An experimental and first-principles study on band alignments at interfaces of Cu$_2$ZnSnS$_4$/CdS/ZnO heterojunctions

This content has been downloaded from IOPscience. Please scroll down to see the full text.

(http://iopscience.iop.org/0022-3727/47/7/075304)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 202.198.62.102
This content was downloaded on 26/06/2014 at 09:27

Please note that terms and conditions apply.
An experimental and first-principles study on band alignments at interfaces of Cu$_2$ZnSnS$_4$/CdS/ZnO heterojunctions

Zi-Yuan Dong$^1$, Yong-Feng Li$^{1,6}$, Bin Yao$^{1,2,6}$, Zhan-Hui Ding$^2$, Gang Yang$^1$, Rui Deng$^3$, Xuan Fang$^4$, Zhi-Peng Wei$^5$ and Lei Liu$^5$

$^1$ Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, People’s Republic of China
$^2$ State Key Lab of Superhard Materials and College of Physics, Jilin University, Changchun 130023, People’s Republic of China
$^3$ School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, People’s Republic of China
$^4$ State Key Laboratory on High-Power Semiconductor Lasers, Changchun University of Science and Technology, 7186 Wei-Xing Road, Changchun 130022, People’s Republic of China
$^5$ State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, No 3888 Dongnanhu Road, Changchun 130033, People’s Republic of China

E-mail: liyongfeng@jlu.edu.cn and binyao@jlu.edu.cn

Received 24 October 2013, revised 10 December 2013
Accepted for publication 17 December 2013
Published 23 January 2014

Abstract

We investigated band offsets at Cu$_2$ZnSnS$_4$(CZTS)/CdS and CdS/ZnO interfaces in a typical CZTS/CdS/ZnO heterojunction solar cell by combining x-ray photoelectron spectroscopy and optical absorption spectroscopy as well as first-principles calculations. X-ray photoelectron spectroscopy and optical absorption spectroscopy measurements indicate that the conduction-band offsets at both CZTS/CdS and CdS/ZnO interfaces show type-II alignment with values of 0.13 eV and 1.00 eV, respectively, which are well supported by first-principles calculations based on the hybrid functional method. Our results suggest that, although type-II alignment for CZTS/CdS heterojunction can form less of a barrier to electron transport across the interfaces, the narrowing of the ‘interface bandgap’ increases recombination of carriers.

Keywords: Cu2ZnSnS4, CdS, ZnO, solar cell, band alignment, x-ray photoelectron spectroscopy, first-principles calculations

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

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSnS$_4$</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>PAW</td>
<td>projector-augmented wave</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>SRPES</td>
<td>synchrotron radiation photoemission spectroscopy</td>
</tr>
<tr>
<td>CBM</td>
<td>conduction-band minimum</td>
</tr>
<tr>
<td>CBO</td>
<td>conduction-band offset</td>
</tr>
<tr>
<td>SLG</td>
<td>soda-lime glass</td>
</tr>
<tr>
<td>VBO</td>
<td>valence-band offset</td>
</tr>
<tr>
<td>VBM</td>
<td>valence-band maximum</td>
</tr>
<tr>
<td>CL</td>
<td>core level</td>
</tr>
<tr>
<td>AEP</td>
<td>average electrostatic potential</td>
</tr>
<tr>
<td>ZB</td>
<td>zinc-blende</td>
</tr>
<tr>
<td>WZ</td>
<td>wurtzite</td>
</tr>
<tr>
<td>$E_g$</td>
<td>bandgap</td>
</tr>
</tbody>
</table>

1. Introduction

With the increasingly serious energy crisis, it is of importance for material research to develop low cost, environment-friendly...
and high-efficiency solar cells [1–3]. Since Cu₂ZnSnS₄ (CZTS) has a direct and suitable bandgap of ~1.5 eV and high absorption coefficient (~10⁴ cm⁻¹), contains Earth-abundant elements and is low cost, it has been considered as a promising absorption layer material in the field of photovoltaic application [4–13]. Recently, a CZTS thin-film solar cell with a conversion efficiency of 9.2% was reported, which is a new efficiency record for such solar cells [14]. A typical structure of CZTS-based solar cell is Mo/CZTS/CdS/ZnO, in which the interface properties, such as CZTS/CdS and CdS/ZnO interface, are very essential for obtaining high energy conversion efficiency [15]. Among the interface properties, the band offset is one of the most important parameters because it influences the transport and recombination of carriers [16–19]. For example, as the photon-generated electrons pass the CZTS/CdS interface, the conduction band alignment at this interface is particularly crucial [20, 21]. However, there are still some conflicting reports on band offset at the interface of CZTS/CdS and CdS/ZnO heterojunctions. Nagoya et al calculated the band offset of a CZTS/CdS interface using first-principles calculations and found that it is a type-II band alignment [21]. However, experimentally, the type-I band alignment at a CZTS/CdS interface has been reported by using ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) methods, in which the conduction band minimum (CBM) of CZTS is lower than that of CdS [22, 23]. Nevertheless, Li et al recently found that the CBM of CZTS is higher than that of CdS by using synchrotron radiation photoemission spectroscopy (SRPES), which is a type-II band alignment [24]. Furthermore, the interface between buffer layer and window layer, CdS/ZnO, is also an important factor to impact carrier transport. Therefore, for the sake of further optimization of efficiency, it is necessary to better understand the CZTS/CdS and CdS/ZnO heterojunction interface characteristics in CZTS-based solar cells.

