



What is the band alignment of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells?



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ARTICLE INFO

Keywords:

CZTS
Kesterite
CdS
Band alignment
XPS
Conduction band offset

ABSTRACT

The band alignment at the $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4/\text{CdS}$ solar cell heterojunction is a controversial issue, as different measurements and calculations point to substantially different conduction band offsets (CBO). As the actual value of the CBO has profound implications on solar cell performance, the aim of this work is to separate genuine process-dependent variations in the CBO from errors in its experimental determination. We argue that the two most likely mechanisms responsible for real CBO variations are Fermi level pinning (which tends to decrease the CBO) and chemical interdiffusion (which tends to increase the CBO). The experimental and computational approaches employed so far to determine the band alignment are analyzed to point out possible limitations for each approach, with an emphasis on photoemission-based approaches. The influence of Fermi level pinning on the CBO should be captured correctly by all types of measurements, except for measurements performed under flat-band conditions. This may explain some particularly large values of the CBO that have been measured under flat-band conditions. On the other hand, the influence of interdiffusion is difficult to resolve completely by most measurement approaches. Interestingly, a rough correlation can be established between the CBO measured at the $\text{Cu}_2\text{ZnSnS}_4/\text{CdS}$ interface by different groups and their corresponding solar cell efficiency: lower-efficiency cells often have a large “cliff-like” offset, whereas most high-efficiency cells have a “spike-like” or nearly flat offset. Control of interdiffusion can be a powerful way to engineer the optimal band alignment in $\text{Cu}_2\text{ZnSnS}_4/\text{CdS}$ solar cells, but it can be detrimental in $\text{Cu}_2\text{ZnSnSe}_4/\text{CdS}$ solar cells, as it may increase the CBO above the optimal range for maximum efficiency.

1. Introduction

The p-type semiconductor $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTS(e)) is among the most promising solar absorber materials on the path to thorough deployment of solar energy [1]. CZTS(e) is usually paired with an n-type CdS buffer layer to form a heterojunction solar cell. While absorbers with a high Se content (CZTSe) have achieved a promising power conversion efficiency of 12.6% at the laboratory scale [2], the record efficiency of higher-band gap absorbers with a low Se content (CZTS) lags at 9.1% [3]. In both cases, the most urgent issue to be solved is the low open circuit voltage (V_{oc}) of the solar cell compared to its theoretical maximum given by the Shockley-Queisser limit [1].

The origin of the large V_{oc} deficit, though, appears to be different in CZTSe- and CZTS solar cells. In fact, temperature-dependent V_{oc} measurements have shown that, in CZTSe solar cells of reasonable efficiency, extrapolation of the open circuit voltage to a temperature of 0 K yields a value that is just a few tens meV lower than the band gap of CZTSe [4]. As the extrapolated V_{oc} at 0 K corresponds to the activation energy of the dominant recombination path in the solar cell (E_A), it is

reasonable to conclude that CZTSe solar cells are limited by bulk recombination, and that the small mismatch between V_{oc} and E_A exists because most bulk recombination occurs to/from bulk tail states [5].

Conversely, the same type of measurement done on CZTS solar cells yields values of E_A that are consistently lower than the CZTS band gap by about 0.3–0.4 eV [6–8]. This is significantly larger than the depth of tail states in CZTS, so it seems as if the dominant recombination path is not located in the CZTS bulk but at some interface instead. There can be different reasons why E_A can be lower than the absorber's band gap when interface recombination is dominant [9]. Among them, a cliff-like conduction band offset (CBO) between CZTS and its typical heterojunction partner CdS (buffer layer) is often invoked because a large fraction of the existing CBO measurements [10–26] and calculations [21,27–33] confirms it. Here, by “cliff-like” or “negative” CBO we intend a lower-lying conduction band maximum of CdS with respect to CZTS(e) at the heterointerface, as shown in Fig. 1(b).

In a generic heterojunction solar cell with a cliff-like CBO at the heterointerface, the activation energy of interface recombination becomes equal to the energy difference between the conduction band

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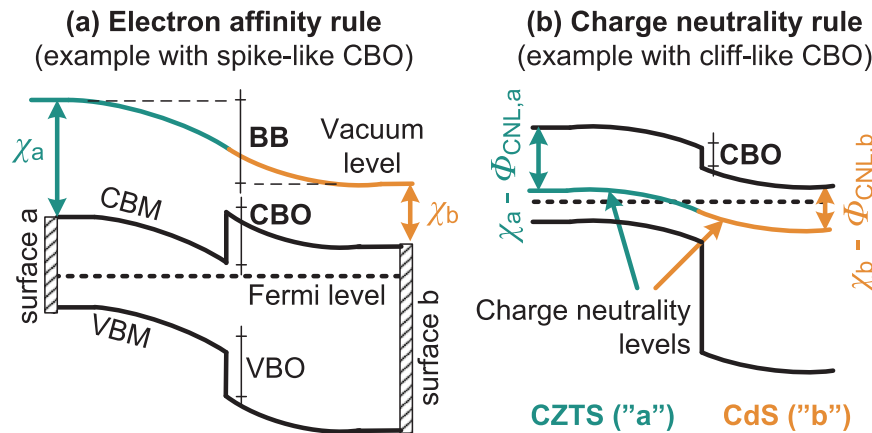


Fig. 1. Band diagram showing the two limiting cases of Eq. (1) in the theoretical determination of band offsets. (a) The Schottky limit (electron affinity rule), where $S=1$ in Eq. (1) and the materials are lined up against a common vacuum level. (b) The Bardeen limit (charge neutrality rule), where $S=0$ in Eq. (1) and the materials are lined up against a common charge neutrality level (CNL). The qualitatively different case of a positive “spike-like” and a negative “cliff-like” CBO are shown to demonstrate the sign conventions. BB stands for band bending.

