Electronic band alignment at CuGaS$_2$ chalcopyrite interfaces

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ABSTRACT

Cu-chalcopyrite semiconductors are commonly used as light absorbing materials on solar cell devices. The study of the heterointerfaces between the absorbent and the contact materials is crucial to understand their operation. In this study, band alignments of the heterojunctions between CuGaS$_2$ chalcopyrite and different semiconductors have been theoretically obtained using density functional theory and more advanced techniques. Band alignments have been determined using the average electrostatic potential as reference level. We have found that the strain in the heterointerfaces plays an important role in the electronic properties of the semiconductors employed here. In this work CuAlSe$_2$/CuGaS$_2$ and CuGaS$_2$/ZnSe heterointerfaces show band alignments where holes and electrons are selectively transferred through the respective heterojunctions to the external contacts. This condition is necessary for their application on photovoltaic devices.

1. Introduction

Solar cells based on chalcopyrite semiconductors of the form Cu(In,Ga)(S,Se)$_2$ have demonstrated high energy conversion efficiencies and their manufacturing is being and important technology in thin film photovoltaics [1,2]. Band-gap value in these chalcopyrite materials goes from 1.0 eV for CuInSe$_2$ [2] to 2.4-2.53 eV for CuGaS$_2$ [3]. This allow to tune the optoelectronic properties using alloys.

Thin film solar cell structure includes layers of different materials. The formation of interfaces between them plays an important role in the optimal performance of the solar cell device. Although the efficiencies found for these chalcopyrite solar cells at laboratory level are close to the maximum theoretical value [4], much lower efficiencies are obtained using the large scale manufacturing fabrication methods. Furthermore, recent studies have shown that the selection of the buffer layer material plays a very important role in the optimal performance of a solar cell device [5].

The changes observed in the performance of solar cells as a function of the layers chosen as current extracting contacts, which will affect the electronic parameters of the heterojunctions, have hindered a systematic approach to the design of optoelectronic devices. In particular it has been reported that one of the properties that characterizes the interface between two semiconductors is the band offsets [6,7]. The importance of knowing the relative alignment of the valence and conduction bands, lies in the confinement of electrons and holes in the heterostructure, i.e., if we have a type I offsets, electrons and holes are confined at the same side of the heterojunction [8].

To determine the band alignment between two semiconductors, we use a periodic solid model [9]. This method arises from the need to associate the energy levels of the semiconductors which comprise the heterostructure with a common reference energy level which will be an average electrostatic potential. The importance of this model lies in the possibility to determine, using first principle calculations, the band alignment shifting due to strain and orientation [10]. However, this model has the same problem as any ab initio DFT calculation which is to subestimate the band-gap. Therefore, a correct reproduction of the bulk band-gap must be necessary for achieving a successful theoretical description. To solve this problem, the use of hybrid functionals in DFT calculations, has been increasingly applied to study a large variety of periodic systems. The aim of this paper is to present accurate theoretical results (using hybrid functionals) of the band alignment between the conduction and valence band edges of CuGaS$_2$ a light absorber which has interest as possible component of inexpensive
chalcopryte-based tandem cells) and those of semiconductor candidates that can be used as contacts for it in solar cells, in particular, CuAlSe₂, CdS, ZnSe and ZnS. The results obtained here, may also provide the fundamentals for the design and development of solar cells with an intermediate band [11], based on CuGaS₂, which has been proposed as a suitable host semiconductor material developing such band when a transition metal is added to substitute the Gallium atoms [12–16].

