Band offsets engineering at $Cd_xZn_{1-x}S/Cu_2ZnSnS_4$ heterointerface*

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(Received 5 June 2016; revised manuscript received 6 September 2016; published online 25 October 2016)

$Cd_{1-x}Zn_xS/Cu_2ZnSnS_4$ (CZTS)-based thin film solar cells usually use CdS as a buffer layer, but due to its smaller band gap (2.4 eV), CdS film has been replaced with higher band gap materials. The cadmium zinc sulfide (CdZnS) ternary compound has a higher band gap than other compounds, which leads to a decrease in window absorption loss. In this paper, the band offsets at $Cd_{1-x}Zn_xS/Cu_2ZnSnS_4$ (CZTS) heterointerface are calculated by the first-principles, density-functional and pseudopotential method. The band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerface are tuned by controlling the composition of Zn in $Cd_{1-x}Zn_xS$ alloy, the calculated valence band offsets are small, which is consistent with the common-anion rule. The favorable heterointerface of type-I with a moderate barrier height (< 0.3 eV) can be obtained by controlling the composition of Zn in $Cd_{1-x}Zn_xS$ alloy between 0.25 and 0.375.

Keywords: band offset, first-principles calculation, $Cd_{1-x}Zn_xS$, heterointerface

PACS: 71.20.–b, 73.40.–c, 71.55.Gs **DOI:** 10.1088/1674-1056/25/12/127102

1. Introduction

Cu_2ZnSnS_4 (CZTS) solar cell material has an ideal band gap ($E_g = 1.5$ eV) and high absorption coefficient.[1,2] As a possible alternative to the commercially available Cu(In, Ga)Se_2 (CIGS), CZTS does not contain indium or gallium. Therefore, it could be a cheaper and more sustainable solar cell material in the future. Recently, a conversion efficiency of 12.6% for selenium containing CZTS[3] has been reported. However more research is needed to understand what prevents the devices from reaching as high efficiency as that of CIGS, which has record efficiency over 20%.[4] As is well known, CZTS-based thin film solar cells usually employ CdS as a buffer layer. However, the development of CdS/CZTS thin film solar cells is restrained by its smaller band gap (2.4 eV). One of the reasons is an unfavorable alignment of the conduction band minimum (CBM) at the CdS/CZTS heterointerface, where CBM of CdS is lower than that of CZTS.[5] This interface leads to an increase in interface recombination and a loss in open circuit voltage, V_{oc}.

Cadmium zinc sulfide (CdZnS) ternary compound has a higher band gap, which leads to a decrease in window absorption loss and thus an increase in the short-circuit current. CdZnS is potentially useful as a window material for p–n junctions without lattice mismatch in the device based on quaternary material like $CuIn_xGa_{1-x}Se_2$ or $CuIn(S_zSe_{1-z})_2$.[6] ZnCdS has a variable band gap energy of 2.4 eV–3.7 eV, primarily dependent on a relative ratio of Cd to Zn.[7–10] The optimum conduction band alignment for CZTS should lie between the CdS and ZnS values. It has been reported that the pure CdS is expected to give a negative conduction band offset with CZTS,[11,12] and ZnS should cause the current to block due to a high barrier. Irvine *et al.* noted that the control of the alloying of ternary $Cd_{1-x}Zn_xS$ and keeping the thickness of the CdS window layer constant can cause the band gap to broaden.[13]

As is well known, the band offset at buffer-absorber interface is one of the most important parameters, which is often used to assess some important interface effects, i.e., quantum confinement and carrier transport, in particular, for the design of solar cells and other optoelectronic devices. There are numerous reports on the electrical and optical properties influenced by Zn substitution in CdZnS material.[14–18] The increasing of Zn composition in $Cd_{1-x}Zn_xS$ will enlarge the band gap, therefore, $Cd_{1-x}Zn_xS$ should lead to an increase of quantum efficiency (QE) in the shorter wavelength regime and also lead to favorable conduction band offset with CZTS. In this paper, we study the effects of Zn composition on the photovoltaic performance by calculating the band offsets for CdZnS/CZTS heterointerface with different Zn compositions. By changing the constituents of $Cd_{1-x}Zn_xS$, the moderate barrier height at the $Cd_{1-x}Zn_xS$/CZTS heterointerface is obtained.

