Valence band offset at the CdS/Cu₂ZnSnS₄ interface probed by x-ray photoelectron spectroscopy

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Abstract

The valence band offset (VBO) at the interface CdS/Cu₂ZnSnS₄ was investigated by x-ray photoelectron spectroscopy (XPS). The VBO was measured by two different procedures: an indirect method involving the measurements of the core levels together with the XPS bulk valence band (VB) spectra and a direct method involving the analysis of XPS VB spectra at the interface. The indirect method resulted in a VBO value of (-1.20 ± 0.14) eV while the direct method returned a similar value of (-1.24 ± 0.06) eV but affected by a lower uncertainty. The conduction band offset (CBO) was calculated from the measured VBO values. These two measured values of the VBO allowed us to calculate the CBO, giving (-0.30 ± 0.14) eV and (-0.34 ± 0.06) eV, respectively. These values show that the CBO has a cliff-like behaviour which could be one of the reasons for the V_{oc} limitation in the CdS/CZTS solar cells.

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years the kesterite compound Cu₂ZnSnS₄ (CZTS) has been attracting increasing interest as a thin-film solar cell absorber. This material has a gap close to the single-junction optimum value for maximum energy conversion efficiency and could potentially substitute Cu(In,Ga)Se₂ (CIGSe) and CdTe thin-film absorbers because of its lower-cost, earth-abundant and non-toxic components [1].

However, thin-film solar cells based on CZTS have achieved so far a maximum conversion efficiency of about 8.4% [2] (11.1% [3] with the Se-containing Cu₂ZnSn(S,Se)₄), which is markedly below the attainable efficiency with CIGSe cells (20%) [4]. One reason for this low efficiency is an open circuit voltage (V_{oc}) value quite lower than the theoretical limit. In order to improve the CZTS solar cell performances, much effort is devoted to improve the synthesis [2, 5–7] of CZTS and to understand theoretically [8–11] and experimentally [12–16]

the electronic properties of the material itself and its behaviour when assembled in a solar cell stack.

Similarly to CIGSe, the p–n junction is obtained by depositing a n-CdS layer on p-CZTS and therefore photogenerated electrons in CZTS move through the CdS/CZTS interface. As most of the solar cells' electronic properties are determined by the emitter/absorber interface and by the absorber/back contact interface, the determination of the band alignment at these interfaces is a crucial point for understanding and optimizing the cell properties. In particular, the relatively low V_{oc} of the CZTS solar cells could be due to an increased interface recombination induced by a cliff-like conduction band offset (CBO) at the CdS/CZTS interface. With this band alignment, the conduction band minimum of the CdS buffer would be located below that of the CZTS and this is equivalent to an interface band gap reduction which favours the recombination processes. A spike-like CBO would be preferable [17].

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To the best of the author's knowledge, only two experimental papers have addressed the band offset issue on CZTS so far. Bär *et al* [14] determined the valence band (VB) and the conduction band (CB) alignment at the CdS/CZTS interface by ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES). They find a 0.33 eV cliff-like CBO and a 1.19 eV valence band offset (VBO) for a non-etched absorber which is reduced to 0.91 eV upon KCN etching. On the other hand, Haight *et al* [12] measured by femtosecond laser, pump–probe UPS, a 0.54 eV VBO value, thereby reporting a spike-like CBO. From the theoretical point of view, Chen *et al* [11] predicted by first-principles calculations a CdS/CZTS VBO of 1.01 eV with a negligible (0.09 eV) cliff-like CBO.

Photoelectron emission spectroscopy with tunable synchrotron radiation and/or with fixed photon energy (x-ray photoelectron spectroscopy—XPS, UPS) has been proved to be a powerful technique to study band offsets in semiconductors [18]. In this work, we have studied the band alignment at the CdS/CZTS interface by XPS core-level spectroscopy and XPS VB spectroscopy. In particular, the VBO has been obtained directly from VB data analysis (direct method) and also indirectly using information from core-level data [19–21] (indirect method).