In this work, the conduction-band offsets (CBOs) of CZTS/CdS and CdS/ZnO interfaces are determined by combining both XPS and optical absorption spectroscopy. The results are well supported by first-principles calculations based on hybrid functional methods.

2. Experiment and first-principles calculations

The thick CZTS, CdS and ZnO thin films were deposited on soda-lime glass (SLG) substrates using pure argon as the working gas by using the rf magnetron sputtering technique. Commercial available high-purity Cu₂ZnSnS₄ and CdS targets (purity > 99.95%) with stoichiometric proportions were used in our experiments. A ZnO target was prepared by sintering a mixture of 99.99% pure ZnO powder at 1000 °C for 10 h in air ambient. The vacuum chamber was evacuated to a base pressure of 10⁻⁴ Pa prior to deposition and the sputtering pressure for CZTS, CdS and ZnO were controlled to 0.1 Pa, 1 Pa and 1 Pa, respectively. For removing oxide layer and impurities on the surface of the CZTS target, the CZTS target was pre-sputtered by Ar gas for 5 min before the CZTS layer was deposited on the substrate. During the whole deposition process, the substrate temperature was fixed at 500 °C and the growth time was 2 h. The thicknesses of the three thick films were estimated to be in the range of 800–1200 nm. For the CdS/CZTS and CdS/ZnO heterojunctions, thin CdS films with a thickness of ~5 nm were deposited on the thick CZTS and ZnO films, respectively, for 20 s using the same growth conditions as the thick CdS films. Energy dispersive x-ray spectroscopy (EDS) measurement was performed for analysing the element ratio in the deposited CZTS film. The element contents for Cu, Zn, Sn and S are 21.7%, 14.7%, 13.4% and 50.2%, respectively, indicating that the CZTS film is Cu-poor and Zn-rich as well as metals/S being equal approximately to 1.

The crystal structures characterization was performed by using x-ray diffraction (XRD) with Cu Kα radiation of 0.15406 nm. The XPS measurements were carried out by using an ESCALAB 250 XPS instrument with an Al Kα (hv = 1486.6 eV) x-ray radiation source and all XPS spectra were calibrated by the C1s peak (284.6 eV). A UV–visible spectrophotometer was used to record the optical absorption spectra of these films.

To better understand the band alignments from XPS measurements, the first-principles calculations were performed using the plane-wave projector-augmented wave (PAW) method [25, 26] applying the semilocal Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [27] and the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional [28] as implemented in the VASP code [29, 30]. We constructed five structures: bulk CZTS, CdS, ZnO and CZTS/CdS as well as CdS/ZnO superlattices for calculating the valence-band offsets (VBOs) of the interfaces. Here we adopted the average electrostatic potential (AEP) as the core level (CL) to align the valence band [31]. The bulk CZTS, CdS and ZnO were first calculated separately to determine the VBM with respect to the corresponding AEP in the bulk, then 1 × 1 × 4 CZTS[0 0 1]/CdS[1 1 1] and CdS[1 1 1]/ZnO[1 1 1] superlattices were constructed and the EᵥBᵥ offset on both sides were extracted. It is noted that the zinc-blende (ZB) ZnO is adopted for matching the crystal structure of CdS. We expect that the results from the ZB ZnO are also applicable for the wurtzite (WZ) ones because some previous reports have indicated that some properties in ZB and WZ are quite similar [32–34]. In the calculation, the cutoff energy for the plane-wave basis set is 500 eV. The atoms are allowed to relax until the Hellmann–Feynman forces acting on them become smaller than 0.01 eV Å⁻¹.

