces.\(^20,21\) For that, we averaged the electrostatic potential within the \(xy\) plane parallel to the interface between the two semi-infinite semiconductors. For sufficiently thick layers (minimum of eight atomic layers for each of the two materials), the electrostatic potentials in the center of each layer become bulk-like and allow the extraction of a band alignment representative of an infinite interface. The valence band offsets at each interface are calculated, as is explained in detail in ref 2 using the equation \(\Delta E_{\text{vb}} = \Delta E_{\text{vb}} - \Delta E_{\text{vb}} + \Delta E_{\text{CB}}\), where \(\Delta E_{\text{vb}}\) is the discontinuity in this reference potential across the interfaces, and \(\Delta E_{\text{vb}}\) and \(\Delta E_{\text{CB}}\) are the differences between the electrostatic potential and the valence band edges, respectively, obtained from the two independent bulk calculations of the single phases. Finally, knowing the relative position of the valence bands, we simply add the theoretical band gaps for each semiconductor forming each slab to obtain the conduction band offsets (\(\Delta E_{\text{CB}}\)).

RESULTS AND DISCUSSION

Lattice Mismatch. To develop a complete systematical analysis of the band alignments between the CuGaS\(_2\)/CuAlSe\(_2\) and CuGaS\(_2\)/ZnSe interfaces, we proposed, as a first step, four interfacial heterostructures: two polar interfaces in the (001) and (112) directions and two nonpolar interfaces in the (110) and (102) directions. This is done to observe the effects of the interface polarity in the behavior of the structural and electronic properties. It is important to ensure that the strain introduced by this way does not alter the electronic properties in an unrealistic way. Based on our experience, we expected that changing the lattice constant of a Cu-chalcopryite surface by \(\pm 1.5\%\) already altered the band gap by \(\sim 0.1\) eV. In contrast, a larger change in the lattice parameter had an even more dramatic effect. A tensile strain of \(\sim 10.0\%\) reduces the band gap by \(\sim 0.6\) eV.\(^8\)

Since the unit cell of CuAlSe\(_2\) (or ZnSe) is slightly larger than that of CuGaS\(_2\), one might expect an increase in the in-plane lattice constant for CuGaS\(_2\) in both heterostructures. To minimize the strain that is introduced by the interface, we constructed the unrelaxed supercell with in-plane lattice constants equal to the average between the lattice constants of the constituent semiconductors. To calculate the strain of the in-plane lattice constant, in the perpendicular direction of the interface, we used the following definition: \(S = 100 \times (a - a_{\text{bulk}})/a_{\text{bulk}}\), where \(a\) and \(a_{\text{bulk}}\) are, respectively, the in-plane lattice constant of the relaxed interface layer and the in-plane lattice constant of the bulk-like constituent semiconductor.

In Table 1, we present the calculated strains between CuGaS\(_2\) and the other semiconductors involved in the four proposed interfaces. According to our results, in all the interfaces, the contact material CuGaS\(_2\) tends to expand the in-plane lattice constants parallel to the interface, and the variation of the lattice constant of the semiconductor on the slab with respect to the bulk-like parameter is less than 4.0%. Nevertheless, this semiconductor suffers the greatest distortion.
CuGaS\(_2\) and the contact semiconductors. Therefore, DFT induced by the interface generates band gap fluctuations in all semiconductors. Finally, according to the theoretical strain of the in-plane lattice constant, the general behavior of the polar interfaces on the lattice mismatch is similar to that of the nonpolar interfaces. However, it can be noticed that the nonpolar configuration (110) presents the lower difference between the absolute value of the change in percentage of the theoretical strains with respect to the bulk-like semiconductors. This can be interpreted as an equitable distribution of the stress induced by the distortion on the lattice parameters, while the polar directions present a higher distortion of the bond lengths because of the difference between the involved ionic nature of the terminations.

