Effect of deposited temperatures of the buffer layer on the band offset of CZTS/In_2S_3 heterostructure and its solar cell performance*

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The effect of the deposition temperature of the buffer layer In_2S_3 on the band alignment of CZTS/In_2S_3 heterostructures and the solar cell performance have been investigated. The In_2S_3 films are prepared by thermal evaporation method at temperatures of 30, 100, 150, and 200 °C, respectively. By using x-ray photoelectron spectroscopy (XPS), the valence band offsets (VBO) are determined to be -0.28 ± 0.1, -0.28 ± 0.1, -0.34 ± 0.1, and -0.42 ± 0.1 eV for the CZTS/In_2S_3 heterostructures deposited at 30, 100, 150, and 200 °C, respectively, and the corresponding conduction band offsets (CBO) are found to be 0.3 ± 0.1, 0.41 ± 0.1, 0.22 ± 0.1, and 0.01 ± 0.1 eV, respectively. The XPS study also reveals that interdiffusion of In and Cu occurs at the interface of the heterostructures, which is especially serious at 200 °C leading to large amount of interface defects or the formation of $CuInS_2$ phase at the interface. The CZTS solar cell with the buffer layer In_2S_3 deposited at 150 °C shows the best performance due to the proper CBO value at the heterostructure interface and the improved crystal quality of In_2S_3 film induced by the appropriate deposition temperature. The device prepared at 100 °C presents the poorest performance owing to too high a value of CBO. It is demonstrated that the deposition temperature is a crucial parameter to control the quality of the solar cells.

Keywords: band offset, deposition temperature, CZTS/In_2S_3 heterostructure, solar cell

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1. Introduction

The Cu_2ZnSnS_4 (CZTS) thin film is one of the most promising light absorbing materials which has attracted much research interests recently.[1–4] In highly efficient CZTS solar cells, CdS is usually utilized as a buffer layer.[4–6] However, since Cd is toxic, great effort has been devoted to developing CZTS solar cells with Cd-free buffer layers.[5–7] Being non-toxic, In_2S_3 is a preferable material to replace CdS as a buffer layer.[5,6] Since conduction band alignment between the p-type CZTS and n-type buffer layers is a key factor to influence the device performance, it is of great importance to investigate the band offset of CZTS/In_2S_3 heterostructures.[6] Yan *et al.* investigated the band alignment of different buffer layers, i.e., CdS, Zn(O,S) and In_2S_3 on CZTS, and they found that the conduction band offset (CBO) of In_2S_3/CZTS is spike-like with a value of 0.41 ± 0.10 eV.[6] However, they did not study the influence of the deposition temperature of In_2S_3 on the band offset. Since heat treatment is a common technology widely used in the fabrication of solar cells, which may modify the surface or interface of CZTS/In_2S_3, it is necessary to carry out systematic experiments to study its influence on the band offset or, furthermore, on the performance of solar cells. In our previous work, the band alignment of In_2S_3/CZTS was investigated, but the influence of the growing temperature of In_2S_3 on the band offset was absent.[8] Sio *et al.* investigated the effect of deposition temperature of In_2S_3 on the optical and electrical properties of In_2S_3 thin film and the performance of CZTS/In_2S_3 solar cells.[9] But they did not study the influence of deposition temperature of In_2S_3 on the band offset of In_2S_3/CZTS heterostructures. In this paper, we studied the deposition temperature of buffer layer In_2S_3 on the band offset of In_2S_3/CZTS heterostructures and its solar cell performance. The CZTS/In_2S_3 heterostructures with the buffer layer In_2S_3 grown at 30 (room temperature), 100, 150, and 200 °C were prepared and the band alignments were investigated by x-ray photoelectron spectroscopy (XPS). Besides, the performance of the CZTS photovoltaic device with the buffer layer In_2S_3 grown at different temperatures was presented and discussed.