2. Experimental details

The sample was obtained by depositing on a soda-lime glass, covered by an RF-sputtered Mo thin-film, a multilayer of ZnS, Cu and Sn by e-beam evaporation. The chemical composition of this precursor is Zn rich because it is commonly accepted that this stoichiometry gives the best performances of final photovoltaic devices. The CZTS layer was successively synthesized by sulfurization of the precursor in a tube oven under a N_2 flux for 1 h at 550 °C. Finally, the CdS/CZTS interface was obtained by depositing a 70 nm CdS layer on CZTS by chemical bath deposition [7]. As reported in [7], both the XRD and Raman spectra do not show any evidence of spurious phases. This does not exclude the possibility of some ZnS segregation since the ZnS XRD peaks are superimposed to those of CZTS and the ZnS Raman signals are quite weak. A XPS quantitative analysis is performed to quantify the concentration of the different elements: it turns out that the film is stoichiometric for most of its thickness except a narrow region near the CZTS/Mo back contact where a Zn excess is detected. This behaviour is commonly reported in almost all papers on CZTS solar cells and it was confirmed also by glow discharge-optical emission spectroscopy (GD-OES) data.

XPS data were acquired in an ultra-high vacuum system operating at 4×10^{-8} Pa base pressure. It is equipped with a VG Al K_α monochromatized x-ray source and a CLAM2 hemispherical analyser working at constant 20 eV pass energy mode and calibrated according to [22]. The total energy resolution resulted to be 0.7 eV as obtained from the fit of the Fermi edge of a clean Au sample. The VB binding energy (BE) was referred to the position of the Fermi level measured on a clean Ta strip in good electrical contact with
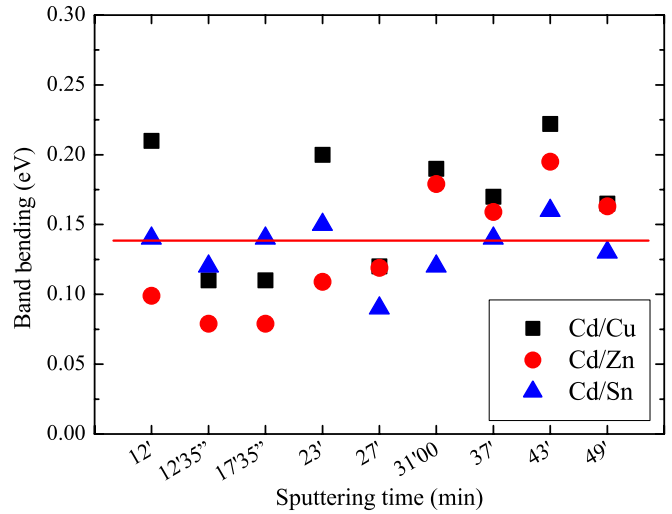
Figure 1. Band bending as a function of sputtering time. The band bending is shown for three data sets: Cd/Cu (filled squares), Cd/Zn (filled circles) and Cd/Sn (filled triangles). A sputtering time of 12 min corresponds to 14% CZTS, while a sputtering time of 23 min corresponds to 75% CZTS. The horizontal solid line indicates the total average of (0.14 ± 0.10) eV. For further explanation see text.

the sample. In order to reach the CdS/CZTS interface, the samples were mildly sputtered with 1 keV Ar ion energy. A careful investigation of the behaviour of the main XPS core-level intensity ratios as a function of sputtering time has allowed us to exclude any preferential sputtering effects. No change in the Cd $3d_{5/2}$, S 2p, Cu $2p_{3/2}$, Zn $2p_{3/2}$, Sn $3d_{5/2}$ core-level lineshapes, relative intensities and BE positions was detected by XPS after sputtering cycles on the CdS and CZTS surfaces, indicating that Ar+ bombardment did not induce any observable surface modifications.

3. Results and discussion

In the indirect method, according to [19], the VBO can be calculated by the formula

$$\text{VBO} = E_{\text{VB}}^{\text{b}} - E_{\text{VB}}^{\text{a}} + V_{\text{bb}}, \qquad (1)$$

where E_{VB}^{a} and E_{VB}^{b} are the energy positions of the VB edges of species 'a' (CZTS) and 'b' (CdS) while V_{bb} is the band bending which is calculated by the well-known formula

$$V_{\text{bb}} = [(E_{\text{CL}}^{\text{a}} - E_{\text{CL}}^{\text{a}}(i)) + (E_{\text{CL}}^{\text{b}}(i) - E_{\text{CL}}^{\text{b}})] \qquad (2)$$

where E_{CL}^{a} and E_{CL}^{b} are the core-level energies of two selected elements in the bulk of material 'a' and 'b' and $E_{\text{CL}}^{\text{a}}(i)$ and $E_{\text{CL}}^{\text{b}}(i)$ are the same core-level energies measured at the interface. In the present case, material 'a' can be chosen from Cu, Zn and Sn and material 'b' is Cd. The band bending is calculated assuming the BE below the Fermi edge negative. According to the configuration used for our calculations (i.e. CZTS/CdS interface), VBO (CBO) results negative if the valence (conduction) band edge of CdS is lower than that of CZTS.