Electronic Properties. As we mentioned earlier, the strain induced by the interface generates band gap fluctuations in CuGaS\(_2\) and the contact semiconductors. Therefore, DFT calculations under the precision of HSE06 approximation\(^{13}\) are needed not only to evaluate the band gaps but also to determine the band alignments. We calculated the band gap of CuGaS\(_2\), CuAlSe\(_2\), and ZnSe from the adjustment of the HF mixing in the hybrid functional. Increasing the HF mixing from the standard value of 0.25 in the HSE06 functional in all semiconductors gives the band gaps of 2.43 eV for CuGaS\(_2\), 2.65 eV for CuAlSe\(_2\), and 2.82 eV for ZnSe,\(^2\) which agree well with the experimental values.\(^{23-25}\)

From Table 2, we can observe how these values change with respect to the strain. Particularly, the CuGaS\(_2\) band gap decreases (respect to the bulk material) by a significant amount (0.06–0.28 eV) depending on the interface orientation and the contact material. For CuGaS\(_2\), the strain of the in-plane lattice constant of the interface increases the Cu–S bond length. The Cu d orbitals are more diffuse, overlapping more effectively with the S orbitals; this leads to a substantial upward repulsion of the anion p states and a reduction in the band gap. The conduction band minimum also contributes in the reduction of the band gap, which could be attributed to the fact that the CBM is conformed by strong Ga s states, whereas the other states in the conduction band are more heavily mixed with atomic orbitals such as S p states.\(^{26,27}\) Inversely, for CuAlSe\(_2\) and ZnSe, the internal compression produced an opening of the band gap. In the case of CuAlSe\(_2\), it increases to 0.19 eV as the lattice mismatch enlarges. For ZnSe, the band gap increases by a negligible amount (∼0.085 eV) as the internal stress augments. On the other hand, the CuAlSe\(_2\) structure responds in an opposite way than CuGaS\(_2\), and the band gap expansion occurs through an upward shift of the CBM, which consists mostly of the antibonding states of Al s and Se s orbitals. Since the selenium atom is closer to the aluminum atom, the antibonding state resulting from Se 4p–Al 3s hybridization is pushed to higher energies and the band gap is increased.\(^{26}\)

The general trend that we can find, according to Table 1, is that, when the strain in the material increases, the band gap reduces; meanwhile, when the strain decreases, the band gap enlarges.

In Figure 2, we show the LDOS projected along the direction perpendicular to the interfaces. In all cases, the band gap varies nonmonotonically across the interface due to the bending of band edges. For the CuAlSe\(_2\)/CuGaS\(_2\) interfaces (Figure 2a–d), the valence manifold near to the Fermi level is almost completely occupied by states lying on CuAlSe\(_2\); meanwhile, the conduction manifold contains mainly CuGaS\(_2\) states near to the Fermi level. However, for the ZnSe/CuGaS\(_2\) interfaces (Figure 2e–h), this behavior is reversed and the larger contribution to the valence manifold near to the Fermi level is due to the CuGaS\(_2\) states, while the conduction manifold conforms to the ZnSe states. All the calculated LDOS show the charge separation in the heterostructures, a characteristic behavior of the type II band alignment. Thus, for the CuAlSe\(_2\)/CuGaS\(_2\) interfaces, the holes are confined to CuAlSe\(_2\), while the electrons are in CuGaS\(_2\), and in the case of the ZnSe/CuGaS\(_2\) interfaces, the holes are now confined to CuGaS\(_2\) and the electrons are localized on ZnSe.

To complement the previous LDOS analysis, we proceeded to develop the study of the behavior of the charge transfer, which was computed based on the Bader’s topological analysis,\(^{18}\) where the three-dimensional space is partitioned into basins, belonging to individual atoms delimited by surfaces through which the flux of the density gradient is zero. In our case, for the Bader analysis, we used the Henkelman group implementation\(^{29-31}\) to quantify the amount of charge transferred across the interfaces. As we can see in Table 3, the absolute values of the charge for both semiconductors are similar at each interface in all the proposed orientations. For the CuGaS\(_2\)/CuAlSe\(_2\) interface, the localization of negative charge is observed on CuGaS\(_2\) while for CuGaS\(_2)/ZnSe\(_2\), it is located on ZnSe, corroborating the charge redistribution found by the LDOS. The largest charge occurs at the interface of the nonpolar (102) CuGaS\(_2)/ZnSe heterostructures, where the Se atoms increase their electron density (1.76 e), making them.

| interface | CuGaS\(_2\)/CuAlSe\(_2\) | CuGaS\(_2\)/ZnSe |
|-----------|--------------------------|------------------|
| (001)     | 2.37                     | 2.26             |
| (112)     | 2.17                     | 2.31             |
| (110)     | 2.19                     | 2.17             |
| (102)     | 2.25                     | 2.16             |
| exp.      | 2.43\(^{25}\)            | 2.43\(^{23}\)    |