2. Experiments

In the experiments, four CZTS/In_2S_3 heterostructure samples were prepared. The CZTS thin films with a thickness of 800 nm were fabricated on floating glass (FG) substrates by sol–gel method, followed by sulphurization in an N_2+H_2S

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gas atmosphere (with 5% H_2S concentration) at 580 °C for one hour.[10] The buffer layers In_2S_3 with a thickness of 5 nm were deposited onto the CZTS thin films by thermal evaporation method in DMDE-450 deposition equipment. The substrate temperature during the deposition of In_2S_3 was chosen to be 30 (room temperature), 100, 150, and 200 °C, respectively. In order to make the deposition of such a thin film possible, the substrate and the source material was kept at a far distance of about 22 cm. In order to find out the right amount of source material (In_2S_3 powder) to deposit an In_2S_3 film of 5 nm, 30-, 50-, and 100-mg In_2S_3 powder were used as the source material, respectively, and the corresponding thicknesses of the In_2S_3 films were determined to be 14, 25, and 49 nm by a step profiler (KLA Tencor D-100). Therefore, to deposit an In_2S_3 film with a thickness of 5 nm, 5-mg In_2S_3 powder was used as the source material. Besides, another four In_2S_3 films with a thickness of 400 nm were also prepared by thermal evaporation method, which were deposited on FG substrates at the four temperatures mentioned above, respectively. The transmittance and reflectance spectra were measured by a Cary 5000-Scan UV-vis-NIR Spectrometer in the wavelength range 350 nm–1200 nm. The XPS measurements were carried out using a ThermoFisher Scientific Escalab 250 electron spectrometer with monochromatic Al Kα ($h\nu$) source, and the XPS spectra were calibrated by the C 1s peak (284.6 eV).

To fabricate a complete solar cell, an intrinsic ZnO film of 60 nm and an ITO film of 270 nm were deposited on top of the glass/Mo/CZTS/In_2S_3 (50 nm) stack by sputtering. Then, 100-nm Al metal grids were fabricated by thermal evaporation. The J–V curves of the fabricated CZTS solar cells with the buffer layer In_2S_3 deposited at different temperatures were measured by a solar simulator with an illumination intensity of 100 mW/cm^2 (Oriel 91192, AM1.5, Global).

3. Results and discussion

According to Ref. [11], the valance band offset (VBO) can be calculated using the formula

$$\mathrm{VBO} = E_{\mathrm{VB}}^{\mathrm{CZTS}} - E_{\mathrm{VB}}^{\mathrm{In_2S_3}} + V_{\mathrm{bb}}. \tag{1}$$

Here $E_{\mathrm{VB}}^{\mathrm{CZTS}}$ and $E_{\mathrm{VB}}^{\mathrm{In_2S_3}}$ are the energy positions of the valence band maximum (VBM) of CZTS and In_2S_3 films, and V_{bb} is the band bending determined by the following expression

$$V_{\mathrm{bb}} = (E_{\mathrm{CL}}^{\mathrm{In_2S_3}} - E_{\mathrm{CL}}^{\mathrm{In_2S_3}}(i)) + (E_{\mathrm{CL}}^{\mathrm{CZTS}}(i) - E_{\mathrm{CL}}^{\mathrm{CZTS}}), \tag{2}$$

where $E_{\mathrm{CL}}^{\mathrm{In_2S_3}}$ ($E_{\mathrm{CL}}^{\mathrm{CZTS}}$) is the core-level (CL) energy of a selected element in the bulk material of In_2S_3 (CZTS), and $E_{\mathrm{CL}}^{\mathrm{In_2S_3}}(i)$ ($E_{\mathrm{CL}}^{\mathrm{CZTS}}(i)$) is the core-level energy of the same element at the heterojunction interface. Then the conduction band offset (VBO) can be obtained by

$$\mathrm{CBO} = (E_{\mathrm{g}}^{\mathrm{In_2S_3}} - E_{\mathrm{g}}^{\mathrm{CZTS}}) + \mathrm{VBO}, \tag{3}$$

