



Theoretical band alignment in an intermediate band chalcopyrite based material



J.E. Castellanos Águila^{a,d}, P. Palacios^{a,b,*}, J.C. Conesa^e, J. Arriaga^d, P. Wahnón^{a,c}

^a Instituto de Energía Solar, Universidad Politécnica de Madrid, 28040 Madrid, Spain

^b Dpt. Física Aplicada a las Ingenierías Aeronáutica y Naval, Universidad Politécnica de Madrid, ETSI Aeronáutica y del Espacio, 28040 Madrid, Spain

^c Dpt. Tecnología Fotónica y Bioingeniería, Universidad Politécnica de Madrid, ETSI Telecomunicación, 28040 Madrid, Spain

^d Instituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, C.U. 72570 Puebla, Mexico

^e Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

ARTICLE INFO

Article history:

Received 25 October 2016

Received in revised form

29 December 2016

Accepted 30 December 2016

Available online 3 January 2017

Keywords:

Photovoltaics

Theoretical calculations

Heterostructures

ABSTRACT

Band alignment is key to enhance the performance of heterojunction for chalcopyrite thin film solar cells. In this paper we report ab initio calculations of the electronic structures of CuGaS₂:Cr with various Cr compositions, CuAlSe₂ and ZnSe and the band alignment between their interfaces. We use density functional theory and the more accurate self-consistent GW scheme to obtain improved bulk band-gaps and band offsets. Band alignments of the interfacial region for CuGaS₂:Cr/CuAlSe₂ and CuGaS₂:Cr/ZnSe systems were aligned with respect of an average electrostatic potential. Our results are in good agreement with experimental values for the bulk band-gaps. These theoretical band alignments show a characteristic staggered band alignment for the design of heterojunction devices in photovoltaic applications.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Current Cu(In,Ga)Se₂ photovoltaics devices, on a laboratory scale, reach conversion efficiencies about 22.3% [1]. This improvement on the efficiency is mainly due to the improvement to the CIGS absorber layer and the junction formation process. However, the efficiency is still lower than the single gap Shockley–Queisser limit [2]. One of the proposals which promises high conversion efficiencies is the intermediate band (IB) solar cells concept [3]. An IB could provide additional optical transitions due to electronic states inside the fundamental band-gap of the host semiconductor. It has been reported that the CuGaS₂ which has a 2.43 eV band-gap, is a suitable host material for the IB concept [4,5]. If we consider Chromium transition atom replacing Gallium atom in a CuGaS₂ semiconductor, additional states within the band-gap are observed due to the Cr, as described in Ref. [6–10]. However, up to date it is not known which will be the behaviour of the intermediate band material taking into account the rest of materials which are in contact in the complete solar cell. For this reason, a precise knowledge of the band structure of these heterojunctions becomes necessary.

In a previous report [11], we have studied the band alignment of the heterointerfaces between CuGaS₂ and several semiconductors. We have found that the CuAlSe₂/CuGaS₂ and CuGaS₂/ZnSe heterointerfaces show good characteristics for the design and development of thin film solar cells. The junctions formed by materials with different band-gaps and lattice constants have strong influence on the valence and conduction band offsets, and moreover the possibility that local states can occur at the interfaces of these heterostructures which might have an influence in the electronic and transport properties. A proper description of the structure and electronic properties of surfaces and heterointerfaces must be taken into account in order to design, to build and to analyze such heterostructures devices.

In this work, we present a systematic procedure for the calculation of the energy band alignment at an abrupt IB material-semiconductor heterojunction [12,13]. The procedures requires only a knowledge of the energy band structures of the participating semiconductors, and does not invoke any properties – empirical or theoretical – of the free surface, but needs to associate the energy levels of the semiconductors which comprise the heterostructure with a common reference energy level. This level is obtained using an average electrostatic potential. The accuracy of the method is believed to reflect directly the quality of the band structures. Once accurate band structures and an adequate sophisticated model of the charge distribution near the interface are obtained, the method should be capable of serving as an accurate tool for the

* Corresponding author at: Dpt. Física Aplicada a las Ingenierías Aeronáutica y Naval, UPM, ETSI Aeronáutica y del Espacio, 28040, Madrid.