Figure 1 shows the band bending values calculated at different thicknesses of the CdS/CZTS interface using the

core-level BEs of Cd $3d_{5/2}$, Cu $2p_{3/2}$, Zn $2p_{3/2}$ and Sn $3d_{5/2}$. While the values of E_{CL}^a and E_{CL}^b are always the same, $E_{CL}^a(i)$ and $E_{CL}^b(i)$ are measured for each different thickness where both the CdS and CZTS signals are present. The core-level BEs for the bulk and for each interface thickness are obtained by a least-square fitting procedure applied to the Shirley background-subtracted photoemission data using Voigt lineshapes. Using this procedure the error on the BEs can be estimated as ±0.025 eV. The band bending values shown in figure 1 are grouped in three sets corresponding to distinct core-level pairs: Cd/Cu (filled squares), Cd/Zn (filled circles) and Cd/Sn (filled triangles). Considering equation (2), the error on the band bending values is conservatively evaluated to be ±0.10 eV. The band bending averages for each set resulted to be (0.17 ± 0.10) eV, (0.13 ± 0.10) eV and (0.13 ± 0.10) eV for Cd/Cu, Cd/Zn and Cd/Sn, respectively. The total average of (0.14 ± 0.10) eV (red line in figure 1) is in good agreement with data reported in [14].

In order to improve the accepted uncertainty of 0.1 eV for the determination of the VB edge position using the linear extrapolation of the leading edges [19], the energy position of the valence band maxima (VBM) is evaluated by modelling the VB onset with the convolution product of a Gaussian function and a Heaviside step function and applying a numerical fitting procedure that, according to our results, allows us to determine the edge position within 0.02 eV.

In our samples, the VBM positions relative to E_F for CdS and CZTS resulted to be (-1.87 ± 0.02) eV and (-0.53 ± 0.02) eV, respectively. These values are in close agreement with those reported in [12–14]. Since it is quite difficult to measure conductivity data on the thin CdS deposited by CBD, its E_F position could well be consistent with XPS measurement. On the other hand, the conductivity data on CZTS samples imply, in the bulk material, a value of $E_V - E_F$ of about 0.25 eV (see [7]). The apparent disagreement can be explained supposing that, even at the surface of pure CZTS, there is a residual downward band bending of the order of 0.25 eV. This effect could be induced by surface defects. However, it is important to note that this background band bending does not influence the VBO determination.

According to (1), the average VBO values obtained with the indirect method, using for the pairs Cd/Cu, Cd/Zn and Cd/Sn at different interface points for each of the above core-level combinations result to be (-1.17 ± 0.14) eV, (-1.21 ± 0.14) eV, (-1.21 ± 0.14) eV, respectively. The resulting average value of (-1.20 ± 0.14) eV is our extracted VBO. The error is calculated by adding the uncertainties in the VBM and BE positions. The VBO calculated by the indirect method results to be in good agreement with (-1.20 ± 0.15) eV of [14] and with the value of 1.01 eV of [11].