with $E_{\mathrm{g}}^{\mathrm{In_2S_3}}$ ($E_{\mathrm{g}}^{\mathrm{CZTS}}$) being the energy band gap of In_2S_3 (CZTS). In this study, we assume that the binding energy below the Fermi energy is positive, and thus a negative VBO (CBO) value indicates a lower valance (conduction) band edge in In_2S_3 than that in CZTS. The reference CLs in CZTS can be chosen from Cu, Zn, and Sn, and that in In_2S_3 is adopted to be In. In this work, the final VBO values are determined by averaging the VBO values obtained by using the CL pairs In/Cu, In/Sn, and In/Zn, respectively. Figure 1 shows the valance band spectra of the In_2S_3 and CZTS films, In 3d core-level spectra of the In_2S_3 and CZTS/In_2S_3 (deposited at 150 °C) samples, Zn 2p core-level spectra of the In_2S_3 and CZTS/In_2S_3 (deposited at 150 °C) samples, respectively. The VBM values of CZTS and In_2S_3 are determined to be -0.07 ± 0.1 eV and 0.43 ± 0.1 eV, respectively, by extrapolating the linear edges of the valence band spectra to the baseline, as shown in Fig. 1. The CL positions are obtained by fitting the CL binding energy spectra to Voigt function, a mixed Lorentzian–Gaussian function with a Shirley background, as shown in Fig. 1. The CL positions in the bulk material and heterostructures deposited at different temperatures are shown in Table 1, where the CL positions in bulk material are measured in the materials deposited at room temperature, since the CL positions of bulk material do not change with deposition temperatures for the current investigated temperature range. Substituting the CL energies and the VBM values into Eqs. (1) and (2) and averaging the values obtained by CL pairs In/Cu, In/Sn, and In/Zn, we determine the V_{bb} to be 0.22 ± 0.1, 0.22 ± 0.1, 0.16 ± 0.1, and 0.08 ± 0.1 eV, and VBO values to be -0.28 ± 0.1, -0.28 ± 0.1, -0.34 ± 0.1, and -0.42 ± 0.1 eV for the heterostructures with the buffer layer In_2S_3 deposited at 30, 100, 150, and 200 °C, respectively, as shown in Table 2. The V_{bb} and VBO values of the sample deposited at 30 °C are in good agreement with that reported in Ref. [6] (V_{bb}: 0.2 ± 0.1 eV, VBO: -0.19 ± 0.1 eV) within experimental errors.

The band gap E_{g} of the CZTS and In_2S_3 films deposited at different temperatures are obtained by the transmittance and reflectance spectra by the following equation

$$\alpha(h\nu) = \frac{A(h\nu - E_{\mathrm{g}})^m}{h\nu}, \tag{4}$$

where α is the optical absorption coefficient of the film, A is a constant related to the effective mass, and the value of m indicates different types of transitions, i.e., m = 0.5 stands for allowed direct, 1.5 for forbidden direct, 2 for allowed indirect and 3 for forbidden indirect transitions, respectively. A linear interval cannot be found for the curve of $(\alpha h\nu)^2$ versus

$h\nu$ indicating that the band gap of In_2S_3 investigated here is not direct. However, a good linear interval can be found in the plot of $(\alpha h\nu)^2$ versus $h\nu$, suggesting an indirect band gap of In_2S_3 films. Thus, the band gap of In_2S_3 films deposited at 30, 100, 150, and 200 °C are determined to be 2.03, 2.14, 2.01, and 1.92 eV, respectively. It can be seen that the band gap of In_2S_3 films varies with deposition temperatures. The band gap of CZTS is direct and determined to be 1.45 eV. Then the CBO values are estimated by Eq. (3) to be 0.30 ± 0.1, 0.41 ± 0.1, 0.22 ± 0.1, and 0.01 ± 0.1 eV corresponding to the heterostructures deposited at 30, 100, 150, and 200 °C, respectively, which are also shown in Table 2.

