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Improvement of the photovoltaic performance of Cu₂ZnSn(SₓSe₁₋ₓ)₄ solar cells by adding polymer in the precursor solution

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Abstract

Kesterite Cu₂ZnSn(SₓSe₁₋ₓ)₄ (CZTSSe) thin films and related solar cells were successfully fabricated by a facile sol-gel method and selenization process. The influence of Polyvinylpyrrolidone (PVP) additive on the properties of the CZTSSe films and the power conversion efficiency (PCE) of the solar cells were investigated. The results reveal that the qualities of CZTSSe films can be manipulated by incorporating a small amount of PVP. With addition of 1 wt% of PVP, the smoothness and grain size of the CZTSSe films were greatly improved. The contact at the CZTSSe/Mo interface was also improved. As a result, the optimized PCE of solar cells improved from 2.24% to 4.34% after the addition of 1 wt% PVP due to the decrease of recombination at the interfaces. These results suggest that polymer addition in the precursor solution is a promising method for obtaining high quality of CZTSSe films and high-performance solar cells.

Keywords: CZTSSe, PVP, additive, morphology, efficiency

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

Introduction

Cu₂ZnSn(S,Se)₄ (CZTSSe) based materials have attracted much attention over the past several years due to its optimum band gap of 1.0–1.5 eV, high absorption coefficient ($>10^4$ cm^{-1}) and earth abundant constituents [1, 2]. Various technologies including co-evaporation [3], sputtering [4], electrodeposition [5] and solution deposition method [6] have been used to fabricate the CZTSSe-based solar cells. Currently, the lab-scale CZTSSe-based solar cell prepared via a hydrazine solution approach yields a world-record efficiency of 12.6% [7]. But the highly toxicity and insecurity of hydrazine limit its application in industrialization production.

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Table 1. Chemical compositions of the CZTS precursor film without PVP and CZTSSe films with different amount of PVP.

Samples	wt% of PVP	Element composition (%)					Composition ratios	
		Cu	Zn	Sn	S	Se	Cu/(Zn + Sn)	Zn/Sn
Precursor films	0 wt%	22.18	15.87	14.17	47.79	—	0.74	1.12
Selenide films	0 wt%	20.76	12.14	11.38	3.45	52.26	0.88	1.07
	1 wt%	21.10	10.89	10.66	3.24	54.12	0.98	1.02
	3 wt%	23.17	12.12	11.59	3.54	49.58	0.98	1.05
	5 wt%	22.67	11.38	11.16	3.52	51.27	1.00	1.02
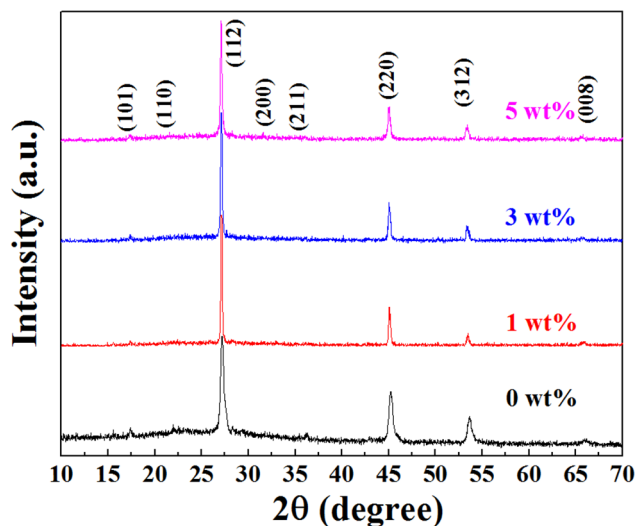
Figure 1. XRD patterns of CZTSSe films with different amounts of PVP additive.