2. Model and computational technique

In this paper we have made ab initio DFT theoretical calculations of the structural and electronic properties for different chalcopryte-semiconductor interfaces. All the calculations were performed using the Vienna ab initio simulation package (VASP) [17]. The core–valence interaction was described by the frozen-core projector augmented wave (PAW) method [18]. The energy cutoff for the plane-wave expansion was set to 350 eV. The Brillouin zone sampling was performed with the Monkhorst-Pack special k-point mesh [19]. For the slab model used here, and explained below, a 6 × 2 × 1 mesh was used (6 × 2 × 2 in the bulk calculations). For standard DFT calculations, the exchange–correlation energy has been treated within the generalized gradient approximation (GGA) approximation using the Perdew, Burke, and Ernzerhof parametrization [20]. It is well known that conventional GGA calculations fail to predict the magnitude of the energy band-gaps. However, it has been shown that the screened hybrid Heyd–Scuseria–Ernzerhof functional (HSE06) [21] presents a significant improvement over the GGA for computing the structural and electrical properties (lattice constant, and band-gaps) of bulk II–VI compound semiconductors [22]. HSE06 functional includes a fraction, $\alpha$, of short-range Hartree–Fock (HF) exchange to improve the derivative discontinuity of the Kohn–Sham potential occurring for an integer number of electron, as well as a length scale defined by a parameter, $\omega$, where the short-range HF exchange is computed.

The $(\alpha, \omega)$ space has been explored only sparsely with results suggesting that different choices of $\alpha$ and $\omega$ may improve in a similar way the accuracy of different physical properties. Since the percentage of HF exchange and length scale in a hybrid functional are not universal constants, and the optimal values may be system-dependent, it is worthwhile to study the variation of the band-gaps as a function of $\alpha$ and $\omega$ in the HSE06 approximation. Fig. 1 shows the effect of the $\alpha$ and $\omega$ parameters on the band-gap for the semiconductors studied in this work. We can observe that a large $\alpha$ value (which is equivalent to a smaller screening of the exchange interaction) increases the band-gap, while the band-gap decreases for large values of $\omega$, as increasing this latter parameter decreases the spatial range in which the exchange interaction is applied. Fig. 1a shows a linear correlation between $\alpha$ and the band-gap; meanwhile Fig. 1b shows a non-linear dependence when $\omega$ increases. The curves displayed in Fig. 1 were obtained by a fit procedure of the obtained results by minimizing the least-square error in the band-gaps. The experimental band-gap values can be reproduced accurately by fitting any (or both) of the two parameters. It has been demonstrated that the mixing parameter $\alpha$ can be made equal to the inverse of the dielectric constant of semiconductors, and adjusted consequently to obtain an accurate value of its band-gap [23]. Based on the above, the parameter $\omega$ in HSE06 is fixed at the standard value of 0.20 Å⁻¹ while $\alpha$ is fitted for each material to reproduce its band gap.

The fraction of HF mixing $\alpha$, is modified to 0.347, to obtain a band-gap of CuGaS₂ (2.43 eV), which agrees with experiment (2.4–2.53 eV) [3]. For CuAlSe₂, CdS, ZnSe and ZnS, the $\alpha$ parameter also is modified (0.352 for CuAlSe₂, 0.354 for CdS, 0.369 for ZnSe, and 0.306 for ZnS) to reproduce as closely as possible their experimental band-gaps (2.49 eV for CuAlSe₂ [24], 2.37 eV for CdS [25], 2.82 eV for ZnSe [25] and 3.52 eV for ZnS [25]). In summary, for each pure semiconductor we determine the $\alpha$ value that allows reproducing exactly the experimental band-gap; with the cell dimensions and atomic parameters obtained through relaxations at the GGA level. This value is significantly higher than the standard one in the HSE06 functional ($\alpha = 0.25$). To calculate the alignment of the band energies between two semiconductors, we construct a supercell that includes one slab for each material and has one interface between them at the center of the supercell. We considered four specific interfaces, CuGaS₂/CuAlSe₂, CuGaS₂/CdS, CuGaS₂/ZnSe and CuGaS₂/ZnS. The surface of contact, (102) for CuGaS₂ and CuAlSe₂, and (110) for CdS, ZnSe and ZnS, was chosen to be a non-polar termination and able to form cation–anion bonds across the interface, minimizing any charge accumulation. The constructed slab contains eight atomic layers for both materials in each slab. For an adequate match between two non-polar surfaces, the 2D surface lattice dimensions must be made equal. The (102) surfaces of CuGaS₂ and CuAlSe₂ have 2D rectangular cells of 5.33 Å × 15.1 Å and 5.66 Å × 15.89 Å size, respectively; while the (110) surfaces of CdS, ZnSe and ZnS have approximately 1 x 2 rectangular 2D cells of 5.88 Å × 16.63 Å, 5.56 Å × 15.73 Å and 5.45 Å × 15.41 Å, respectively. We have different lattice parameters to the left and right side of the interface. We construct the unrelaxed supercell with inter-planar distance equal to the average between the inter-planar distances of the