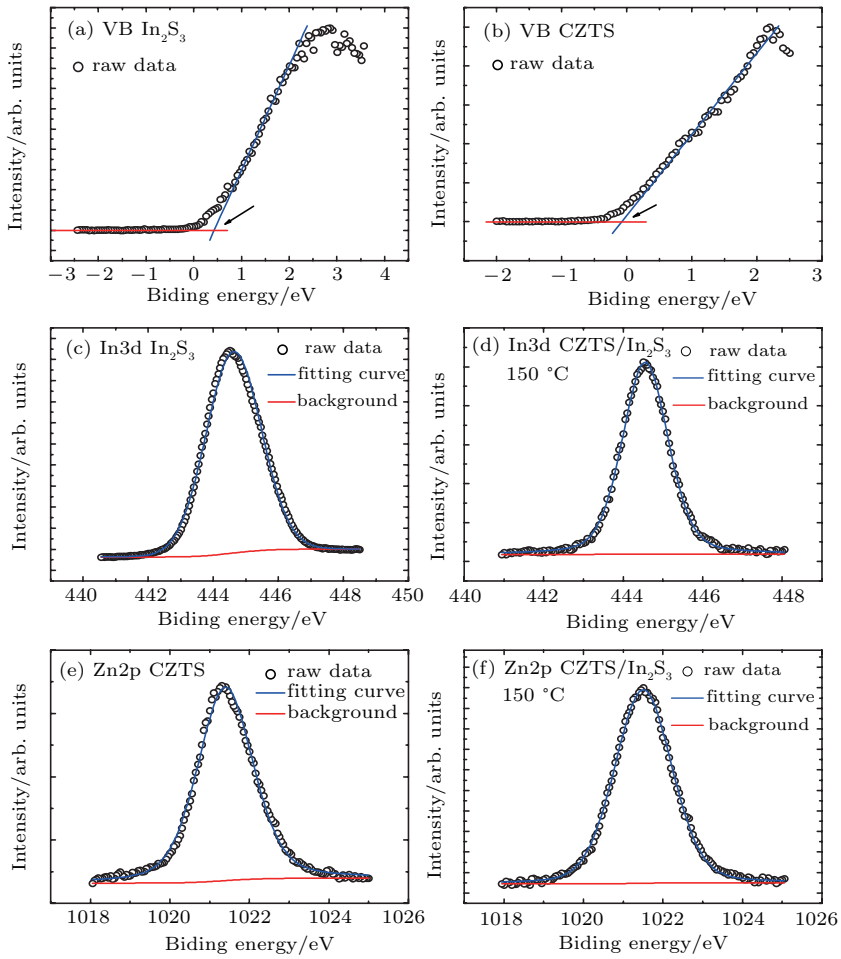


Fig. 1. (color online) Valance band spectra of (a) the In_2S_3 and (b) CZTS film samples, (c) In 3d core-level spectra of the In_2S_3 and (d) CZTS/In_2S_3 (deposited at 150 °C) samples, (e) Zn 2p core-level spectra of the In_2S_3, and (f) CZTS/In_2S_3 (deposited at 150 °C) samples. The VBM positions are determined by extrapolating the linear edges of the VB spectra to the baseline, and the CL spectra are fitted to Voigt function.

Table 1. Core-level energies obtained by the XPS spectra fitting for the bulk In_2S_3, bulk CZTS, and CZTS/In_2S_3 heterostructures deposited at different temperatures.