A series of non-harmful, low-cost and environmentally-friendly solutions were widely used in the fabrication of CZTSSe solar cells. Hillhouse's group demonstrated a conversion efficiency over 8% using dimethyl sulfoxide (DMSO) as the solvent [8]. A $Cu_2Zn_{1-x}Cd_xSnS_4$ solar cell with efficiency of 9.24% was also accomplished by dissolving raw materials in 2-methoxyethanol [9]. However, two main issues still exist in the common solution processes. On the one hand, the incomplete evaporation of the solvents during the annealing processes will lead to thick fine-grain sub-layers in the absorbers [10, 11]. On the other hand, too rapid volatilization process and/or the instability of the precursor solutions will cause some holes and cracks on the surfaces of the CZTSSe thin films, eventually lead to the deterioration of the film micro-structures [12]. Recently, the stable dimethylformamide (DMF)-based solution has been used for fabricating CZTSSe solar cells. Although ideally-large grains extended parallel to the substrate were obtained, a large number of large voids observed in the bulk absorber and at the absorber/back electrode interface have great influence on the performance of devices [13].

At present, one of the main challenges in the preparation of CZTSSe solar cells by solution method is to obtain CZTSSe films with large grains, high density surfaces and without fine-grain layers. Doping metal cations (Na, K, Sb, Ge) in the precursor solutions has been used successfully to improve the grain size and the coverage of CZTSSe thin films [14–16].

However, the incorporated cations will bring more detrimental defects and secondary phases which usually act as recombination centers. Therefore, the polymer additive that will not leave behind in the lattices of CZTS material might be a better option. It has been reported that polymer additives have a great influence on the growth of the perovskite films. Jen *et al* utilized 1,8-diiodooctance (DIO) as an additive in the $CH_3NH_3PbI_{3-x}Cl_x$ thin film to improve the coverage of perovskite film [17]. Su *et al* reported the controllable film morphology by incorporating a polymer additive polyethylene glycol (PEG) into the N,N-dimethylformamide (DMF) based perovskite precursor solution [18]. Other polymers, such as polyethylenimine (PEI), polyvinylpyrrolidone (PVP) were also applied as the additive to control the crystal-growth of perovskite films [19].

We suppose that these polymer additives also have great influence on the growth of the solution based CZTSSe films. In this paper, DMF was used as the solvent to form CZTS precursor solution, and the polymer PVP which easily dissolved in DMF was introduced as additive. The effects of PVP additive on the crystallinity, morphologies of CZTSSe layers and the efficiencies of the solar cells were studied in details.

Experimental details

The Cu_2ZnSnS_4 (CZTS) precursor solution was prepared by dissolving copper (II) acetate monohydrate (6 mmol), zinc (II) chloride (3.7 mmol), tin (II) chloride dihydrate (3.3 mmol) and thiourea (26 mmol) in 10 ml dimethylformamide (DMF, AR) and stirring for 1 h to get a light-yellow solution. To study the effects of PVP additive on the CZTSSe films, various amount of PVP (0%, 1%, 3% and 5% with respect to the content of metal salts) were added into the solution during the stirring process. The solution can be stable for several weeks in the air.

The CZTS precursor films were obtained by spin-coating the precursor solutions on soda-lime glass (SLG) and Mo coated SLG substrates at 3000 rpm for 30 s, followed by drying at 300 °C for 5 min on a hot plate. The coating and drying processes repeated six times to achieve the required thickness of 1.5 μm. The CZTS precursor films were selenized for 15 min at 530 °C in a rapid thermal processing (RTP) furnace under nitrogen flow (70 ml min^{-1}) with a ramping rate of 300 °C min^{-1}, and then cooled down to room temperature naturally.