minimum (CBM) of CdS and the valence band maximum (VBM) of CZTS due to cross-recombination [9]. Therefore, if interface recombination is the dominant recombination path, a cliff-like CBO will result in a lower E_A than the absorber’s band gap and in a lower V_{oc} , as shown in device simulation work [27,34,35]. The ideal CBO for heterojunction solar cells is a moderately positive (spike-like) CBO between $+0$ eV and $+0.4$ eV [27,34,35] as shown in Fig. 1(a). If the spike becomes too large ($> +0.4$ eV) the light-generated electrons flowing from CZTS toward the top contact are blocked by the large electron barrier at the heterointerface. As will be discussed later, this problem can be encountered in (selenide) CZTSe/CdS solar cells. The valence band offset (VBO) at the heterointerface is not of primary importance as long as the band gap of the buffer is significantly larger than that of the absorber.

The above arguments may lead to the conclusion that the V_{oc} of CZTS/CdS solar cells is fundamentally limited by a cliff-like CBO. To confirm or reject this conclusion, we will try to understand the factors that determine the actual band alignment between CZTS(e) and CdS, and the factors that may lead to an incorrect measurement or calculation of the band offsets. In Section 2, general theory on semiconductor band alignment will be reviewed. In Section 3 (Section 4), the experimental (computational) methods employed to measure (calculate) the CBO between CZTS(e) and CdS will be discussed. In Section 5, previously published CBO measurements and calculations will be presented. In Sections 6–10, different physical and chemical mechanisms that may influence the CBO will be proposed. Possible measurement errors related to those mechanisms will be discussed in parallel. Section 11 will present measurement issues related to sample preparation. Finally, Section 12 will propose how the CBO of CZTS(e)/CdS solar cells can be engineered within a certain range and Section 13 will summarize the most important findings of this paper.

2. Theory of band alignment of semiconductor heterojunctions

Most of the basic models of heterojunction band alignment are based on concepts developed in the 1970s and 1980s. A recent review can be found in [36]. A specific review on the band alignment of other chalcogenide semiconductors for solar cells can be found in [37]. It is now generally accepted that, in most situations, the band alignment between two ideal semiconductors is just a function of their bulk properties [36,38–40]. By this it is intended that any contribution to the band alignment due to interfacial charge transfer can be predicted from bulk properties of the two materials without explicitly modeling the interface itself. Two interesting bulk models for the prediction of band alignment are the “electron affinity rule” (Schottky limit) and the

“charge neutrality rule” (Bardeen limit). The electron affinity rule (Fig. 1(a)) aligns semiconductors based on the distance χ (electron affinity) between their conduction band and the vacuum level. The charge neutrality rule (Fig. 1(b)) aligns semiconductors based on the distance $\chi - \Phi_{CNL}$ between their conduction band and their charge neutrality level (CNL). Interestingly, those two models are simply two limiting cases of the following generalized expression for the CBO between semiconductors a and b [36].

$$\text{CBO} = (\chi_a - \Phi_{\text{CNL},a}) - (\chi_b - \Phi_{\text{CNL},b}) - S(\Phi_{\text{CNL},b} - \Phi_{\text{CNL},a}) \quad (1)$$

The dimensionless screening parameter S ($0 \leq S \leq 1$) is a bulk property of the wider band gap semiconductor (CdS in the case of the CZTS(e)/CdS interface). S depends on the high-frequency dielectric constant ϵ_∞ of the material, according to an expression shown in [41]. If $S=0$, we are in the limiting case of the charge neutrality rule and the semiconductors can be aligned against a common CNL (Fig. 1(b)). If $S=1$, we are in the limiting case of the electron affinity rule and the semiconductors can be aligned against a common vacuum level (Fig. 1(a)). For intermediate S values, there is no universal reference level and Eq. (1) must be used instead. Taking $\epsilon_\infty \approx 5$ for CdS [36], the above theory predicts $S \approx 0.4$ for the interface between CdS and any absorber material such as CZTS(e), Cu(In,Ga)Se₂ (CIGS) or CdTe. Therefore, Eq. (1) should be used instead of the electron affinity rule or the charge neutrality rule.

The charge neutrality level of CIGS has been calculated [38]. By substituting it in Eq. (1), one obtains very good agreement with experimental band offsets on CIGS/CdS interfaces without process-induced non-idealities (e.g. interdiffusion or interface defects) [37,38,42]. Unfortunately, the charge neutrality levels of CZTS and CZTSe have not been explicitly calculated yet and theoretical predictions of the CZTS(e)/CdS band alignment have so far been based on the computation of the full electronic structure of explicit CZTS(e)/CdS interface models. Those models will be introduced in Section 4.

As mentioned already, Eq. (1) is expected to be valid for “ideal” interfaces. However, a number of non-idealities can occur at real interfaces. Two widely discussed non-idealities are Fermi level pinning and interface polarization. Their influence on the band alignment of CZTS(e)/CdS solar cells will be discussed in Sections 6 and 7 respectively. Other mechanisms that may change the “ideal” band alignment involve changes in the band edge positions, band gap changes, alloying between the two materials at the interface, and formation of interface phases. Those mechanisms are not often discussed in relation to band alignment but they will be covered in this work (Sections 8–10) as they may have a decisive role in determining the CBO of the CZTS(e)/CdS system.

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