Sample	E_{CL}^{In3d}/eV	E_{CL}^{Cu2p}/eV	E_{CL}^{Zn2p}/eV	E_{CL}^{Sn3d}/eV
Bulk In_2S_3	444.60 ± 0.05			
Bulk CZTS		931.55 ± 0.05	1021.34 ± 0.05	486.21 ± 0.05
CZTS/In_2S_3 (30 °C)	444.56 ± 0.05	931.51 ± 0.05	1021.61 ± 0.05	486.53 ± 0.05
CZTS/In_2S_3 (100 °C)	444.58 ± 0.05	931.53 ± 0.05	1021.61 ± 0.05	486.56 ± 0.05
CZTS/In_2S_3 (150 °C)	444.57 ± 0.05	931.47 ± 0.05	1021.51 ± 0.05	486.50 ± 0.05
CZTS/In_2S_3 (200 °C)	444.67 ± 0.05	931.58 ± 0.05	1021.47 ± 0.05	486.49 ± 0.05

Table 2. V_{bb} values and the band offsets of the heterostructures deposited at different temperatures.

Samples	V_{bb}/eV	VBO/eV	CBO/eV
CZTS/In_2S_3 (30 °C)	0.22 ± 0.1	-0.28 ± 0.1	0.30 ± 0.1
CZTS/In_2S_3 (100 °C)	0.22 ± 0.1	-0.28 ± 0.1	0.41 ± 0.1
CZTS/In_2S_3 (150 °C)	0.16 ± 0.1	-0.34 ± 0.1	0.22 ± 0.1
CZTS/In_2S_3 (200 °C)	0.08 ± 0.1	-0.42 ± 0.1	0.01 ± 0.1

The CBO can also be easily calculated by using the Anderson model,[12] if electron affinity χ of In_2S_3 and CZTS are known. Electron affinity χ of In_2S_3 and CZTS are estimated to be 4.25 ± 0.3[13] and 4.33 eV,[14] respectively. Therefore, the CBO of In_2S_3/CZTS heterostructures is estimated to be 0.08 ± 0.3 eV, which agrees with that obtained by XPS within the experimental errors.