2. Calculation

Alloying is a good approach to performing band-gap engineering to extend the available band gap. In bulk $Cd_{1-x}Zn_xS$ alloyed crystal, its composition (x)-dependent band gap en-

*Project supported by the Special Funds of the National Natural Science Foundation of China (Grant Nos. 11547226 and 11547180).
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ergy $E_g(x)$ can be expressed by Vegard's law[19]

$$E_g(x) = xE_g(\mathrm{ZnS}) + (1-x)E_g(\mathrm{CdS}) - bx(1-x), \quad (1)$$

where E_g(ZnS) and E_g(CdS) are the band gap energies for bulk ZnS and CdS, respectively, and b is the bowing parameter and has a value 0.61.[19,20]

The calculation of density of states (DOS) was performed on the basis of the first-principles, density-functional and pseudopotential method by using the PHASE code developed by Institute of Industrial Science, University Tokyo.[21] We used the generalized gradient approximation (GGA) for the exchange-correlation interaction,[22] with valence electron configurations of S ($3s^2$, $3p^4$), Cu ($3d^{10}$, $4s^1$), Zn ($3d^{10}$, $4s^2$), Cd ($4d^{10}$, $5s^2$) and Sn ($4d^{10}$, $5s^2$, $5p^2$). For a given atomic arrangement, the lattice constants and atom positions were optimized to minimize the total energy.

We first obtained the energy level difference between the reference core levels (take the S 3s, Zn 3d, Cd 4d, and Sn 4d as reference core levels in the pseudopotential calculation method) and valence band maximum (VBM), from the band structures of $Cd_{1-x}Zn_xS$ and CZTS. Then, the core level difference was obtained from the band structure of the (001) $Cd_{1-x}Zn_xS$/CZTS superlattice. The valence band offset E_{VBM} and conduction band offset E_{CBM} were obtained as[23,24]

$$\Delta E_v = \Delta E^{\mathrm{CZTS}}_{\mathrm{VBM-core}} - \Delta E^{\mathrm{Cd_{1-x}Zn_xS}}_{\mathrm{VBM-core}} - \Delta E^{\mathrm{Cd_{1-x}Zn_xS/CZTS}}_{\mathrm{Core}}, \quad (2)$$

$$\Delta E_c = \left|\Delta E_g - \Delta E_v\right|, \quad (3)$$

where $\Delta E^{\mathrm{CZTS}}_{\mathrm{VBM-core}}$ $\left(\Delta E^{\mathrm{Cd_{1-x}Zn_xS}}_{\mathrm{VBM-core}}\right)$ is the energy difference between the reference core levels and VBM for the CZTS (CdZnS) bulk, and $\Delta E^{\mathrm{Cd_{1-x}Zn_xS/CZTS}}_{\mathrm{Core}}$ is the difference between core levels in the $Cd_{1-x}Zn_xS$/CZTS supercell. This equation is based on the idea that the energy difference between the core level and VBM in the respective bulk material is conserved in the heterostructure. ΔE_g is the band gap difference between CdZnS and CZTS. For CdZnS/CZTS heterointerface, the lattice parameter of CdZnS is well matched to that of the CZTS layer: the lattice parameters are $a = 0.541$ nm for zinc-blende ZnS, $a = 0.582$ nm for zinc-blende CdS, and $a = 0.551$ nm and $c = 1.123$ nm for kesterite CZTS. Thus, the (001)-face lattice mismatch is smaller than 5.6% (with respect to CZTS) between CdZnS and CZTS layers, the effects of strain caused by lattice mismatch in the CdZnS/CZTS interface are negligible. So, in this work, we assume that the ΔE_g for CdZnS/CZTS is the same as the difference between their bulk energy levels.

