Promising Cd-free double buffer layer in CZTSSe thin film solar cells

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ABSTRACT Zn(O,S) film is widely used as a Cd-free buffer layer for kesterite thin film solar cells due to its low-cost and eco-friendly characteristics. However, the low carrier concentration and conductivity of Zn(O,S) will deteriorate the device performance. In this work, an additional buffer layer of In₂S₃ is introduced to modify the properties of the Zn(O,S) layer as well as the CZTSSe layer via a post-annealing treatment. The carrier concentrations of both the Zn(O,S) and CZTSSe layers are increased, which facilitates the carrier separation and increases the open circuit voltage (V_{OC}). It is also found that ammonia etching treatment can remove the contamination and reduce the interface defects, and there is an increase of the surface roughness of the In₂S₃ layer, which works as an antireflection layer. Consequently, the efficiency of the CZTSSe solar cells is improved by 24% after the annealing and etching treatments. Simulation and experimental results show that a large band offset of the In₂S₃ layer and defect energy levels in the Zn(O,S) layer are the main properties limiting the fill factor and efficiency of these CZTSSe devices. This study affords a new perspective for the carrier concentration enhancement of the absorber and buffer layers by In-doping, and it also indicates that In₂S₃/Zn(O,S) is a promising Cd-free hybrid buffer layer for high-efficiency kesterite solar cells.

Keywords: double buffer layer, CZTSSe, In-doping, band offset

INTRODUCTION

In recent years, Cu₂ZnSn(S,Se)₄ (CZTSSe) has been regarded as a promising absorber material due to its merits and promising photovoltaic performance compared with that of Cu(In,Ga)Se₂ (CIGS) [1–6]. To date, over-11%-efficient CZTSSe solar cells using CdS layer as the buffer

layer have been reported [7–9]. The application of a CdS buffer layer in CZTSSe solar cells enables good efficiency due to the appropriate conduction band offset (CBO) at the CdS and CZTSSe heterojunction [10,11]. However, the toxic and hazardous cadmium in CdS buffer layers remains a serious problem [12].

To solve this problem, Cd-free buffer layers, such as (Zn,Mg)O, Zn(O,S), and Zn_{1-x}Sn_xO (ZTO), have been proposed to replace the CdS layer [13–15]. Among those Cd-free buffer layers, the Zn(O,S) buffer layer has been widely studied due to its controllable bandgap, low-cost, and low-toxicity characteristics. Recently, many groups have demonstrated over-5% CZTSSe solar cells using Zn(O,S) as a buffer layer [16,17]. Neuschitzer *et al.* [18] reported a 6.5%-efficient CZTSe solar cell with a 10-nm-thick Zn(O,S) buffer layer by adjusting the sulfur content in the Zn(O,S) buffer layer. However, making an excessively thin Zn(O,S) buffer layer with uniform coverage remains an unsolved problem. In order to improve the coverage of the Zn(O,S) buffer layer at the junction interface, our group [19] reported a 7.2%-efficient CZTSSe solar cell with 25-nm-thick Zn(O,S) as the buffer layer (with an anti-reflectivity layer). The CZTSSe solar cell with a Zn(O,S) buffer layer has good performance, but the low carrier concentration and low conductivity of the Zn(O,S) layer can increase the contact resistance and reduce the carrier collection efficiency, and thus the performance of the device is deteriorated [20,21]. Therefore, it is necessary to find a way to increase the carrier concentration and conductivity of the Zn(O,S) layer.

Herein, we deposited a thin In₂S₃ layer on Zn(O,S)/CZTSSe/Mo. After annealing at low temperature, the

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buffer layer was etched by concentrated ammonia. It is found that indium diffuses into the Zn(O,S) layer as well as the CZTSSe layer during the annealing treatment, which increased the carrier concentration of both the absorber and buffer layers. The concentrated ammonia can remove the contaminants at the interface and enhance the light absorption by increasing the surface roughness of the In_2S_3 layer. After the treatments, both the open circuit voltage (V_{OC}) and short-circuit current density (J_{SC}) of CZTSSe solar cells were improved, and, as a result, the efficiency of the CZTSSe solar cells was improved by 24%. Subsequently, simulation was employed to understand the limitations of $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ solar cell efficiency taking into account the interface between In_2S_3 and Zn(O,S).

