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# Band offset of the $ZnO/Cu_2O$ heterojunction from ab initio calculations

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ABSTRACT

The $ZnO/Cu_2O$ system has known a recent revival of interest in solar cells for its potential use as a heterojunction able to highly perform under visible light. In this work, we are interested on the characterization of the interface through nanoscale modelization based on ab initio (Density Functional Theory (DFT), Local Density Approximation (LDA), Generalized Gradient Approximation (GGA–PBE), and Pseudopotential (PP)). This work aims to build a supercell containing a heterojunction $ZnO/Cu_2O$ and study the structural properties and the discontinuity of the valence band (band offset) from a semiconductor to another. We built a zinc oxide in the wurtzite structure along the [0001] on which we placed the copper oxide in the hexagonal structure ($CdI_2$-type). We choose the method of Van de Walle and Martin to calculate the energy offset. This approach fits well with the DFT. Our calculations of the band offset gave us a value that corresponds to other experimental and theoretical values.



## 1. Introduction

More fundamental research is being carried out with the aim of developing radically lower-cost and/or higher-efficiency modules for the longer term [1,2]. A promising strategy to install novel concepts, incorporates often enabling technologies such as nanotechnology, which aim to modify the active layer to better match the solar spectrum, or to preferentially modify the incoming solar radiation before it impinges on the active layer. Design, growth and characterization of new

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generation solar cells are nowadays an important research field [3,4]. In the recent years, a large amount of experimental and theoretical work focused on heterostructures composed of ultrathin layers designed for new solar energy converters working under a low light intensity. However, the development of new solar cells with improved performances and lower cost requires new approaches based on the use of clean, low cost and non-toxic materials prepared via low energy processes. Simulation methods are used to predict the characteristics of a semiconductor which would operate with an optimum efficiency as a photovoltaic solar energy converter. The existence of such an optimum material results from the interaction between the optical properties of the semiconductor which determine what fraction of the solar spectrum is utilized and its electrical properties which determine the maximum efficiency of conversion into electricity [5].

Photovoltaic cell requires two semiconductor slabs (n-type and p-type). Zinc oxide (ZnO) attracted researcher's attention for a long time, owing to its potential applications in many scientific and industrial areas [6]. Actually, its non-toxicity and natural abundance make it an ideal candidate for many industrial manufacturing processes [7]. ZnO belongs to the family of the transparent conductive oxides (TCO). It is an n-type semiconductor, with a wide band gap of 3.4 eV and an exciton binding energy of 60 meV. These features make ZnO, like GaN, a candidate for applications to blue and ultra-violet optical devices [8]. Cuprous oxide ($Cu_2O$) is a potential material for the fabrication of low cost solar cells [9,10]. The first $Cu_2O$-based solar cell was manufactured at the end of 1920. However, at that time, and until the first space explorations, the energy production from the sun light by the photovoltaic effect was just a curiosity. $Cu_2O$ is a p-type semiconductor with a direct band gap of about 2 eV, which is suitable for photovoltaic conversion.

The ZnO/$Cu_2O$ heterojunction has been fabricated longtime ago and studied for a long time [11]. This heterojunction has recently attracted a renewed interest thanks to the low cost and non-toxic character of its constituents [12–15]. Its efficiency is still quite small (2%), but better performances can be expected by improving the crystalline order and the interface features. Considerable attention is devoted to improve the electronic properties at interfaces and to grow the heterostructure along crystallographic directions that provide stability and increase efficiency. ZnO has a hexagonal (wurtzite) structure, while $Cu_2O$ is cubic (cuprite). An epitaxial growth of (1 1 1)-oriented $Cu_2O$ film on the (0 0 0 1) surface of ZnO is thus possible as it was reported in several papers [16,17]. Nevertheless, studies of $Cu_2O$ under pressure [18,19] show that this crystal underlies to a transition to a hexagonal phase, which is a polytype of the $CdI_2$ structure. This suggests that a growth of $Cu_2O$ films according to the $CdI_2$ structure on a ZnO substrate is also possible. This kind of growth would have the advantage of giving superlattices preserving the stoichiometry. In the present work, we will investigate this kind of growth.

Many important properties of semiconductors are not solely determined by the band gap. For instance, the relative band energies between different semiconductors and corresponding band offsets are of fundamental interest in solid state physics and are indispensable for the design of heterojunction devices [20,21]. Band offsets of semiconductors are important and necessary parameters in material and device design [22]. They are among the most important properties of heterostructure. Their precise knowledge is extremely important to engineer electronic [23] and optoelectronic [24] devices. More specifically, the band offsets are critical to many properties such as quantum confinement [25] doping ability, [26] and chemical activity [27]. In the theoretical approach, the valence and conduction band offsets are formed by two terms:

$$E(V,C)_{\text{offset}} = \Delta E_{\text{band}}(V,C) + \Delta V_{av} \tag{1}$$

where $\Delta E_{\text{band}}(V, C)$, known as the band structure contribution, is defined as the difference between the valence band maxima (VBM) or the conduction band minima (CBM) relative to the average of the electrostatic potential in each material. $\Delta V_{av}$ is the lineup of average of the electrostatic potential across the interface [28]. Most of the heterojonction physics is determined by the band offset, which is usually described by models [29–31]. The model proposed by Van de Valle and Martin [32] will be used here and, will be combined with ab initio calculations, which will allow us to calculate the band offset of the ZnO/$Cu_2O$ heterojonction. Previous experimental studies of this heterojonction can be found in Refs. [15,33], while theoretical results are reported in Ref. [17].