The devices were prepared as the traditional CZTSSe solar cells configuration: SLG/Mo/CZTSSe/CdS/i-ZnO/ITO/Al. A cadmium sulfide (CdS) buffer layer with thickness of 50 nm was deposited on top of the CZTSSe absorbers by

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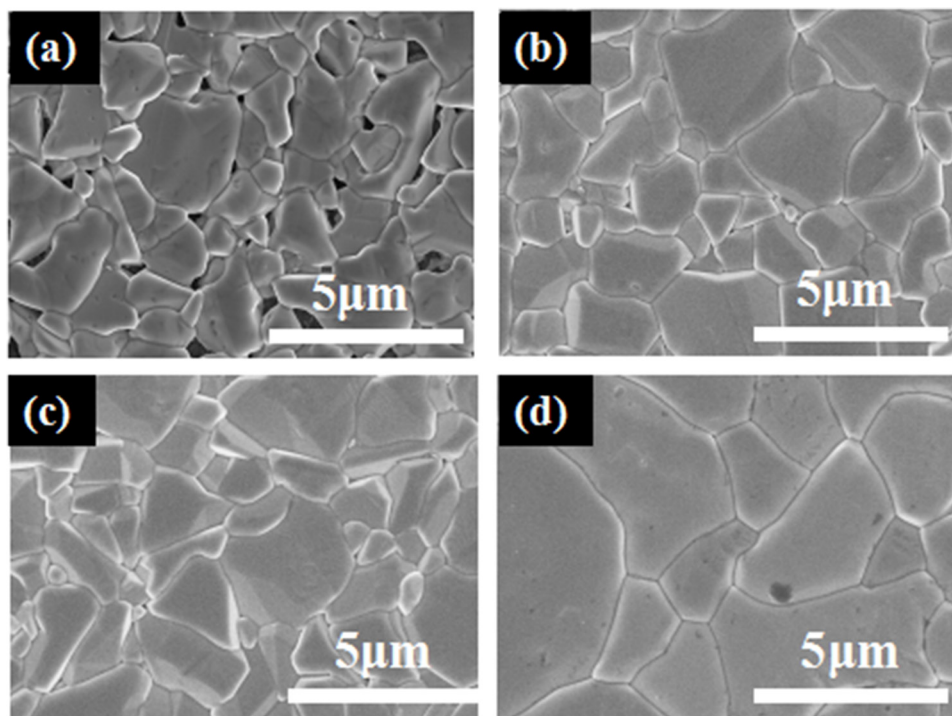
Figure 2. SEM images of CZTSSe based films with different amount of PVP additive. (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.

chemical-bath deposition. Then, transparent window layer of i-ZnO (60 nm) and ITO (400 nm) were sputtered on the top of the CdS layer by using RF magnetron sputtering technique followed by thermal evaporation of the Al grid electrode. Finally, all the devices were mechanically scribed into 9 small cells with an active area of about $0.19\,cm^2$.

Structural characterization of the selenized CZTSSe films were carried out by x-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.5406$ Å). The surface and cross-sectional morphologies of the thin films were characterized by scanning electron microscope (SEM, Hitachi S-4800) images. An energy dispersive x-ray spectroscopy (EDS) system (EDAX Genesis 2000) was used to check the elemental composition. The efficiencies of the CZTSSe based solar cells were determined by measurement of current density–voltage (*J–V*) curves under simulated AM 1.5 G solar illumination, calibrated with an official certified crystalline Si reference cell.

Results and discussion

We first investigated the effect of the additives on chemical compositions. The results for the as-grown and selenized precursor films without PVP and the selenide films with different amount of PVP were listed in table 1. The precursor films show an average Cu/(Zn + Sn) ratio of 0.74 and Zn/Sn ratio of 1.12, which is close to the reported optimum values for high efficiency devices. But the contents of S element are slightly low, which may be due to the decomposition and volatilization of thiourea during the drying processes. The thermal decomposition mechanism of the metal-thiourea complexes has been investigated in detail in previous literatures [20–22]. The deficiency of the chalcogen elements can be compensated by subsequent high temperature selenization

process. Compared with the precursor films, the contents of Cu element in all the selenized CZTSSe films did not change significantly. However, the obvious losses of Sn and Zn elements during annealing were observed. As a result, the ratio of Cu/(Zn + Sn) increases a little after 530 °C selenization, while Zn/Sn ratio decreases somewhat. The decrease in Zn/Sn ratio is due to that the volatilization of Zn is more serious than that of Sn [23, 24]. More importantly, we found that the amount of PVP additive has not significant effect on the element contents.