E-mail address: pablo.palacios@upm.es (P. Palacios).

quantitative prediction of band lineups at heterojunctions for which no experimental data yet exist.

2. Model and computational technique

We perform first-principles calculations based on the GGA approximation [14] and many body perturbation theory (quasi-particle energy calculations) [15,16] as implemented in the Vienna ab initio simulation package (VASP) [17]. The interactions between the ionic cores and the valence electrons were introduced using the projector-augmented wave method (PAW) [18,19]. The valence configurations used in the PAW pseudopotentials were: $3d^{10}4s^1$ for Cu; $4s^24p^1$ for Ga; $3s^23p^4$ for S, $3d^54s^1$ for Cr, $4s^24p^4$ for S, $3s^23p^1$ for Al and $4s^23d^{10}$ for Zn. Ga potential without semi-core d states reproduces quite well the experimental valence band levels in CuGaS_2 semiconductor so they have not been included. The Perdew–Burke–Ernzerhof (PBE) [14] functionals are employed for the GGA exchange–correlation potential. The valence electronic wave-functions are expanded in a plane wave basis set up to a kinetic energy cut-off of 450 eV. The quasi-particle energy calculations are based on a restricted self-consistent scGW schemes, where, the wave-functions and energies of the PBE calculations were used as the starting point to compute the quasiparticle band structure, subsequently, we update the quasi-particle wave-function four times in both Green's function G and screened potential W [20]. The total number of valence and conduction band states in the scGW procedure was set to 320 for all materials.

To calculate the band alignment from first principles calculations we use non-polar interfaces because their structures are relatively well established. The heterointerfaces between the IB material and CuAlSe_2 or ZnSe phases are studied using a typical supercell approach. Basically a supercell consists of a unit cell of n monolayers of one semiconductor followed by m monolayers of the other. Eight atomic layers for each of the two materials are stacked in the [110] direction. Supercells composed of 16 layers, correspond to a ~ 32 Å thickness. Here, Γ -centred k -point Monkhorst–Pack [21] mesh of $6 \times 6 \times 1$ was used, due to the relatively large supercell size. For the bulk calculations we use a $6 \times 6 \times 2$ k -point mesh. The plane wave cut-off and the Brillouin zone sampling both were verified to provide convergence in total lattice energy within 1 meV. The calculation for $\text{CuGaS}_2\text{:Cr}$ was carried out using a monoclinic unit cell in which one of the Ga atoms was replaced by a Cr atom (at tetrahedral sites), which corresponds to the 25% dopant concentration.

Two types of calculations were performed to obtain three types of energy level differences. First, heterointerface calculations were carried out at the GGA level to obtain the difference between electrostatic potentials near the centre of slabs of the two phases. Second, bulk calculations provide the difference from the electrostatic potential to the valence band maximum for each phase. It should be noted that in the first calculation, we incorporated the effect of the strain due the lattice-mismatch heterojunction, however, this $\text{CuGaS}_2\text{:Cr}$ mismatch and the different semiconductors are reduced respect to the lattice-mismatch without chromium, for the $\text{CuGaS}_2\text{:Cr/CuAlSe}_2$ the lattice mismatch is 4.72% and for the $\text{CuGaS}_2\text{:Cr/ZnSe}$ is 5.9%, meanwhile in the $\text{CuGaS}_2\text{/CuAlSe}_2$ interface, the lattice mismatch is 5.96% and for the $\text{CuGaS}_2\text{/ZnSe}$ interface is 5.68%. This is due for the presence of three cationic species. For that reason we took the lattice constant and atomic position without distortion. Finally, for these undistorted cells, we have used the many body GW approximation to carried out quasiparticle energy calculations. Using this method we have predicted the electrostatic potential and the band structures more accurately.