3. Methods

In this work, the VBOs of CZTS/CdS and CdS/ZnO heterojunctions were first measured by XPS, it is often used experimentally to probe core states and hence provide a reference to align the valence-band maximum (VBM) of two systems [35]. Then bandgaps of CZTS, CdS, ZnO films were determined by optical absorption spectroscopy. Finally, the CBO is also determined by the VBO and bandgap. The VBO of CZTS/CdS can be calculated by the following formula [36]:

\[ \Delta E_v = \Delta E_{CL} + (E_{VBM}^{CdS} - E_{VBM}^{CdS}) - (E_{VBM}^{CZTS} - E_{VBM}^{CZTS}) \] (1)
grown on SLG substrates. and CZTS films deposited on SLG substrates. For the three

Figure 1 illustrates the typical XRD patterns of the ZnO, CdS and (c) CZTS films grown on SLG substrates.

where \( E_{\text{CdS}}^{\text{CdS}} - E_{\text{VBM}}^{\text{CdS}} \) is the energy difference between Cd 3d and VBM in the CdS thin film, and the \( E_{\text{CZTS}}^{\text{CZTS}} - E_{\text{VBM}}^{\text{CZTS}} \) is the energy difference between Sn 3d and VBM in the CZTS thin film. While

\[
\Delta E_{\text{CL}} = E_{\text{CdS}}^{\text{CdS}} - E_{\text{VBM}}^{\text{CdS}} - E_{\text{CZTS}}^{\text{CZTS}} / \Delta E_{1}\text{eV}
\]

is the energy difference between CZTS and CdS CLs in the CZTS/CdS heterojunction. The CBO can be calculated by the following,

\[
\Delta E_{\text{C}} = E_{\text{g}}^{\text{CZTS}} - E_{\text{g}}^{\text{CdS}} - \Delta E_{\text{V}}.
\]

Similarly, the VBO of CdS/ZnO heterojunction can be also calculated by

\[
\Delta E_{\text{V}} = \Delta E_{\text{CL}} + (E_{\text{CdS}}^{\text{CdS}} - E_{\text{VBM}}^{\text{CdS}}) - (E_{\text{ZnO}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}}).
\]

\( E_{\text{CdS}}^{\text{CdS}} - E_{\text{VBM}}^{\text{CdS}} \) is the energy difference between Cd 3d and VBM in the CdS, \( E_{\text{ZnO}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}} \) is the energy difference between Zn 2p and VBM in the ZnO and while

\[
\Delta E_{\text{CL}} = E_{\text{ZnO}}^{\text{ZnO}} / \Delta E_{1}\text{eV}
\]

is the energy difference between CdS and ZnO CLs in the CdS/ZnO heterojunction.

\[
\Delta E_{\text{C}} = E_{\text{g}}^{\text{ZnO}} - E_{\text{g}}^{\text{CdS}} - \Delta E_{\text{V}}.
\]

For the first-principles calculations of band offset, we adopted the AEP as the referenced CL to align the valence band. To calculate the CBO, the experimental bandgaps are used because the first-principles usually underestimate them, even though the hybrid functional method is used here.

4. Results and discussion

Figure 1 illustrates the typical XRD patterns of the ZnO, CdS and CZTS films deposited on SLG substrates. For the three films, no extra phases of other compounds were observed, indicating that the three films are all single phase under the optimal deposition conditions.

To determine VB states, we first measured VB spectra of the thick CZTS, CdS and ZnO films, as shown in figure 2. The valence-band edges are determined to be 0.47 ± 0.1 eV, 1.50 ± 0.1 eV and 2.20 ± 0.1 eV for CZTS, CdS and ZnO films, respectively, by linear extrapolation of the leading edge to the extended baseline. To determine the VBO of the CdS/CZTS heterojunction, the CLs of the thick CZTS and CdS films, as well as the CdS/CZTS heterojunction, were measured as reference levels. Figures 3(a)–(d) show the CLs of Cd 3d and Sn 3d in the thick CdS and CZTS films, as well as in the CdS/CZTS heterojunction, respectively. The peaks of Cd 3d \( \frac{1}{2} \) and Sn 3d \( \frac{1}{2} \) in the CdS and CZTS films are located at 404.98 ± 0.05 eV and 486.36 ± 0.05 eV, respectively. Compared with the spectra recorded on the CdS and CZTS films, the CdS 3d \( \frac{1}{2} \) peak in CdS/CZTS shifts to a binding energy of 405.11 ± 0.05 eV, and the Sn 3d \( \frac{1}{2} \) peak shifts to 486.46 ± 0.05 eV, respectively. According to equation (1), the VBO of the CdS/CZTS interface is determined to be 1.06 ± 0.1 eV. The VBO of the CdS/ZnO heterojunction is also determined by the same method. Figures 4(a)–(d) show the CLs of Cd 3d and Zn 2p in the thick CdS and ZnO films, as well as in the CdS/ZnO heterojunction, respectively. According to equation (4), the VBO of the CdS/ZnO interface is determined to be 1.86 ± 0.1 eV.