To reveal the effects of the PVP additive on the crystal quality of the CZTSSe film, the x-ray diffraction (XRD) measurements were carried out for all the CZTSSe films prepared with different amount of PVP additive. As shown in figure 1, all the diffraction peaks can be indexed to kesterite CZTSSe [25]. The XRD peak positions for all CZTSSe films on SLG substrates are nearly the same. The absence of second phases indicates that single phase CZTSSe films can be obtained regardless of the amount of the PVP additive. However, the values of full width at half maximum (FWHM) and the intensities of the main diffraction peaks of the (1 1 2) planes are quite different. The FWHM decreases from 0.32° to 0.16° as the amount of PVP was increased from 0% to 1%, suggesting that the PVP additive improve crystal quality of the CZTSSe films, but it increases from 0.16° to 0.21° as the amount of PVP increase to above 3 wt%, indicating degradation of the crystal quality. Therefore, we speculate that 1 wt% of PVP in the precursor solution is the optimal additive amount.

The dense and flat morphologies of CZTSSe films are crucial to the performance of solar cells. The top-view SEM images of the CZTSSe absorbers with different amounts of PVP additives were shown in figure 2. As shown in the figure 2(a), for the pristine CZTSSe film without additive,
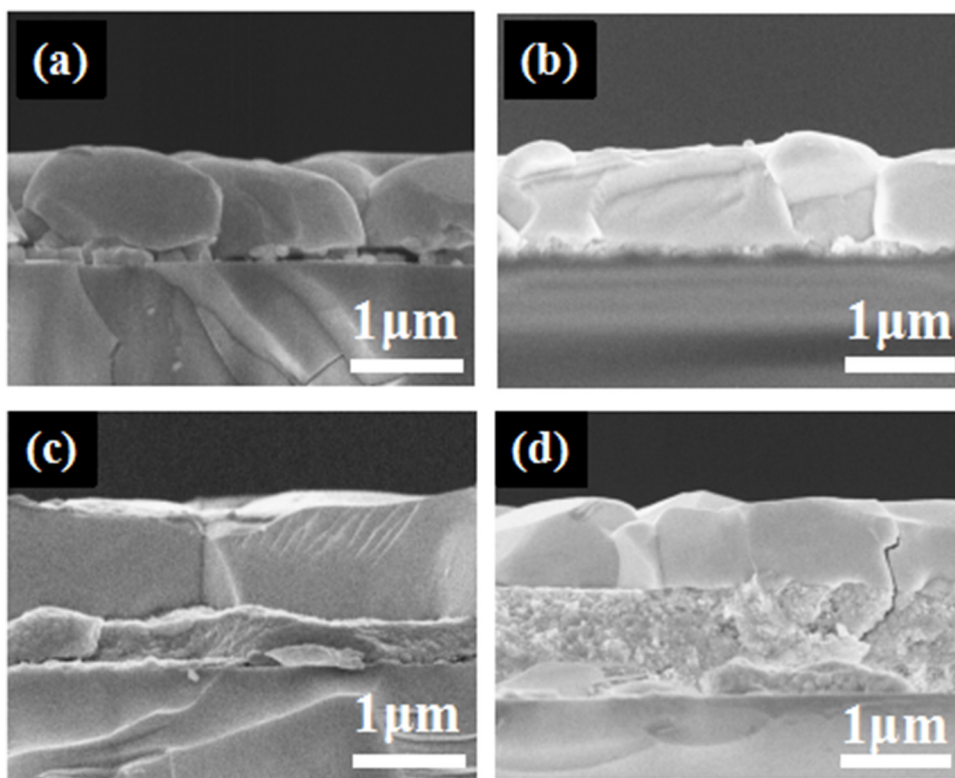
Figure 3. Cross-sectional SEM images of CZTSSe based films with different amount of PVP additive. (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.