EXPERIMENTAL SECTION

Preparation of films and solar cells

CZTSSe absorbers were fabricated by sol-gel and then a selenization process. The detailed fabrication process was described in Ref. [22]. Next, the Zn(O,S) layers were deposited on the CZTSSe absorbers using the chemical bath deposition (CBD). The preparation process of the Zn(O,S) was described in Ref. [21]. The In_2S_3 layers were spin-coated onto the samples at 2000 r min^{-1} for 20 s and then dried. The In_2S_3 solution was prepared by dissolving 1.1 g In_2S_3 and 0.38 g thiourea into 10 mL 2-methoxyethanol (AR). The In_2S_3 layers underwent the optimal annealing treatment in Ar atmosphere at 280°C for 5 min. Subsequently, the samples were etched by 25%–28% concentrated ammonia for 5 min followed by rinsing in deionized (DI) water. The CZTSSe solar cell fabrication was finished with the sputtering of a 500-nm ZnO:Al layer and evaporated Ni/Al grid contacts. The active area of each CZTSSe solar cell was 0.34 cm^2 .

Characterization

A PANalytical X'Pert PRO X-ray diffractometer (XRD) was used to measure the crystal structures with Cu K α as the radiation source. The morphologies of the films were measured using a Hitachi S-4800 scanning electron microscope (SEM). Atomic force microscope (AFM) on a Dimension Icon (Bruker) was used to measure the surface morphology and roughness of these films over an area of $25 \mu\text{m}^2$. The current density-voltage (J - V) characteristics of the solar cells were measured under a solar simulator at room temperature (RT) with the illumination intensity of 1000 W m^{-2} and the standard AM 1.5 spectrum. The surface chemical compositions of the films were char-

acterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) with Al K α as the X-ray source. Raman measurement was performed to characterize the surface phases of the films with an excitation wavelength of 514 nm. The carrier density profiles of these solar cells were measured by the capacitance-voltage (C - V) technique with a 100-kHz alternating current (AC) excitation source and a direct current (DC) bias from 0.5 to -1 V . A chopped white light source was used to measure the external quantum efficiency (EQE) spectra on a system calibrated using a certified Si solar cell and InGaAs solar cell. The bandgap of In_2S_3 was calculated from the transmittance and reflection spectra, which were measured with a Varian Cary 5000 UV-Vis-NIR Spectrophotometer between 200 and 2000 nm.

RESULTS AND DISCUSSION

Annealing and ammonia etching treatments on the In_2S_3 thin films

To study the effect of annealing and ammonia etching treatments on the In_2S_3 films, XRD, SEM, and AFM were used to measure the In_2S_3 films. The In_2S_3 films are polycrystalline and grow with a (103) preferred orientation for the as-grown (reference) sample and the samples annealed at 280, 330 and 380°C , as shown in Fig. S1. The intensity of the (103) peak of the In_2S_3 film annealed at 280°C is the strongest. SEM images of the surfaces of the annealed In_2S_3 films are shown in Fig. S2a–d. The images indicate that the surface morphology of In_2S_3 films is not significantly changed after annealing. However, the grain size of the In_2S_3 layer annealed at 280°C is larger than those of the In_2S_3 films with other annealing temperatures, as seen in the cross-sectional images in Fig. S2e–h, and this is consistent with the XRD results.

After the 280°C annealing treatment, we soaked the samples in the concentrated ammonia solution for 0, 3 and 5 min. AFM images of the In_2S_3 layers shown in Fig. 1 indicate that the R_a (arithmetic average of the absolute roughness) values of the samples etched in concentrated ammonia for 0, 3 and 5 min are 16.1, 18.1 and 21.4 nm, respectively. Fig. S3 shows the reflectance spectra of In_2S_3 films etched by the concentrated ammonia for 0, 3 and 5 min. The reflectance of the samples decreases with the etching time increasing. These results mean that the ammonia etching treatment can effectively increase the surface roughness of the In_2S_3 layer, which can reduce the reflectance losses in the films and enhance the light trapping. Thus, the performance of In_2S_3 films should be best after annealing at 280°C followed by a

5-min concentrated ammonia etching treatment.