3. Results and discussion

3.1. Electronic structures and band gap

The total density of states for zinc-blend structures of ZnS and CdS are calculated as shown in Fig. 1. The zero point energy is taken as VBM. For the ZnS and CdS binary materials, cation d state and anion p state will repeal upward the VBM as shown in Fig. 1, Zn 3d states are shallower than the Cd 4d states. The calculated band gaps are 2.8 eV and 1.2 eV for ZnS and CdS, respectively. These calculated band gaps are smaller than the experimental values of 3.8 eV and 2.4 eV. It is due to the limitation of DFT, but it has less effect on the investigated electronic structure in the present work. As shown in Fig. 1, Cd-d states show two peaks and Zn-d states show a single peak, when a small amount of Zn content exists in $Cd_{1-x}Zn_xS$. The Zn-d states change into two peaks while Cd-d states change into one single peak with the increase of Zn content. It means that the interaction of Zn-d and S-p states will play an important role in VBM nearby, when higher content Zn exists in $Cd_{1-x}Zn_xS$. The calculated band gaps are 1.3, 1.5, and 1.8 for $Cd_{1-x}Zn_xS$ with the composition x values of 0.25, 0.5, and 0.75, respectively. As the Zn content increases, $Cd_{1-x}Zn_xS$ shifts toward the higher band gap; this trend is consistent with Vegard's law[19] and other investigations.[25]

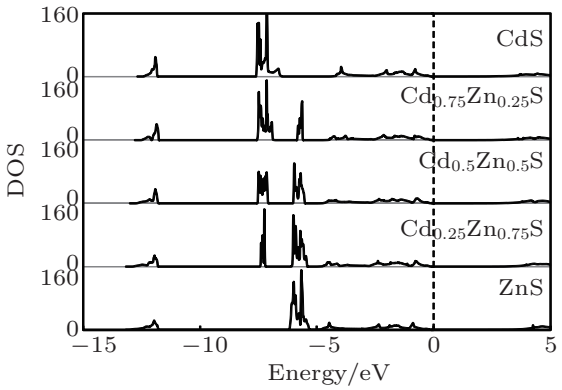


Fig. 1. Densities of states (DOS) for $Cd_{1-x}Zn_xS$ at composition x of 0, 0.25, 0.5, 0.75, and 1.

3.2. Band offsets for $Cd_{1-x}Zn_xS$/CZTS heterointerfaces

The band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces are tuned by controlling the Zn composition (x) in $Cd_{1-x}Zn_xS$ ($x = 0$, 0.125, 0.25, 0.375, 0.5, 0.75, 1) alloy. Since the band gap is generally underestimated in the calculation based on GGA, the band gap energy of $Cd_{1-x}Zn_xS$ as a function of Zn composition (x) is determined using Eq. (1). The calculated values of band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces with different Zn content values are given in Table 1. The minus value means that the VBM (or CBM) of $Cd_{1-x}Zn_xS$ is lower than that of CZTS. The obtained valence band offsets are almost the same, i.e., about -1.0 eV~ -1.3 eV. This result is in consistence with the common-anion rule, where two semiconductors sharing the same anion would have a small valence-band offset.[26] The obtained conduction band offsets are $-0.3 \sim 1.0$ eV, the CBM of $Cd_{1-x}Zn_xS$ increases with the increase of Zn composition in $Cd_{1-x}Zn_xS$ alloy. The conduction band offset becomes plus value when the composition content of Zn is higher than 0.25, that means the type of heterointerface is changed.

Table 1. Calculated band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces with different values of Zn composition (x) in $Cd_{1-x}Zn_xS$ ($x = 0$, 0.125, 0.25, 0.375, 0.5, 0.75, 1).