though some grain size can reach about 2 μm, many pinholes and big holes were observed at the surfaces. These existed defects would lead to poor charge transport and weak light absorption in CZTSSe thin films. In addition, the pinholes were therefore filled with chemical bath deposited CdS, this will destroy the quality of p-n junctions and lead poor performance of the devices. However, by incorporating PVP additive, the thin films with smoother surface and densely packed large grains can be obtained, nearly no voids can be found in the films. It's worth noting that grain size became larger and more uniform after PVP addition. As the amount of PVP additive increases to 5 wt%, the grain size can reach more than 5 μm, as shown in figure 2(d). We speculate that the polymer additive helps the spread of precursor solution on the substrates and facilitates homogeneous nucleation to obtain continuous CZTSSe films with large grains [18].

　　The SEM images of the cross-sectional morphologies of the CZTSSe films were shown in figure 3. It is shown that CZTSSe film without PVP additive is composed of micrometer scale grains, and the grains also stack densely at the top of the films, however, there are some obvious holes at the bottom, as shown in figure 3(a), the unsatisfactory contacts between the films and the substrates will hinder the transport of electron holes. The images of CZTSSe films prepared with 1 wt% PVP were shown in figure 3(b), we can see that film is in good contact with the substrates without voids at the interfaces, and has large columnar grains extended parallel through the film, the thickness of the CZTSSe film is about 1 μm. However, thin film containing 3 wt% PVP exhibits an obvious bi-layer morphology consisting of a dense large
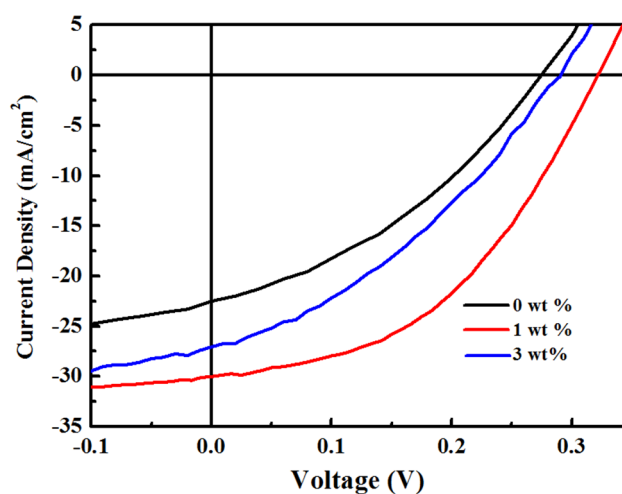

Figure 4. Current–voltage characteristics of the CZTSSe-based solar cell using the CZTSSe absorber layer prepared with 0 wt%, 1 wt% and 3 wt% of PVP additive.

grained top layer of about 1 μm and a fine-grain layer of about 500 nm, this phenomenon is more obvious for the film with 5 wt% PVP, in which the thickness of the fine-grain layer can reach 1.5 μm. The existence of fine-grain sub-layer may be related to the incomplete selenization of the CZTS films. On the one hand, the dense top layer will hinder the diffusion of Se element into the bottom of the films. On the other hand, the addition of PVP to the solution may increase its viscosity, therefore, thicker precursor CZTS films were obtained in the same preparation condition. As a result, CZTS films with

Table 2. Characteristics of CZTSSe based solar cells with 0 wt%, 1 wt% and 3 wt% of PVP additive.