The VBO determined by the indirect method is affected, in our case, by an error that is mainly due to the band bending calculation by means of the core-level positions. On the other hand, the direct method can allow the determination of VBO without an explicit knowledge of the band bending. According to [18], it consists of measuring directly the VB at the interface CdS/CZTS and determining the two band edges relative to the material components. The VBO value is simply obtained by
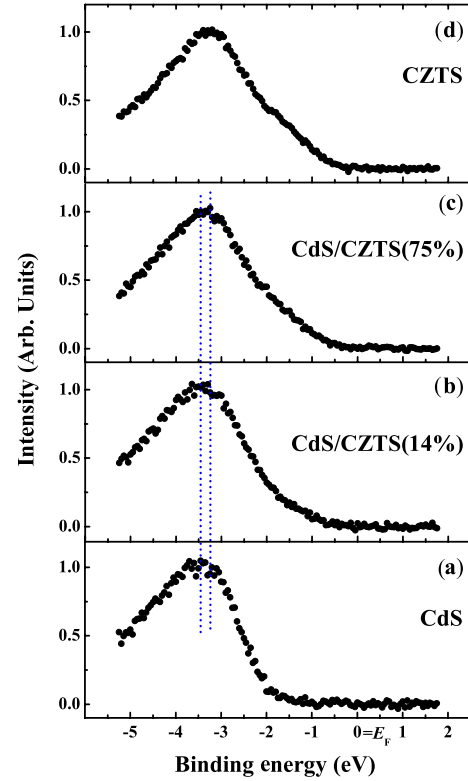

Figure 2. VB measured by XPS at different interface thicknesses. (*a*) VB of the clean CdS surface; (*b*) VB of the CdS/CZTS interface at 14% of measured CZTS total intensity; (*c*) VB of the CdS/CZTS interface at 75% of measured CZTS total intensity; (*d*) VB of the CZTS substrate only. The two vertical blue lines are guides for the eye indicating a peak shift of about 0.15 eV.

the difference between the band edges positions. Figure 2 shows the clean CdS VB (panel (*a*)), the sequence of the VBs measured at two different thicknesses at the interface CdS/CZTS corresponding to about 14% (panel (*b*)) and 75% (panel (*c*)) of detected CZTS intensity and the clean CZTS VB (panel (*d*)). These spectra are normalized to the same height.

Data show that the main VB peak at about -3.5 eV, moves towards the Fermi level by about 0.15 eV on going from the clean CdS surface to the 75% CZTS. The VB shape evolution from pure CdS to pure CZTS does not show significant changes in the overall shape except for the growth of spectral intensity at about 1 eV from VBM. The shoulder at 1 eV, visible in the 14% CZTS VB (figure 2(*b*)), is clearly bigger in the 75% CZTS VB (figure 2(*c*)) and it is still observed nearly unchanged in the bulk CZTS VB data (figure 2(*d*)). The experimentally observed VB spectral intensity at about 1 eV from VBM, growing with increasing amount of detected CZTS can be explained with the onset of CZTS Cu 3d states which dominate the DOS up to 2 eV from VBM [8, 9].

Due to the nature of the CdS/CZTS system, the VB shape at the interface (Figures 2(*b*) and (*c*)) does not show well distinct VB contributions from CdS and CZTS, making impossible a direct determination of the VBO as discussed in [18]. Indeed, the CdS VB in the region close to the VB edge consists of features originating from the outermost cation and anion s- and p-electrons [23], mainly Cd 5s and S 3p, with maximum intensity at about 3 eV from VB maximum [24] and,
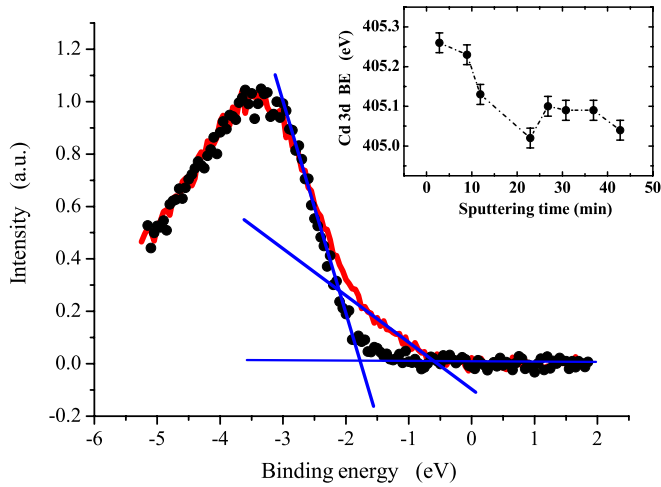
Figure 3. VBO measurement by direct VB analysis. VB measured on the 14% CZTS interface (full red line) with superimposed the clean CdS VB (black dots) shifted by a band bending of 0.10 eV. Data are normalized to the same height. The straight blue lines are only guides for the eye and indicate the approximate VBM positions and the background according to the linear extrapolation method. The inset shows the Cd $3d_{5/2}$ binding energy as a function of sputtering time. A sputtering time of 12 min corresponds to 14% CZTS.

as discussed above, the CZTS VB has a high DOS within 2 eV from VBM due to Cu 3d states.

