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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]. Bang-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 heterostructure, whereas if we have a type II offset, electrons and holes are confined at different sides 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

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chalcopyrite-based tandem cells) and those of semiconductor candidates that can be used as contacts for it in solar cells, in particular, $CuAlSe_2$, 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 $CuGaS_2$, 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 chalcopyrite-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 $6 \times 2 \times 1$ mesh was used ($6 \times 2 \times 2$ 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 Ernzerhoff 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, α, 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, ω, where the short-range HF exchange is computed.

The (α, ω) space has been explored only sparsely with results suggesting that different choices of α and ω 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 α and ω in the HSE06 approximation. Fig. 1 shows the effect of the α and ω parameters on the band-gap for the semiconductors studied in this work. We can observe that a large α 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 ω, as increasing this latter parameter decreases the spatial range in which the exchange interaction is applied. Fig. 1a shows a linear correlation between α and the band-gap; meanwhile Fig. 1b shows a non-linear dependence when ω 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 α 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 ω in HSE06 is fixed at the standard value of 0.20 $Å^{-1}$ while α is fitted for each material to reproduce its band gap.

The fraction of HF mixing α, is modified to 0.347, to obtain a band-gap of $CuGaS_2$ (2.43 eV), which agrees with experiment (2.4–2.53 eV) [3]. For $CuAlSe_2$, CdS, ZnSe and ZnS, the α parameter also is modified (0.352 for $CuAlSe_2$, 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 $CuAlSe_2$ [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 α 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 (α = 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, $CuGaS_2/CuAlSe_2$, $CuGaS_2$/CdS, $CuGaS_2$/ZnSe and $CuGaS_2$/ZnS. The surface of contact, (102) for $CuGaS_2$ and $CuAlSe_2$, 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 $CuGaS_2$ and $CuAlSe_2$ 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 × 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

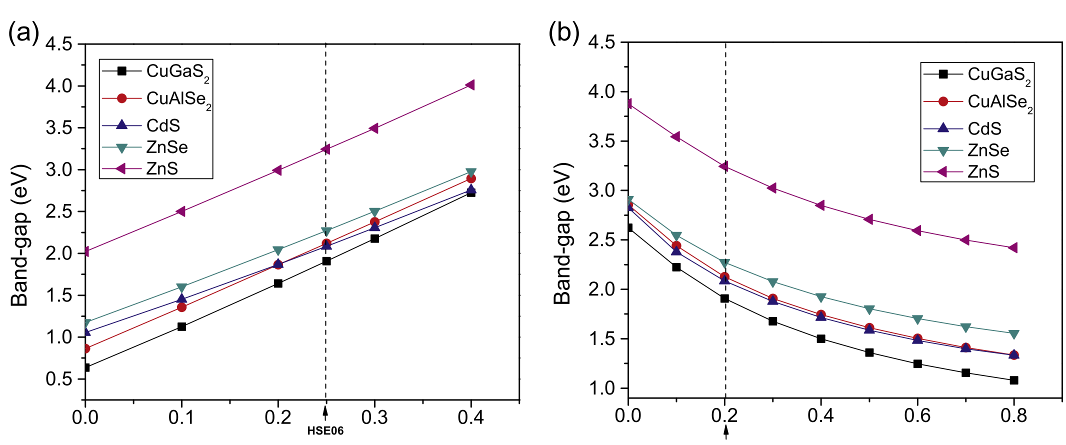

Fig. 1. Calculated band-gap vs (a) fraction of α HF mixing, and (b) the parameter ω (in units of $Å^{-1}$) which defines the range of the exchange interaction.