![Fig. 1. Calculated band-gap vs (a) fraction of $\alpha$ HF mixing, and (b) the parameter $\omega$ (in units of Å⁻¹) which defines the range of the exchange interaction.](image-url)
constituent semiconductors. The same was done for the lattice constants parallel to the interface. The basic unit cell is periodically repeated in space in order to generate an infinite system. For the non-polar surface chosen (102), the minimum number of atomic layers to reproduce the structural and electronic properties of CuGaS$_2$ are eight layers, giving a total of 64 atoms for each slab, and 128 atoms for the heterostructure. Increasing the size of the supercell in a direction parallel to the interface involves duplicating the number of layers. This is too much to be handled with our present resources. We have studied a supercell with 16 layers of CuGaS$_2$ and 8 layers for the semiconductor contact. The changes of the structural properties and the electrostatic potential for the slab model are negligible.

Fig. 2 shows the structure of the supercell used to represent the interface in the direction (102). Even though periodic boundary conditions are imposed along the planes parallel to the interface to simulate an infinite system, the heterointerface displays the special constraints of the relatively small size of the slabs used in the simulation. Consequently, it is favorable for the atomic spacing on either side of the interface to slightly contract and expand the lattice parameters of each material to align with adjacent atoms, while the atoms farthest away from the interface optimize their respective lattice parameters in the direction perpendicular to the interface. Since the structures exhibit a smooth transition from the CuGaS$_2$ to semiconductor material, the interfacial strain is minimized and the only strain remaining in either material just a few atomic planes away from the interface is that due to the change in the lattice dimensions parallel to the slabs.

To obtain the valence- and conduction-band discontinuities, we used an electrostatic potential-based alignment method [9,26] following a three-step computational procedure. The first step is the determination of the appropriate $\alpha$ value for each bulk semiconductor, carried out as said above. Next, structural relaxations for the slab models are carried out at GGA-PBE level. The electrostatic potential distribution is then determined for the optimized geometry results. The electrostatic potential calculations for the slab models were not made with the HSE-$\alpha$ functional, since these calculations are computationally too demanding for large unit cells and the electrostatic potential is already well described using GGA functionals. Besides, it is no clear which $\alpha$ values should be used for such calculation involving two different semiconductors. In the third step it is necessary to perform electronic and electrostatic calculations for the corresponding bulk materials forming the interface. But 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. This is done to calculate the band-gap of the semiconductors under conditions similar to those in the interface model. These calculations were done with the HSE hybrid functional, using the optimum $\alpha$ value obtained before for each relaxed, non-strained pure semiconductor. Then the positions of the band edges relative to the electrostatic potential distribution in each bulk semiconductor were noted, and transferred to the corresponding slab interface model to locate the positions of the band edges for the constituting semiconductors.

### 3. Results and discussion

Generally thin films develop a large amount of intrinsic stress during the growth of the heterostructures. The presence of stress can not only affect the layer morphology but can also severely modify the electronic properties.

In Table 1, we present the calculated lattice mismatch (only for the $x$ direction) between the CuGaS$_2$ and the different semiconductors involved in the four interfaces proposed. The lattice mismatch is defined as $\delta = (a - a_{\text{CuGaS}_2})/a_{\text{CuGaS}_2}$, where $a$ and $a_{\text{CuGaS}_2}$ are, respectively, the lattice constant in the $x$ direction of the contact material and of CuGaS$_2$, respectively. In all cases we can observe that the theoretical values of the lattice mismatch are larger than the experimental values, this is due to the overestimation of the lattice constant produced by standard GGA calculations. Furthermore, the lattice mismatch determines the magnitude of the structural variation displayed by the different types of heterointerfaces, whose magnitude modifies the electronic properties of the semiconductors when forming the heterostructure [27,28]. This modification will affect the type of band alignment.