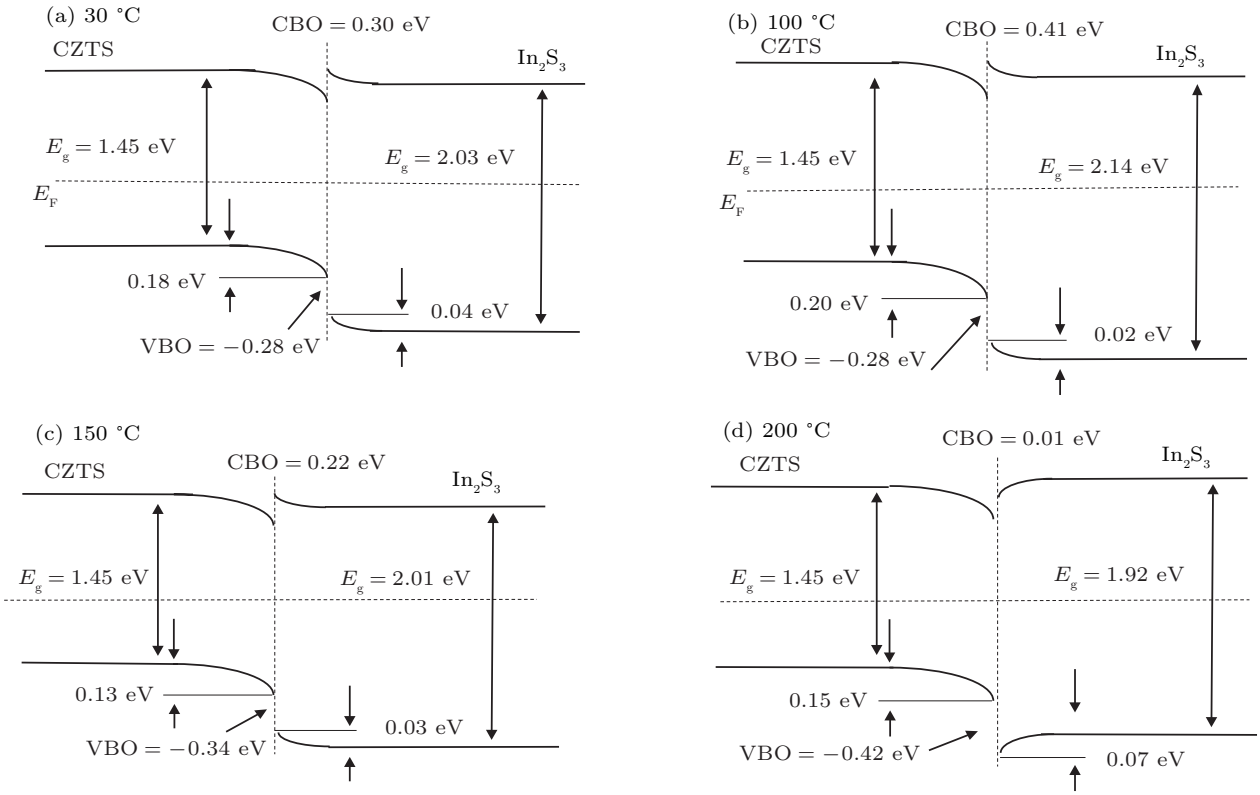


Fig. 2. Band offset diagram for the heterostructures deposited at different temperatures.

With the values of VBO, CBO, and V_{bb} available, the band alignment at the interface of the heterostructures are obtained, whose diagrams are plotted in Fig. 2. The band bendings at the interface on the side of In_2S_3 and CZTS are calculated by the first and second part of Eq. (2), respectively. One can see that the band alignments of the heterostructures belong to 'type I' no matter at which temperature they are deposited. With the increase of the growth temperature, the value of VBO increases and that of CBO decreases. It is worth noting that the band of In_2S_3 deposited at 200 °C bends down at the interface, indicating a large number of interface defects or a p-type compound forming at the interface. In order to figure out the possible impurity at the interface of the heterostructure deposited at 200 °C, we perform the element content analysis of the four heterostructure samples by XPS, and the results are shown in Table 3. It can be seen that, at the interface, the concentration of In element decreases with increasing temperatures (from 13.8 at.% to 6.3 at.%), while that of Cu decreases with increasing temperatures (from 5.8 at.% to 25.4 at.%). The element contents of Sn and Zn do not show significant change with temperatures. Therefore, it is obvious that strong interdiffusion of In and Cu occurs at the interface of CZTS/In_2S_3 heterostructure, which are especially serious at high temperatures. Since there are a lot of cationic vacancies in In_2S_3, it can be easily doped by Cu.[15–17] According to the phase diagram of the Cu–In–S system and considering the high copper concentration in the interface of heterostructure deposited at 200 °C, we infer that a compound of $CuInS_2$ with a p-type conductivity may be formed at the interface, which may lead to the downward bending of the band on the side of In_2S_3 at the interface.

Table 3. Element content at the interface of the heterostructures deposited at different temperatures.

Element	30 °C/at.%	100 °C/at.%	150 °/at.%	200 °C/at.%
In	13.8	10.6	8.6	6.3
Sn	52.3	50.3	47.5	44.2
Cu	5.8	9.5	15.7	25.4
Zn	28.1	29.6	28.2	24.2

In order to investigate the influence of the deposition temperature of the buffer layer as well as the band alignments of the heterostructures on the device performance, the CZTS solar cells with the buffer In_2S_3 deposited at temperatures of 30, 100, 150, and 200 °C, named as samples A, B, C, and D, respectively, are prepared. *J*–*V* curves of the devices are shown in Fig. 3 and the detailed parameters of the devices are also summarized in Table 4. From Table 4, one can see the short circuit current J_{sc} of sample A is nearly equal to that of sample C, but the open circuit voltage V_{oc} of sample C is higher than that of sample A, leading to a higher conversion efficiency. The performance of the solar cell may be closely related to the band alignment of the heterostructure. According to the simulation