Samples	η (%)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	R_{sh} ($\Omega\cdot$cm^2)	R_s ($\Omega\cdot$cm^2)	n	J_0 (mA cm^{-2})
0 wt%	2.24	274.47	22.49	36.27	66.05	2.47	2.48	0.63
1 wt%	4.34	321.68	30.01	44.95	119.90	2.79	1.80	0.017
3 wt%	2.75	290.45	27.04	35.01	76.92	2.57	2.18	0.65
IBM CZTSSe	12.6	513.4	35.2	69.8	621.11	0.72	1.24	7×10^{-5}
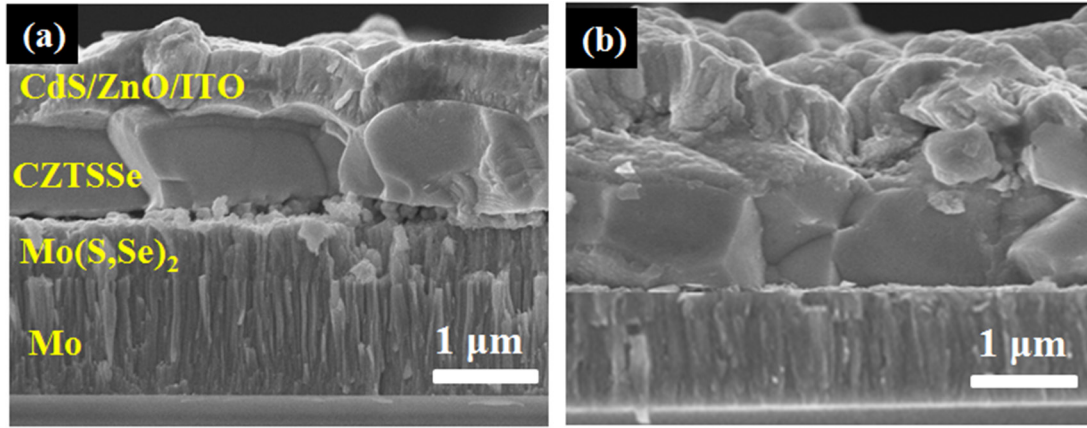
Figure 5. Cross-sectional SEM images of the completed CZTSSe solar cells. s(a) without PVP and (b) with 1 wt% of PVP additive.

3 wt% and 5 wt% PVP cannot be selenized completely. It is known that the CZTSSe films with smooth surface and large columnar grains are favorable to the fabrication of high efficiency solar cells. Hence, the optimized additive amount of PVP should be 1 wt% judging from the films' morphologies of figures 2 and 3.

Solar cell devices with conventional structure were fabricated by using CZTSSe films as absorbers. To investigate the effect of additives on device performance, current density–voltage (J–V) curves of the devices were measured under AM1.5 G illuminations, as illustrated in figure 4. The parameters including open-circuit voltage (V_{oc}), short-circuit density (J_{sc}), fill factor (FF) and PCE are listed in table 2 for clarity. For the reference device without any PVP additive, the obtained PCE was 2.24% with V_{oc} of 274.47 mV, J_{sc} of 22.49 mA cm^{-2}, and FF of 36.27%. While for the CZTSSe solar cell fabricated with 1 wt% PVP, a PCE of 4.34% was achieved, with a V_{oc} of 321.68 mV, a J_{sc} of 30.01 mA cm^{-2} and a FF of 44.95%. But the efficiency for the device with 3% PVP was just 2.75% with V_{oc} of 290.45 mV, J_{sc} of 27.04 mA cm^{-2}, and FF of 35.01%. Unfortunately, there is no efficiency observed for the solar cells with 5 wt% PVP. The results indicate that the incorporation of PVP in the CZTS precursor solutions has a great effect on the efficiencies of the solar cells, which could be ascribed to the variation of J_{sc}, V_{oc} and FF.