In order to determine the CBO of the CdS/CZTS and CdS/ZnO heterojunctions, the bandgaps of the CZTS, CdS and ZnO films are determined by the optical absorption spectra. Figure 5 shows the optical absorption spectra of the CZTS, CdS and ZnO films. The bandgaps \( (E_g) \) can be determined by

\[
\alpha(h\nu) = A(h\nu - E_g)^{\frac{1}{2}},
\]

where \( \alpha \), \( h\nu \) and \( A \) are absorption coefficient, photon energy and a constant, respectively. Thus, the bandgaps of the CZTS, CdS and ZnO films were estimated to be about 1.50 eV, 2.43 eV and 3.29 eV, respectively, which is good agreement with previous reports [37–42]. According to
equation (3), the CBO of the CdS/CZTS interface is determined to be 0.13 ± 0.1 eV, and the CBM of CZTS is higher than that of CdS, indicating a type-II alignment at the interface CdS/CZTS heterojunction. Similarly, according to equation (6), the CBO of the CdS/ZnO interface is determined to be 1.00 ± 0.1 eV, and the CBM of CdS is higher than that of ZnO, also indicating a type-II alignment at the interface CdS/ZnO heterojunction. The schematic diagram of band alignment of a CZTS/CdS/ZnO heterojunction is shown in figure 6.

At the interface of the CZTS/CdS heterojunction, the electron–hole pairs excited by photons are easy to separate, and the electrons easily cross the interfaces of CZTS/CdS and CdS/ZnO heterojunctions. However, the narrower ‘interface bandgap’ between the CBM of CdS and the VBM of CZTS increases the recombination due to type-II band alignment, which leads to low open circuit voltage and small fill factor [43]. Therefore, the CZTS/CdS interface with type-II band alignment is unsuitable for improving the efficiency of solar cells.

To better understand the band alignments at the interfaces of CZTS/CdS and CdS/ZnO heterojunctions, we calculated electronic structure and VBO of CZTS/CdS and CdS/ZnO based on the first-principles method. The detailed calculation method and configuration are described in the sections 2 and 3, respectively. To calculate the VBO of CZTS/CdS and CdS/ZnO interface, we constructed CZTS/CdS and CdS/ZnO superlattices, as shown in figure 7. The calculated VBOs are 0.98 and 1.15 eV for the CZTS/CdS and CdS/ZnO interfaces, respectively. The experimental bandgaps of CZTS, CdS and ZnO are used to determine the CBO at the CZTS/CdS and CdS/ZnO interfaces because the bandgap is generally underestimated for the first-principles calculations, even
Figure 6. Schematic diagram of band alignment of a CZTS/CdS/ZnO heterojunction determined by XPS (energy unit in eV).

Figure 7. Supercells of the (a) CZTS/CdS and (b) ZnO/CdS superlattices.

through the hybrid functional method is used here. The calculated CBOs are 0.05 eV and 0.29 eV for the CZTS/CdS and CdS/ZnO interfaces, respectively. The schematic diagram of the calculated band alignment of a CZTS/CdS/ZnO heterojunction is shown in figure 8, indicating also the II-type alignment at both CZTS/CdS and CdS/ZnO interfaces. The calculated results support our experimental results.

5. Conclusions

In conclusion, we have presented an experimental and first-principles study on the band alignment of the CZTS/CdS/ZnO heterojunction. Both CZTS/CdS and CdS/ZnO interfaces possess type-II alignment, which is well supported by first-principles calculations based on hybrid functional method. Our results suggest that, although type-II alignment for a CZTS/CdS heterojunction can form less of a barrier to electron transport across the interfaces, the narrowing of the ‘interface bandgap’ increases the recombination of carriers.

Figure 8. Schematic diagram of band alignment of a CZTS/CdS/ZnO heterojunction determined by hybrid functional first-principles calculations (energy unit in eV).

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grant Nos 10874178, 11074093, 61205038 and 11274135, the National Science Foundation of Jilin Province under Grant No 201115013 and the National Fund for Fostering Talents of Basic Science under Grant No J1103202. This work was supported by the High Performance Computing Center of Jilin University, China.

References

[16] Li Y et al 2008 Appl. Phys. Lett. 92 192116
[40] Li Y F et al 2007 Appl. Phys. Lett. 91 021915