Table 1. Theoretical Strain S between a Relaxed Interface Layer and the Bulk-like Semiconductors (in % with Respect to the Change in the Lattice Parameter for Each Proposed Semiconductor when Conforming to the Interface)

| interface | CuGaS\(_2\)/CuAlSe\(_2\) | CuGaS\(_2\)/ZnSe |
|-----------|--------------------------|------------------|
| (001)     | 2.21                     | 2.00             |
| (112)     | 3.11                     | 3.05             |
| (110)     | 2.12                     | 2.37             |
| (102)     | 3.41                     | 3.76             |

Table 2. Theoretical Band Gap (in eV) Obtained for the Semiconductors Forming the Interfaces at the Different Orientations, Modified from the Experimental One Due to the Strain
less positive; the larger contribution to this charge increment occurs in the second layer of the interface.

The same behavior can be recognized from the plotting of the electronic charge density difference, as shown in Figure 3. The red and blue regions in the figure represent electron accumulation and depletion, respectively. In Figure 3a,c, it can be seen that there is electron enrichment around the sulfur atoms, whereas electron deficiency appears around the aluminum atoms, indicating an electron transference from the CuAlSe$_2$ surface to CuGaS$_2$. Meanwhile, in Figure 3b,d, the transferred electrons to the ZnSe material are mostly contributed by the sulfur atoms of CuGaS$_2$. All the presented electronic properties are in good agreement with the band alignment obtained from the electrostatic potential-based alignment method (Table 4), as we present in the next section.

**Band Alignments.** To determine how the band alignments take place between CuAlSe$_2$/CuGaS$_2$ and ZnSe/CuGaS$_2$, we first calculated the electrostatic potential difference between the two semiconductors that conform to the interface. For this purpose, we plot the plane-averaged electrostatic potentials along the heterostructure, and then we determine the mean of these potentials in the corresponding materials. Using this method, we obtain a value of $\Delta \text{EP}_{\text{int}}$ for each interface, and then we compute the band edges relative to the electrostatic potential for each bulk semiconductor. Since these are distorted due to the epitaxial strain, we took the lattice constants and atomic coordinates from the central part of each slab in the model. The change in the local averaged electrostatic potentials between the two semiconductors at the proposed polar and nonpolar interfaces is presented in Figure 4 to facilitate their comparison and analysis. In all the cases, we can notice that the energy range of the averaged electrostatic potential of CuGaS$_2$ is smaller than the ones of the other semiconductors. Also, in Figure 4, we included the estimated electronic properties are in good agreement with the band alignment obtained from the electrostatic potential-based alignment method (Table 4), as we present in the next section.

**Table 3.** Calculated Bader Charges for CuGaS$_2$/CuAlSe$_2$ and CuGaS$_2$/ZnSe at the Polar and Nonpolar Interfaces

| Interface | CuGaS$_2$/CuAlSe$_2$ | CuGaS$_2$/ZnSe |
|-----------|----------------------|-----------------|
| (001)     | $-0.119250$          | $0.119106$      |
| (112)     | $0.005508$           | $0.005521$      |
| (110)     | $-0.142819$          | $0.142823$      |
| (102)     | $-0.235446$          | $0.235408$      |
| (001)     | $0.824569$           | $-0.824779$     |
| (112)     | $0.835758$           | $-0.835735$     |
| (110)     | $0.770182$           | $-0.770270$     |
| (102)     | $1.543017$           | $-1.543125$     |
For all three interfaces, the valence band positions were determined with respect to the reference potential energy, as shown in Table 4. The calculated valence band offsets (ΔE_{VB}) and conduction band offsets (ΔE_{CB}) are reported for each interface. These values indicate the degree to which the electronic states of the semiconductors are aligned at the interface.

Table 4. Calculated Valence $\Delta E_{VB}$ and Conduction $\Delta E_{CB}$ Band Offsets (in eV) for the Different Interfaces Referred to the Valence and Conduction Bands of CuGaS$_2$

| Interface       | CuGaS$_2$/CuAlSe$_2$ | CuGaS$_2$/ZnSe |
|-----------------|----------------------|----------------|
|                 | $\Delta E_{VB}$     | $\Delta E_{CB}$| $\Delta E_{VB}$ | $\Delta E_{CB}$ |
| (001)           | 0.03                 | 0.32           | −0.74           | −0.15           |
| (112)           | 0.18                 | 0.79           | −1.27           | −0.67           |
| (110)           | 0.21                 | 0.86           | −1.03           | −0.34           |
| (102)           | 0.16                 | 0.62           | −0.87           | −0.15           |

This table highlights the differences in band offsets for the different interfaces, which can have significant implications for the performance of photovoltaic devices. The calculated values for $\Delta E_{VB}$ and $\Delta E_{CB}$ provide insight into the alignment of electronic states and the potential for charge transfer across the interfaces. These results are crucial for optimizing the design of heterostructures for improved photovoltaic performance.