Device performance after annealing and ammonia etching treatments

In this work, we analyzed three groups of $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ solar cells with different interface treatments. All the CZTSSe absorbers and $\text{Zn}(\text{O,S})$ buffer layers were fabricated by the same process. In the first group, the In_2S_3 films without treatment (Sample Reference) were deposited on the $\text{Zn}(\text{O,S})/\text{CZTSSe}$ films. In the second group, the In_2S_3 films were deposited on the $\text{Zn}(\text{O,S})/\text{CZTSSe}$ films and then the samples were annealed at 280°C (Sample Annealed). In the third group, the In_2S_3 films were deposited on the $\text{Zn}(\text{O,S})/\text{CZTSSe}$ films and then the samples were annealed at 280°C followed by the concentrated ammonia etching for 5 min (Sample Annealed&Etched). The CZTSSe solar cells were fabricated using the Sample Reference, Sample Annealed, and

Sample Annealed&Etched as the absorber layers. The corresponding solar cells are denoted as Cell Reference, Cell Annealed, and Cell Annealed&Etched.

Fig. 2a presents the J - V curves of the Cell Reference, Cell Annealed, and Cell Annealed&Etched devices. The photovoltaic parameters of these devices are listed in Table 1. The V_{OC} and J_{SC} of the Cell Annealed and Cell Annealed&Etched devices are higher than those of the Cell Reference. The fill factors (FF) of Cell Annealed and Cell Annealed&Etched are higher than that of Cell Reference, which is attributed to both lower ideality factor (A) and reverse saturation current density (J_0) extracted from the J - V curves, as shown in Fig. 2b, c. This indicates that the interface recombination is inhibited, which will also be proved below. As a result, after the annealing and etching treatments, the V_{OC} and J_{SC} of the CZTSSe solar cells are improved, and, as a result, the efficiency of the CZTSSe solar cell is improved by 24%.

Figure 1 AFM topography images of In_2S_3 films with the ammonia etching for (a) 0, (b) 3 and (c) 5 min.

Figure 2 (a) The J - V curves of Cell Reference, Cell Annealed, and Cell Annealed&Etched. (b) The R_s , A , and (c) the J_0 of Cell Reference, Cell Annealed, and Cell Annealed&Etched from fitting with light J - V curves. G in (b) is shunt conductance.

Table 1 The photovoltaic parameters of the representative Cell Reference, Cell Annealed, and Cell Annealed&Etched devices

Cell	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	η (%)	R_s ($\Omega \text{ cm}^2$)	A	J_0 (mA cm^{-2})
Reference	328	31.18	45.28	4.63	1.71	2.42	1.42×10^{-1}
Annealed	358	32.89	46.72	5.50	1.96	2.32	8.38×10^{-2}
Annealed&Etched	346	34.76	47.80	5.75	1.86	2.06	4.70×10^{-2}

To investigate the reason why the device performance changes after the heterojunction interface treatments, the quality of the $\text{In}_2\text{S}_3/\text{Zn}(\text{O},\text{S})/\text{CZTSSe}$ interfaces was characterized firstly. Fig. 3a–c show the surface SEM images of Sample Reference, Sample Annealed, and Sample Annealed&Etched. It is obvious that the fabricated $\text{In}_2\text{S}_3/\text{Zn}(\text{O},\text{S})$ hybrid buffer layers formed with uniform and dense coverage on the absorbers. The grains and grain boundaries of Sample Annealed are clear, and the thickness of the buffer layer of Sample Annealed is thinner than that of Sample Reference, which can be ascribed to the elemental inter-diffusion caused by the annealing treatment. Additionally, the crystallization and the coverage of the buffer layer are improved by the annealing treatment, which improves both the V_{OC} and FF; however, extra clusters at the surface of the buffer layer, which formed during the annealing treatment, will lead to an increase of interfacial recombination at the CZTSSe/AZO interface and a corresponding increase of the series resistance (R_s) [23]. The clusters are removed effectively by the concentrated ammonia etching treatment, which will thus improve the contact of the CZTSSe/AZO interface and result in a decrease of A and J_0 . Fig. 3d–f show the cross-sectional morphologies of Sample Reference, Sample Annealed, and Sample Annealed&Etched. It is clear that the hybrid buffer layers can be well-preserved on the top of the absorbers after the series of post-treatments.