According to the solar cell theory, the performance of the solar cells can be evaluated by parameters of shunt conductance (G_{sh}), series resistance (R_s), diode ideality factor (n), and reverse saturation current density (J_0) of the solar cell, which can be obtained by analyzing the J–V curves of solar cells with the Sites' method. Table 2 also shows the G_{sh}, R_s, n, and J_0 of the solar cells. It can be seen that the R_s are similar for all the devices, but the G_{sh}, n, and J_0 decrease a lot as

the incorporation of 1 wt% polymer PVP. As we are known, the relationship between the V_{oc} and these parameters can be expressed as a transcendental equation:

$$G_{sh}V_{oc} = J_{sc} - J_0(e^{\frac{qV_{oc}}{nkT}} - 1). \quad (1)$$

Therefore, the decrease of the G_{sh} and J_0 are beneficial to the improvement of the V_{oc}. In addition, the increase of J_{sc} and FF are also related to these parameters. In one word, the increase of PCE should be ascribed to the variation of these diodes parameters, especially G_{sh}, J_0 and n which are related to the recombination rate of photogenerated carriers. It is should be noted that n is larger than 2 for the reference device, indicating the serious recombination occurs at the interface, including CZTSSe/CdS front interfaces and CZTSSe/Mo back interfaces [26, 27]. It should be noted that these diodes parameters have similar values for solar cell with 3 wt% PVP and reference device. As discussed above, the thick fine-grain sublayers appeared in the CZTSSe films with 3 wt% and 5 wt% PVP may lead to the serious carrier recombination in the CZTSSe bulks. Therefore, the relatively high value of J_0 should be responsible for the lower V_{oc} and efficiency of these devices.

In order to further track down the effect of PVP additive on PCE of the solar cells, the cross-sectional SEM images of reference devices and CZTSSe solar cell with 1 wt% PVP were characterized and the results were depicted in figure 5. It can be seen that only a small amount of PVP make a big difference. First, the thickness of the CZTSSe absorber layer of the device without PVP has decreased significantly, which may be due to the sub-layer CZTSSe react with the back-electrode Mo to form a thick MoSe$_2$ layer [28, 29]. The thinner CZTSSe layer may result in incomplete absorption of the light, affecting the J_{sc} of the device. Second, the contact

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between the CZTSSe layer and the Mo back electrode was significantly improved after the addition of PVP. As shown in the figure 5(b), CZTSSe films are adhered well with the Mo electrode due to the thickness of Mo(S,Se)$_2$ layer decreases markedly, there is also no void and fine-grain sub-layer at the back interfaces, large columnar grains extended parallel through the films. Such characters are favorable to decrease the amount of grain boundaries and the defects that usually act as recombination centers [30]. In addition, a CZTSSe/CdS heterojunction with better quality can be expected due to the improvement of the crystal quality as discussed above, this is also beneficial to reduce the recombination of photogenerated carriers. Therefore, the enhanced PCE of the devices mainly attributed to the improvement of quality of the CZTSSe films as well as the CZTSSe/CdS p-n junction and the CZTSSe/Mo back contact by adding small amount of PVP in the CZTS solution. However, the values of G_{sh} and J_0 are still too large compared with the solar cell with an efficiency of 12.6%, implying serious recombination still exist in our CZTSSe films. Further optimization should focus on the reduction of the defects in the CZTSSe films and the improvement of interfacial properties in the solar cells.

Conclusions

In this study, CZTSSe thin film solar cells were fabricated using DMF-based solution, an easily-accessible polymer PVP was employed to tune the crystallinity and the morphologies of CZTSSe thin films. Compared with the pristine CZTSSe film without the PVP additive, the holes and pinholes on the surfaces decrease obviously by adding 1 wt% PVP additive in the precursor solution. In addition, the contact between the CZTSSe layer and the Mo back electrode was also significantly improved. The CZTSSe-based solar cell with 1 wt% PVP achieved a PCE of 4.34%, which demonstrated a large increase compared with the PCE of 2.24% for the reference device (without PVP). The enhancement of efficiency can be attribute to the reduction of recombination which is related to the improvement of interfacial (both CZTSSe/CdS and CZTSSe/Mo) properties of the solar cells by using PVP as an additive.

Acknowledgments

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