Composition	Band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces	
x	Valence band offset/eV	Conduction band offset/eV
0	–1.2	–0.3
0.125	–1.2	–0.2
0.25	–1.0	0.1
0.375	–1.0	0.3
0.5	–1.0	0.4
0.75	–1.0	0.8
1	–1.3	1.0

Figure 2 shows the band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces with different Zn content values. The VBM of ZnS is higher than that of CdS, it is due to the Zn 3*d* state being shallower than the Cd 4*d* state. The CBM of $Cd_{1-x}Zn_xS$ is higher than that of CZTS (type-I heterointerface), when the composition content of Zn is higher than 0.25 in $Cd_{1-x}Zn_xS$ alloy, the conduction band offset forms a barrier (spike) for the photoexcited electrons crossing the interface. Height of this barrier is larger than 0.4 eV; when the composition content of Zn is higher than 0.5 in $Cd_{1-x}Zn_xS$ alloy, this will considerably reduce the photocurrent.[27] On the other hand, if the composition content of Zn is smaller than 0.25 in $Cd_{1-x}Zn_xS$ alloy, the barrier against photogenerated electrons is not formed at the heterointerface, but the open-circuit voltage will be reduced by increasing the recombination rate for the majority carriers at the interface. Accordingly, it is generally consistent with the fact that the type-I interface with a moderate barrier height (< 0.3 eV) is the most favorable. Thus, it will obtain higher conversion efficiency by controlling the composition content of Zn in $Cd_{1-x}Zn_xS$ alloy to be between 0.25 and 0.375. Bhattacharya *et al.*[17] reported the 19.52%-efficient CIGS-based solar cells using a single-layer chemical bath deposited CdZnS buffer layer with a compositional ratio of Cd:Zn being 80:20. Song *et al.*[18] experimentally investigated the dependences of $Cd_{1-x}Zn_xS$/CIGS device performance parameters on the Zn content in $Cd_{1-x}Zn_xS$ buffer layers with $x = 0$, 0.1, 0.2, 0.3, 0.4 and reported the higher conversion efficiency with $x = 0.2$ than other Zn content in $Cd_{1-x}Zn_xS$, which is consistent with our prediction.

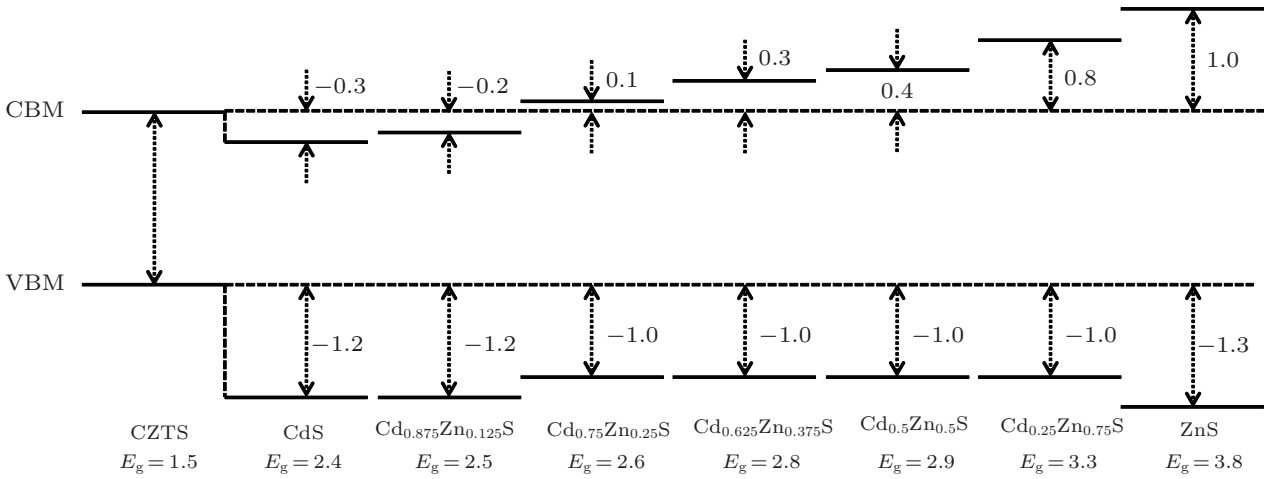


Fig. 2. Band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerfaces with different Zn content values (in unit eV).

4. Conclusions

In the present paper, we calculated the band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerface for different values of x, based on the first-principles, density-functional, and pseudopotential method. The band offsets at $Cd_{1-x}Zn_xS$/CZTS heterointerface are tuned by controlling the composition content of Zn in $Cd_{1-x}Zn_xS$ alloy. $Cd_{1-x}Zn_xS$/CZTS is a type I of heterointerface with a moderate barrier height smaller than 0.3 eV, when the composition content of Zn in $Cd_{1-x}Zn_xS$ alloy is between 0.25 and 0.375.