Table 2 contains the values of band-gaps obtained for each semiconductor using such HSE modified functional (i.e. with the $\alpha$ value giving for the relaxed bulk semiconductor the exact experimental gap) but with the cell parameters obtained from the relaxed slabs. As mentioned above, the structurally induced variations from the band-gaps are a consequence of the internal stresses produced by compression or stretching of the bonds and by changes in the bond angles. In all cases showed in Table 1, for CuGaS$_2$ the band-gap decreases because the lattice constant increases [29]. This is mostly attributed to the coupling between filled anion p and cation d levels, which is large in these chalcopyrites because the elements of the group IB in the periodic table have high d orbital energies, and the coupling is inversely proportional to the energy separation between the anion p and cation d energy states; this coupling is then rather sensitive to the anion-cation distances and to the symmetry around the atoms. On the other hand, all the semiconductors forming the other side of the four interfaces are under internal compression, which is accompa-

![Fig. 2. Structure of the supercell for the CuGaS$_2$/CuAlSe$_2$ (102) interface. Other chalcopyrite heterointerfaces supercells are constructed similarly.](image)
The difference between £PcuGas and £PcuAlSe can be seen in Fig. 3b), which includes the top of the valence and the lowest of the conduction band (EcB) for both semiconductors in the interface. However, HSE-£z predicts the nature and magnitude of band-gaps accurately. This is especially relevant in the CdS case which shows the largest band-gap error in our GGA calculations. The importance of considering the distortion and the HSE-£z approximation in the band alignments, is reflected in comparison with Anderson’s electron affinity rule results.

In this rule the main contribution to the change in the type of alignment is due to a modification in the band-gap caused by the tensile stress generated by the interface. The £Eg of CuGaS2/AlSb interface is type II, meaning that the CdS interface is of type I, meaning that the band-gap of CuGaS2 lies completely inside the band-gap of CdS. More specifically, the £Ev of CuGaS2 is 0.62 eV higher than that of CdS while its £Ec is only 0.12 eV less than that of CdS. This result is consistent with the empirical work of Singh et al. [5], where the CuGaS2/CdS interface exhibits poor conversion efficiency. They suggest that the lattice mismatch is an important factor in the performance of the solar cell device; we show here that in any case the band alignment is inadequate in this system. The CuGaS2/ZnS heterointerface exhibits type II (staggered) band lineup. The corresponding band offset for this interface gives £Ev and £Ec equal to 0.87 eV and 0.20 eV, respectively.
Fig. 3. (a) Planar average of the electrostatic potential of CuGaS$_2$/CuAlSe$_2$(102) oriented along this direction. The reference level is determined by this potential at positions intermediate between the atomic planes which are far from the interface. (b) Electrostatic potential and energy levels of the gap edges, obtained for CuAlSe$_2$ and CuGaS$_2$ single phases distorted due to the epitaxial strain.

Fig. 4. Electrostatic potential and band-gap variation of CuGaS$_2$ versus the lattice mismatch. The lattice mismatch values are taken from Table 1 and correspond to the four interfaces studied here. The EP and band-gap are obtained from the corresponding four distorted bulk calculations.

0.15 eV respectively, with CuGaS$_2$ bands lying higher. Finally, the CuGaS$_2$/ZnS interface is of type I. The conduction and the valence bands of the CuGaS$_2$ are inserted within the band-gap of the wide-gap semiconductor (ZnS). A downward step of 0.84 eV for the valence band is theoretically obtained which implies a $\Delta E_C$ of 0.38 eV. In this case, the large band-gap differences are the main factor in the type of alignment. So the electrons and holes are thermalized on the same side of the interface.