Fig. 4a–c show the S 2p/Se 3p XPS spectra of Sample Reference, Sample Annealed, and Sample Annealed&Etched. From Fig. 4 and Fig. S4, the locations of the S 2p peak and In 3d peak indicate that the indium bonds to the sulfur atom and forms In_2S_3 phases [24]. On the other hand, the peaks at 159.9 and 166.29 eV belong to Se 3p_{3/2} and Se 3p_{1/2} (Fig. 4) [25–27]. Comparing the in-

tensity of the Se 3p peaks shown in Fig. 4a, b, the increase of the Se 3p peak intensity in Fig. 4b indicates that a lot of selenium from the CZTSSe diffuses into the In_2S_3 and the $\text{Zn}(\text{O},\text{S})$ during the annealing treatment. The thickness of the In_2S_3 layer is reduced after the sample is annealed and then etched in concentrated ammonia solution. X-rays can penetrate the absorber layer deeply, thus the intensity of the Se 3p peak is enhanced dramatically (Fig. 4c). Similarly, the indium should also diffuse into the $\text{Zn}(\text{O},\text{S})$ and CZTSSe layers. To prove that the indium diffuses into the $\text{Zn}(\text{O},\text{S})$ and CZTSSe layers, Raman spectra are also collected and shown in Fig. 5. The Raman spectra of all samples show strong Raman peaks at 172, 196 and 238 cm^{-1} , which is consistent with the Raman peaks of CZTSe in previous reports [28–30]. The Raman peak at 250 cm^{-1} belongs to the ZnSe phase. The intensity of the Raman peak at 172 cm^{-1} for Sample Annealed&Etched is decreased and the intensity of its peak at 250 cm^{-1} is increased compared with Sample Reference, which proves a decrease of Cu and an increase of Zn after annealing treatment. In addition, the Raman peaks of Sample Annealed&Etched at 172 and 196 cm^{-1} shift toward lower wave number compared with Sample Reference. The shift of the Raman peaks is due to the smaller Sn ions (0.69 Å) substituted by larger In ions (0.80 Å) [31,32]. Above results indicate that the detrimental $[\text{2Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}]$ defect cluster is reduced, which is partly responsible for the improvement of device performance.

To further explain the correlation between the diffusion mechanism and photovoltaic (PV) properties, the C-V measurement was performed on Cell Reference and Cell Annealed&Etched. Fig. S5 shows the C-V scanning curves of Cell Reference and Cell Annealed&Etched. The carrier density (N_A) of CZTSSe solar cells at the different bias is calculated by Equation (1):

$$N_A = \frac{2}{qS^2\varepsilon} \left[\frac{d(1/C^2)}{dV} \right]^{-1}, \quad (1)$$

$$w_d = \frac{\varepsilon S}{C}, \quad (2)$$

where w_d is the depletion region width at the different bias calculated by Equation (2), S is the total area of CZTSSe solar cells, C is the capacitance at different bias, and ε is the dielectric constant of CZTSSe absorber. Combining the C-V measurement results shown in Fig. S5 and the calculation with Equations (1) and (2), plots of N_A versus the distance to the junction for Cell Reference and Cell Annealed&Etched are obtained, as shown in Fig. 6. The N_A and w_d of Cell Reference and Cell Annealed&Etched can be obtained when the V is at 0 V

Figure 3 The (a–c) surface and (d–f) cross-sectional SEM images of Sample Reference, Sample Annealed, and Sample Annealed&Etched.

Figure 4 The S 2p/Se 3p XPS spectra of (a) Sample Reference, (b) Sample Annealed, and (c) Sample Annealed&Etched (black line: spectra as measured; red line: spectra as fitted).

Figure 5 Raman spectra of Sample Reference and Sample Annealed&Etched.

Figure 6 The carrier density profiles of Cell Reference and Cell Annealed&Etched measured by C-V.