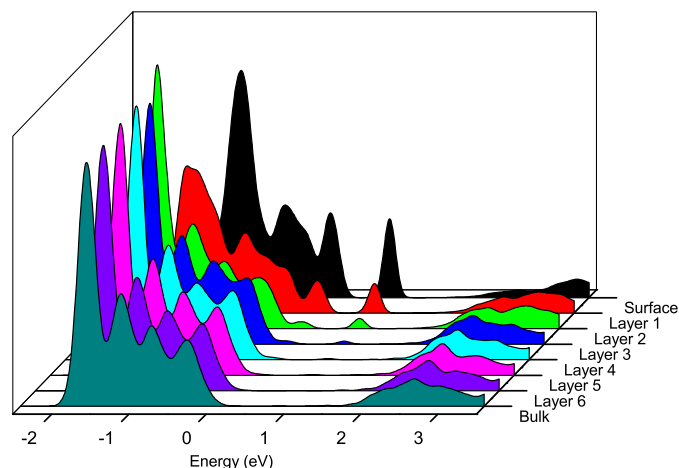


Fig. 1. Densities of states in the first seven top-layer CuGaS_2 (110), compared to the bulk density of states. The zero of energy is at the Fermi level.

3. Results

In a previous study, we found that non-polar surfaces of CuGaS_2 are technologically very important because in thin film solar cell structures are the most suitable to form cation–anion bonds across the interface, minimizing any charge accumulation. We consider for the interface the (110) plane, which is formed by an atomic layer having the stoichiometric Cu–S–Ga–S composition. In this case we use slabs which stack eight such monolayers.

Fig. 1 shows the projected density of states (PDOS) for the unrelaxed surface and the first six sub-surfaces layers for the CuGaS_2 (110), compared with the bulk-DOS. According to the well known DFT problem, the predicted band-gaps are underestimated and the trends in the predicted gap should be meaningful. Is important to note that the purpose of this part of the work is to determine the depth of the surface states in the chalcopyrite, which allows us to determine an integer number of CuGaS_2 formula units to ensure that the effect of the interface on the level positions at the slab centre is negligible.

We see that the PDOS of the topmost atomic layer reflects the density of surface states whereas the PDOS of deeper layers become identical to the density of bulk states. Significant perturbations arising from the surface do not penetrate deeper than three layers into the bulk, which justifies using slabs containing eight atomic planes each. For the surface layer, two surface states (E_1 and E_2) appear at 0.3 eV and 1.2 eV from the valence band. These levels correspond to $3d$ of Cu and $4p$ of Ga, respectively. A more extensive analysis of the LDOS shows that this is a consequence of two covalent Cu–S and Ga–S bonds breaking in the z direction of a primitive translation vector of the surface unit cell. Particularly, E_1 are mostly of d_{z^2} symmetry (where the normal to the surface is taken as z direction), meanwhile the state E_2 is primarily of p_z symmetry.

From this, the created supercell contains sixteen atomic layers for both the $\text{CuGaS}_2\text{:Cr/CuAlSe}_2$ and $\text{CuGaS}_2\text{:Cr/ZnSe}$ interfaces, as it is shown in Fig. 2a for the interface to CuAlSe_2 case. The total numbers of layers of the slab are checked to guarantee that the effects of the interfaces do not affect the electronic properties and the electrostatic potential for the slab model. Fig. 2b shows the PDOS (from the GGA calculation) for the interface and the first three sub-interface layers (one of them containing the transition metal). We observe that the electronic properties of each material are maintained in the heterostructure. Surface states such as those in Fig. 1 do not appear because broken bonds are absent. In the interface layers, the effect of the lattice mismatch is observed in the edge of the valence and conduction band, where the band-gap is almost

Download English Version:

<https://daneshyari.com/en/article/5350011>

Download Persian Version:

<https://daneshyari.com/article/5350011>

[Daneshyari.com](https://daneshyari.com)