As stated in Table 3 and considering the difference between type I and type II heterojunctions, the band offsets have different signs at the type I interface. For this type of band alignment, occurring here at the interfaces with CdS and ZnS, electrons and holes are localized on the same side of the interface, i.e. in the narrow-gap layer which in this cases is CuGaS$_2$. This leads to an easy recombination of the carriers inside CuGaS$_2$, from which they cannot escape. At the type II interface, where the band offsets have the same sign, electrons and holes localize on different sides of the interface, facilitating thus only recombination through spatially indirect transitions.

According to the results obtained in this work, in a photovoltaic device using as light absorber CuGaS$_2$, CuAlSe$_2$ can be used to achieve selective hole collection, while ZnSe can be used for selective electron collection. For CuGaS$_2$/CdS interface, for which the Anderson’s rule predicts a staggered gap, meaning that the valence
4. Conclusions

Table 3

<table>
<thead>
<tr>
<th>CuGaS₂/CuAlSe₂</th>
<th>CuGaS₂/CdS</th>
<th>CuGaS₂/ZnSe</th>
<th>CuGaS₂/ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>HSE-α</td>
<td>GGA</td>
<td>HSE-α</td>
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<tr>
<td>ΔE₀</td>
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<td>-0.71</td>
<td>-0.65</td>
</tr>
<tr>
<td>ΔEₐ</td>
<td>0.69</td>
<td>-0.08</td>
<td>0.42</td>
</tr>
</tbody>
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Fig. 5. Band alignments between the CuGaS₂ and several wide band gap semiconductors proposed as contacts, computed with HSE-α.

and conduction bands in CdS are lower in energy than the valence and conduction bands in CuGaS₂, our result shows on the contrary, as said above, a straddling gap, which is an incorrect band alignment for photovoltaic applications, but is often used to fabricate light emitting diodes and lasers [35,36]. This example shows how the effects of the lattice mismatch can modify the valence and conduction bands discontinuities at which the CuGaS₂/CdS interface switches from type II to type I. Finally, the structural and electronic results suggest that the nanostructure CuAlSe₂/CuGaS₂/ZnSe may improve the carrier collection efficiency, which would allow to build a p-i-n heterostructure. Tandem solar cells can thus be made using this structure for the front (high band gap) side of the cell. Alternatively, if suitable transition metals are used to substitute for Gallium atom in the CuGaS₂ chalcopyrite, an intermediate band solar cell could be made, which could potentially improve the performance of a solar cell [16]. The appropriate level of cationic substitution to form and intermediate band using transition metal atoms is about a 10%. At this level of metal concentration the main gap will be affected by less than one or two tenths of eV [37] so the band alignment should not change significantly.

4. Conclusions

In summary, we have presented density functional calculations of the band alignment and structural properties for the CuAlSe₂/CuGaS₂, CuGaS₂/CdS, CuGaS₂/ZnSe and CuGaS₂/ZnS heterointerfaces. The HSE-α hybrid functional used reproduces accurately experimental band-gaps and hence correct band offsets can be expected using it. We also discuss the effects of the lattice mismatch on the electrostatic potential and on the band-gap, that describe the variation on the type of the band alignments. This effect is relevant for the study of the CuGaS₂/CdS interface where the band alignment changes from type II to type I. The alignment using as reference the average electrostatic potential predicts that the CuGaS₂/CuAlSe₂ and the CuGaS₂/ZnSe interface are type II and possess a staggered alignment. The valence and conduction bands of CuGaS₂ lie at energies below the corresponding ones of CuAlSe₂. For ZnSe just the opposite happens, CuGaS₂ valence and conduction bands lie at energies above the corresponding ZnSe bands. These are the appropriate conditions to match two interfaces into a heterostructure with three semiconductors (CuAlSe₂/CuGaS₂/ZnSe) so that electrons and holes photo-generated in CuGaS₂ (used as light absorber) can be extracted selectively, as desired, at both device sides. The detailed model employed here, should serve as an accurate tool for the quantitative prediction of band alignment at heterojunctions for which no experimental data yet exist.

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