bias. From Fig. 6, with annealing and etching treatments, the N_A in the depletion region and interface increases from $3.17 \times 10^{15} \text{ cm}^{-3}$ for the Sample Reference to $3.12 \times 10^{16} \text{ cm}^{-3}$. Meanwhile, the w_d decreases from 200 to 145 nm. The increase of N_A of Sample Annealed&Etched is due to not only the suppression of interface recombination but also the indium diffusion into the CZTSSe absorber. As the Raman result indicates, the indium diffuses from In_2S_3 into $\text{Zn}(\text{O},\text{S})$ and CZTSSe during the annealing treatment. As a consequence, In^{3+} replaces Sn^{4+} to form In_{Sn}^- defects and then increases the N_A of the absorber. Simultaneously, In^{3+} substitutes Zn^{2+} to form In_{Zn}^+ defects and then increases the N_A of the $\text{Zn}(\text{O},\text{S})$ layer [31,33]. The effects of the increased carrier concentrations on the performances of CZTSSe solar cells have been simulated by wxAMPS. The set parameters of the simulation process are listed in Table S1. In accord with the C-V results, the carrier concentrations of the CZTSSe layer of Sample Reference and Sample Annealed&Etched are set to 1×10^{15} and $1 \times 10^{16} \text{ cm}^{-3}$, respectively. From Ref. [33], the carrier concentration of the $\text{Zn}(\text{O},\text{S})$ layer of Sample Reference is set to $1 \times 10^{14} \text{ cm}^{-3}$ and that of Sample Annealed&Etched is set to $1 \times 10^{15} \text{ cm}^{-3}$. The simulated energy band diagrams of Cell Reference and Cell Annealed&Etched are shown in Fig. S6. From Fig. S6, the quasi-Fermi level of holes (E_{fp}) of Sample Annealed&Etched moves toward valence band energy level (E_v) of the CZTSSe layer compared with that of Sample Reference, and the quasi-Fermi level of electrons (E_{fn}) of Sample Annealed&Etched moves toward conduction band energy level (E_c) of the CZTSSe layer compared with that of Sample Reference. Therefore, the value of $E_{\text{fn}} - E_{\text{fp}}$ increases after the annealing and etching treatments. This result will facilitate the carrier separation, reduce the interface recombination, and lead to an improvement of the V_{OC} [28].

Fig. 7a presents the EQE responses of Cell Reference, Cell Annealed, and Cell Annealed&Etched. This result is consistent with the J - V data of these solar cells. The EQE

response of Cell Annealed is enhanced in the wavelength region of 500–950 nm compared with Cell Reference. This is because the annealing process increases the built-in electric field strength across the Zn(O,S)/CZTSSe p-n junction by inter-diffusion of the elements, and thus improves the carrier collection and J_{sc} (Fig. 7b, c). After etching treatment, the EQE response of Cell Annealed&Etched is enhanced throughout the whole wavelength region, which is due to not only the suppression of interface recombination but also the enhancement of light absorption by the increased surface roughness after the etching treatment (Fig. 1). As shown in the inset of Fig. 7a, the bandgaps of Cell Reference, Cell Annealed, and Cell Annealed&Etched are determined from fits to the EQE data [34]. The bandgaps of these devices are almost unchanged after the treatments, in accordance with the bandgap of CZTSSe in a previous report [28].

The reason for the efficiency limitation of devices

Based on the above discussion, it is promising to use $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})$ as the Cd-free hybrid buffer layer, and the annealing and ammonia etching treatments can be used to improve the performance of CZTSSe solar cells with the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})$ buffer layer. However, the efficiency is still low compared with those of the reported Cd-free kesterite solar cell devices [18,19]. As shown in Table 1, the overall efficiency of these devices is mainly limited by low FF as a consequence of high R_s and high diode A.

To further reveal the reason for the low FF, a possible band alignment of the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ interface is shown in the schematic diagram in Fig. 8. As shown in

Table 1, the A of these devices are all higher than 2.0, which indicates that there is serious recombination at the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ interface. Our group's previous report [19] indicated that a possible defect energy level (E_D) very close to the Fermi level aids the transport of the negative charges across the Zn(O,S) layer even though a large conduction band spike exists at the Zn(O,S)/CZTSSe interface. This result indicates that there is no recombination at the Zn(O,S)/CZTSSe interface. So the low FF may arise because a large barrier exists at the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})$ interface [35]. The electron affinity (χ_e) of In_2S_3 is calculated according to Equation (3) [36]:

$$E_g = 6.75 - \chi_e. \quad (3)$$

The band gap energy (E_g) of In_2S_3 is estimated to be 2.9 eV from the transmittance and reflection spectra, as shown in Fig. S7. The calculated χ_e of In_2S_3 is 3.85 eV according to Equation (3), and the χ_e of CZTSSe is 4.35 eV [28]. Based on the above results, the CBO of the In_2S_3 and CZTSSe is 0.5 eV, and thus the band offset of E_D and In_2S_3 is higher than 0.5 eV. The large band offset (>0.4 eV) will lead to the abrupt decrease of FF. We used wxAMPS to simulate the effects of the band offset of E_D and In_2S_3 on the performance of the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ devices. The set parameters of the simulation process are listed in Table S2. It is found that as the bandgap of In_2S_3 decreases from 2.9 to 2.7 eV and χ_e of In_2S_3 increases from 3.85 to 4.05 eV, the band offset of E_D and In_2S_3 is decreased and the FF increases significantly with the other parameters unchanged (Table S3). This result indicates that the large band offset is a reason for

Figure 7 (a) The EQE responses of Cell Reference, Cell Annealed, and Cell Annealed&Etched. Inset: the bandgaps of these devices from fitting with the EQE data. The built-in electric field strength of (b) Cell Reference and (c) Cell Annealed&Etched estimated by C-V.

Figure 8 The schematic diagram of the band alignment of the $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})/\text{CZTSSe}$ interface for devices.

the low FF, and the band offset can be decreased by decreasing the bandgap of the In_2S_3 to improve the FF.

CONCLUSIONS

In conclusion, we developed CZTSSe solar cells with $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})$ hybrid buffer layers. The In_2S_3 buffer layer was used to provide indium, which will diffuse into the $\text{Zn}(\text{O,S})/\text{CZTSSe}$ layer via annealing. Further, the effect of annealing and ammonia etching treatments on the CZTSSe device performance was investigated. We find that the indium diffuses into the $\text{Zn}(\text{O,S})$ forming In_{Zn}^+ as well as into the CZTSSe forming In_{Sn}^- with annealing treatment, which increases the carrier concentrations of both the $\text{Zn}(\text{O,S})$ and CZTSSe and increases the value of $E_{\text{fn}} - E_{\text{fp}}$. This facilitates the carrier separation and increases the built-in electric field strength, which leads to an increase of the V_{OC} and J_{SC} . In addition, it is found that the ammonia etching treatment can reduce the interface recombination and enhance the absorption of light by increasing the surface roughness of the In_2S_3 layer. Finally, the efficiency of the CZTSSe solar cell with sequential treatments is improved. Then, we use wxAMPS software to simulate the device performance. The simulation and experimental results reveal that a large band offset of E_{D} and In_2S_3 is the physical origin of the low FF and efficiency, and the simulation also indicates that the FF and efficiency can be further improved by decreasing the bandgap of In_2S_3 . This study provides a new method to increase the carrier concentrations of absorber and buffer layers and also proposes a mean to further improve the efficiency of chalcopyrite solar cells with an $\text{In}_2\text{S}_3/\text{Zn}(\text{O,S})$ buffer layer.

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experiments for device fabrication, optimization and characterization; Wu L, Zhang J, Ao J and Wang H participated the design of experiment and the discussion of experimental results; Zhang Y supervised the whole project. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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铜锌锡硫硒薄膜太阳能电池中有希望的无镉双缓冲层

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摘要 Zn(O,S)薄膜由于低成本和生态友好的特性而被广泛用作锌黄锡矿薄膜太阳能电池的无镉缓冲层。但是Zn(O,S)缓冲层的载流子浓度和电导率较低, 这将会导致器件性能的降低。在这项工作中, 我们引入了一层额外的In₂S₃缓冲层, 并通过后退火处理来改进Zn(O,S)层以及CZTSSe层的属性。经过退火处理后, 我们发现Zn(O,S)和CZTSSe层的载流子浓度均增加, 这有助于载流子分离并增加开路电压。此外还发现, 氨水蚀刻处理可以去除污染物, 减少界面缺陷, 并且增加In₂S₃层的表面粗糙度以用作减反层。因此, 经过退火和蚀刻处理后, CZTSSe太阳能电池的效率提高了24%。仿真和实验结果表明, In₂S₃层和Zn(O,S)层中的缺陷能级之间较大的能带偏移是限制CZTSSe器件的填充因子和效率的主要原因。以上研究表明In₂S₃/Zn(O,S)是一种有希望的高效锌黄锡矿太阳能电池的无镉双缓冲层。本研究还为通过铜掺杂提高吸收层和缓冲层的载流子浓度提供了新的视角。