Figure 3. Electronic charge density differences for CuGaS$_2$/CuAlSe$_2$ and CuGaS$_2$/ZnSe at (a, b) polar and (c, d) nonpolar interfaces, respectively. The red region represents charge accumulation, and the blue region indicates charge depletion. Similar results found for the other proposed systems are not shown here.

In conclusion, the calculated band offsets and charge density distributions provide a comprehensive understanding of the electronic properties of the proposed heterostructures. The alignment of the valence and conduction bands is critical for the efficient transfer of charge carriers, which is essential for the operation of photovoltaic devices. The results from this study offer valuable insights into the design of future photovoltaic materials.
Fermi level mainly correspond to CuAlSe$_2$, demonstrating a donor character; meanwhile, in contrast, the conduction band edge contains CuGaS$_2$ states near the Fermi level for the most part. This is in good agreement with the charge separation, as can we see in Figure 3.

According to Figure 5 and Table 4, the band alignment of the CuGaS$_2$/CuAlSe$_2$ polar surfaces agrees with those for the nonpolar surfaces within 0.1 eV, which is consistent with the experimental observation.$^5$ However, we find that the band alignment in the (001) surface orientation leads to a dramatic decrease in the $\Delta E_{CB}$ to 0.3 eV with those for the (112), (110), and (102) surfaces. This could be attributed to the surface atomic arrangements of the different surfaces and the distance between atomic planes in the unit cell, which could affect the surface chemistry. The (001) polar surfaces of CuGaS$_2$ can be terminated by cationic layers that consist of either 50% of Cu atoms and 50% of Ga atoms (see Figure 1); meanwhile, the anionic layers consist of 100% of S atoms, so they can generate a total interfacial dipole that can slightly shift the charge density distribution but not in a dominant way. This behavior can be observed on the charge density isosurface for the (001) or (112) interfaces (see Figure 5a,c), where the charge density distribution at VBM is localized on the Cu atoms of CuAlSe$_2$; meanwhile, the charge density distribution at CBM is localized mainly in the sulfur atoms of CuGaS$_2$. That is the reason why the transition from the valence band to the conduction band mainly occurs between the S and Cu states, which is beneficial to the separation of electron–hole pairs. On the other hand, for the nonpolar interfaces, the charge density is distributed...
uniformly along the layers of each band. Similar results were found for the CuGaS2/ZnSe interfaces.

Finally, our studies show that the electrostatic potential is not affected by the polarity on the interfaces. Nevertheless, we notice that the termination cation and anion surfaces affect the length of the bonds between the atoms that conform to the interface, and this modifies the electronic properties of each semiconductor at the interface and can shift the band offsets, which reflects the importance of atomic relaxations at this interface.

**CONCLUSIONS**

In summary, we have presented results of first-principles calculations, which properly include strain and relaxation effects at the polar and nonpolar interfaces between CuGaS2 and the CuAlSe2 and ZnSe semiconductors, to achieve a complete understanding of the physical process that is involved in the band alignment. Based on the above analysis, we can determine that the distortions of the lattice at the interface induced shifts in ΔE\text{cb}

and as a consequence, the E\text{F} values of both materials change with respect to the bulk values; for that reason, correct treatment of the band gap is important to obtain an accurate ΔE\text{cb}.

From the electronic properties, we can conclude that, in the CuAlSe2/CuGaS2 systems, CuAlSe2 acts as a electron donor material and CuGaS2 as an acceptor compound. Meanwhile, in the case of the ZnSe/CuGaS2 interfaces, the holes are confined to CuGaS2, and the electrons are localized on ZnSe. This is clearly observed from the LDOS and the charge density distributions since we can notice that the semiconductor with the larger electron number on the unit cell transfers electrons to the semiconductor with the lowest electron number.

The confinement of the charge carriers on a specific side of the interface, presented on the obtained results in this study, guarantees the correct carrier mobility and avoids their recombination. Finally, the polarity configuration does not play an important role in the band alignment; rather, it is determined by the intrinsic nature of the atoms at both sides of the interface and the induced strain.

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**Notes**

The authors declare no competing financial interest.

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