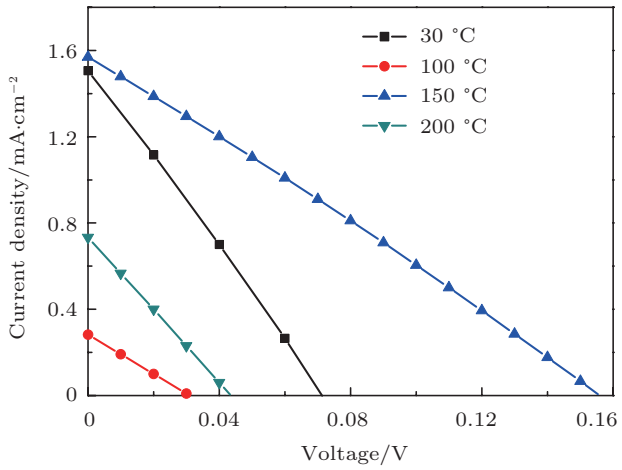


Fig. 3. (color online) J–V measurements of the solar cells with the buffer layer deposited at different temperatures under AM1.5 solar illumination conditions.

Table 4. Performance characteristics of the solar cells with the buffer layer deposited at 30 (room temperature), 100, 150, and 200 °C, respectively.

Sample	J_{sc}/(mA/cm^2)	V_{oc}/mV	FF	η_e/%
Sample A (30 °C)	6.04	80	0.23	0.11
Sample B (100 °C)	1.12	30	0.24	0.01
Sample C (150 °C)	6.28	160	0.26	0.26
Sample D (200 °C)	2.92	40	0.27	0.03

by Minemoto *et al.*,[18] when the CBO value is larger than 0 eV, V_{oc} should be nearly constant. Thus, the V_{oc} values of samples A and C are expected to be nearly equal since their CBO values are all larger than 0 eV. However, the V_{oc} of sample C is much larger than that of sample A. The possible reason for this phenomenon may be attributed to the suppression of the defects, which will cause undesirable recombination, by the appropriate deposition temperature (150 °C). Specifically speaking, when the growth temperature of In_2S_3 is increased to 150 °C, much of the water vapor and other impurities will leave the substrate surface and, moreover, the In_2S_3 particles just arriving at the substrate surface will get more kinetic energy to get together to form a much denser film. As a result, the interface defects are dramatically reduced, leading to the increase of V_{oc}. One can note that sample B presents the poorest performance, which can be owing to the large value of CBO (0.41 ± 0.1 eV). This CBO value is much larger than the optimal value of being in the range of 0 eV–0.3 eV,[5] and it will act as a barrier against the photo-generated electrons, leading to the extremely small value of J_{sc}.[18] When the deposition temperature is increased up to 200 °C, the performance of the device is also not good, although its CBO value (0.01 ± 0.1 eV) is within the optimal range. This phenomenon may be attributed to the large amount of interface defects or the formation of $CuInS_2$ compound at the interface induced by the high deposition temperature, as we mentioned above. Specifically, acting as a recombination center, interface defects will greatly reduce J_{sc}, and, due to the p-type conductivity of $CuInS_2$, its formation will degrade the quality of the heterostructure resulting in poor performance of the solar cell. A similar effect is also observed in Cu(In,Ga)Se_2 solar cells buffered with In_2S_3,[17] i.e., the solar cell efficiency is dramatically decreased when the deposition temperature is increased from 130 °C to 200 °C, which is possibly due to the formation of the p-type $CuInS_2$ compound at the heterostructure interface. It can be seen that the deposition temperature of the buffer layer has a significant influence on the performance of the solar cell.