Although our VB data do not allow a direct VBO determination, it is still possible to obtain the VBO by another approach. According to Klein *et al* [25] the VBO can be evaluated by shifting the starting surface VB by the band bending related to a defined interface thickness and successively by subtracting the shifted surface VB from the VB measured on the interface at the same interface thickness.

Figure 3 shows the clean CdS VB shifted by 0.10 eV and superimposed onto the VB measured on the interface at 14% CZTS. Both spectra are normalized to the same height. The shift on going from CdS to the CdS/14% CZTS interface is measured by means of a least-squares method to be (0.10 ± 0.02) eV. From the good matching of the two superimposed curves up to the CZTS-induced features shown in figure 3, it is reasonable assuming that the observed shift is rigid and hence due to the band bending. This finding is also supported by a similar shift observed on the measured Cd $3d_{5/2}$ BE on going from the clean CdS to the CdS/14% CZTS interface. The Cd $3d_{5/2}$ shift is shown in the inset of figure 3 and was calculated to be (0.13 ± 0.05) eV, the bigger error being due to the uncertainty in peak position.

Therefore, using the VB-determined shift, the VBO results to be (-1.24 ± 0.06) eV. This VBO value is again in good agreement with experimental data by Bär *et al* [14], who report a VBO of (-1.20 ± 0.15) eV, and with theoretical calculations [11] that predicted for the CdS/CZTS interface a VBO value of 1.01 eV.

The CBO can be calculated from the VBO value and the difference of the energy gaps of the two materials: CBO = $(E_{gap}^{b} - E_{gap}^{a})$ + VBO. Using 1.5 and 2.4 eV for the CZTS (*a*) and CdS (*b*) band gaps, respectively, the CBO calculated with the indirect method results to be (-0.30 ± 0.14) eV while
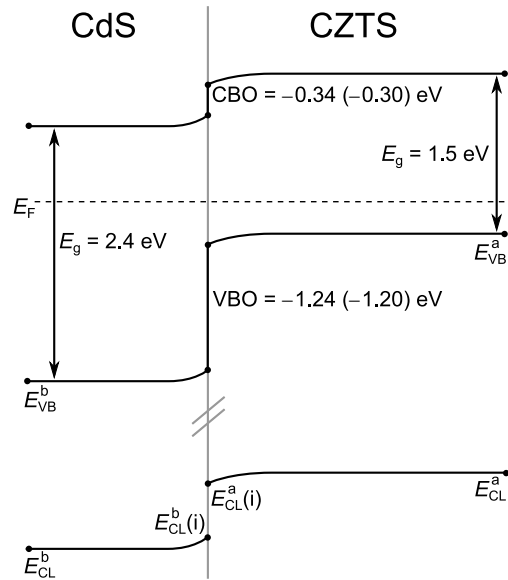
Figure 4. Band diagram of the CdS/CZTS interface resulting from this work. The values of the CBO and VBO reported in parentheses are obtained by the indirect method.

the CBO resulting from VB analysis is (-0.34 ± 0.06) eV, pointing to a cliff-like behaviour in good agreement with [14]. A schematic band diagram of the CdS/CZTS interface with the values measured in this paper is shown in figure 4.

In summary, the interface CdS/CZTS was fabricated by depositing a 70 nm CdS layer by chemical bath on a CZTS thin film, synthesized by sulfurization of an e-beam evaporated multilayer of ZnS, Cu and Sn. The VBO was measured by two different procedures: an indirect method involving the measurements of the core levels together with the XPS VB spectra and a direct method involving the XPS VB spectra only. The indirect method gave a VBO value of (-1.20 ± 0.14) eV while the direct method gave a VBO value of (-1.24 ± 0.06) eV. These results are in agreement with theoretical predictions. The CBO was calculated from the measured VBO values, obtaining (-0.30 ± 0.14) eV for the indirect method and (-0.34 ± 0.06) eV for the direct one. These values show that the CBO has a cliff-like behaviour which could be one of the reasons for the V_{oc} limitation in the CdS/CZTS solar cells.

Acknowledgments

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