References

[1] Katagiri H 2005 *Thin Solid Films* **480–481** 426
[2] Shin B, Gunawan O, Zhu Y, Bojarczuk N A, Jay Chey S and Guha S 2013 *Prog. Photovoltaics* **21** 72
[3] Wang W, Winkler M, Gunawan O, Gokmen T, Todorov T, Zhu Y and Mitzi D 2014 *Adv. Energy Mater.* **4** 1301465
[4] Jackson P, Hariskos D, Wuerz R, Kiowski O, Bauer A and Friedlmeier T M 2015 *Phys. Status Solidi* **9** 28
[5] Bär M, Schubert B, Marsen B, Wilks R, Pookpanratana S, Blum M, Krause S, Unold T, Yang W, Weinhardt L, Heske C and Schock H W 2011 *Appl. Phys. Lett.* **99** 222105
[6] Prem Kumar T, Saravana kumar S, Sankaranarayanan K 2011 *Appl. Surf. Sci.* **257** 1923
[7] Al Kuhaimi S A and Tulbah Z 2000 *J. Electrochem. Soc.* **147** 214
[8] Chen P, Nicholls J E, O'Neill M, Stirner T and Hogg J H C 1998 *J. Appl. Phys.* **84** 5621
[9] Dmitrienko A O, Bukesov S A and Mikhailova V V 1993 *Inorg. Mater.* **29** 960
[10] Salem A M 2002 *Appl. Phys. A* **74** 205
[11] Barkhouse D A R, Haight R, Sakai N, Hiroi H, Sugimoto H and Mitzi D B 2012 *Appl. Phys. Lett.* **100** 193904

[12] Nagoya A, Asahi R and Kresse G 2011 *J. Phys.: Condes. Matter* **23** 404203
[13] Irvine S J C, Barrioz V, Lamb D, Jones E W and Rowlands-Jones R L 2008 *J. Cryst. Growth* **310** 5198
[14] Peter A J and Chang W L 2012 *Chin. Phys. B* **21** 087302
[15] Azizi S, Rezagholipour Dizaji H and Ehsani M H 2016 *Optik-International Journal for Light and Electron Optics* **127** 7104
[16] Thahab S M, Omran Alkhayat A H and Saleh S M 2014 *Mater. Sci. Semicond. Process.* **26** 49
[17] Bhattacharya R N, Contreras M A, Egaas B, Noufi R N, Kanevce A and Sites J R 2006 *Appl. Phys. Lett.* **89** 253503
[18] Song J, Li S S, Chen L and Noufi R 2006 *IEEE World Conference on Photovoltaic Energy Conference* **1** 534
[19] Singh J 1996 *Optoelectronics: an introduction to materials and devices* (New Delhi: Macgraw Hill)
[20] Sze S M 1969 *Physics of Semiconductor Devices* (New York: Wiley)
[21] http://www.ciss.iis.u-tokyo.ac.jp/rss21/en/index.html
[22] Perdew J P, Burke K and Ernzerholf M 1996 *Phys. Rev. Lett.* **77** 3865
[23] Nelson A J, Schwerdtfeger C R, Wei S H, Zunger A, Rioux D, Patel R and Hochst H 1993 *Appl. Phys. Lett.* **62** 2557
[24] Wei S H and Zunger A 1993 *Appl. Phys. Lett.* **63** 2549
[25] Wei S H, Ren X, Han Z, Li T, Su Y, Wei L, Cong F and Zhang Y 2013 *Mater. Lett.* **102–103** 94
[26] Wei S H and Zunger A 1988 *Phys. Rev. B* **37** 8958
[27] Minemoto T, Matsui T, Takakura H, Hamakawa Y, Negami T, Hashimoto Y, Uenoyama T and Kitagawa M 2001 *Sol. Energy Mater. Sol. Cells.* **67** 83