4. Conclusion

In summary, we have studied the influence of the deposition temperature of the buffer layer on the band alignment of CZTS/In_2S_3 heterostructures. It is found that the VBO values are -0.28 ± 0.1, -0.28 ± 0.1, -0.34 ± 0.1, and -0.42 ± 0.1 eV for the deposition temperature of 30, 100, 150, and 200 °C, respectively, and the corresponding CBO values are 0.3 ± 0.1, 0.41 ± 0.1, 0.22 ± 0.1, and 0.01 ± 0.1 eV, respectively. By XPS analysis, we find that a strong inter-diffusion of In and Cu occurs when the deposition temperature is increased up to 200 °C, which results in plenty of interface defects or the formation of $CuInS_2$ phase at the interface leading to the degradation of the heterostructure. The performance of the CZTS solar cell buffered with In_2S_3 deposited at different temperatures is also investigated. The best performance is obtained in the device deposited at 150 °C, due to the proper CBO value at the heterostructure interface and the improved crystal quality of In_2S_3 film induced by the appropriate deposition temperature. The device prepared at 100 °C shows the poorest performance owing to too high a value of CBO. The performance of devices grown at room temperature and at 200 °C are also not desirable, which may be attributed to the large amount of defects introduced by too low or too high deposition temperatures, respectively. The formation of $CuInS_2$ phase at the interface may also be responsible for the poor performance of the solar cell prepared at 200 °C. Our study demonstrates that the deposition temperature is a crucial parameter to influence the quality of solar cells.

References

[1] Guo Q J, Hillhouse H W and Agrawal R 2014 *J. Am. Chem. Soc.* **131** 11672
[2] Katagiri H, Jimbo K, Maw W S, Oishi K, Yamazaki M, Araki H and Takeuchi A 2009 *Thin Solid Films* **517** 2455
[3] Paier J, Asahi R, Nagoya A and Kresse G 2009 *Phys. Rev. B* **79** 115126
[4] Santoni A, Biccari F, Malerba C, Valentini M, Chierchia R and Mittiga A 2013 *J. Phys. D: Appl. Phys.* **46** 175101
[5] Barkhouse D A R, Haight R, Sakai N, Hiroi H, Sugimoto H and Mitzi D B 2012 *Appl. Phys. Lett.* **100** 193904

[6] Yan C, Liu F Y, Song N, Ng B K, Stride J A, Tadich A and Hao X J 2014 *Appl. Phys. Lett.* **104** 173901
[7] Rajeshmon V G, Poornima N, Kartha C S and Vijayakumar K P 2013 *J. Alloys Compd.* **553** 239
[8] Lin L Y, Yu J L, Cheng S Y, Lu P M, Lai Y F, Lin S L and Zhao P Y 2014 *Appl. Phys. A-Mater. Sci. Process.* **116** 2173
[9] Siol S, Dhakal T P, Gudavalli G S, Rajbhandari P P, DeHart C, Baranowski L L and Zakutayev A 2016 *ACS Appl. Mater. Interfaces* **8** 14004
[10] Long B, Shuying Cheng S Y, Qiao Zheng Q, Jinling Yu J L and Hongjie Jia H J 2016 *Mater. Res. Bull.* **73** 140
[11] Kraut E A, Grant R W, Waldrop J W and Kowalczyk S P 1980 *Phys. Rev. Lett.* **44** 1620
[12] Anderson R L 1962 *Solid State Electron.* **5** 341
[13] Bernede J C, Barreau N, Marsillac S and Assmann L 2002 *Appl. Surf. Sci.* **195** 222
[14] Zhou X, Meng W, Dong C, Liu C, Qiu Z, Qi J, Chen J and Wang M 2015 *RSC Adv.* **5** 90217
[15] Barreau N 2009 *Sol. Energy* **83** 363
[16] Zheng Z M, Yu J L, Cheng S Y, Lai Y F, Zheng Q and Pan D M 2016 *J. Mater. Sci.* **27** 5810
[17] Gall S, Barreau N, Harel S, Bernede J C and Kessler J 2005 *Thin Solid Films* **480** 138
[18] 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