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High efficiency CZTSSe thin film solar cells from pure element solution: A study of additional Sn complement

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ABSTRACT

CZTSSe based thin film solar cells have received considerable interests due to low material cost, suitable band gaps and high absorption coefficient of CZTSSe materials. Achieving high efficiency CZTSSe based thin film solar cells often need a high temperature selenization process that always causes Sn loss in the form of gaseous $SnSe_2$. Additional Sn complement may decrease the loss of Sn during selenization process and improve the performance of fabricated CZTSSe based thin film solar cells. Here, we investigate the effect of additional Sn complement on the performance of CZTSSe based thin film solar cells fabricated from pure element solution. XRD and Raman characterizations indicate that additional Sn complement could reduce the secondary phase that may cause the voltage loss and decrease of efficiency. The solar cell fabricated with 15% additional Sn complement shows the best conversion efficiency of 8.71% (V_{OC}=0.42 V, J_{SC}=32.73 mA cm^{-2}, FF=63.19%). To the best of our knowledge, it is the highest efficiency of CZTSSe based thin film solar cells fabricated from pure element solution.

1. Introduction

$Cu_2ZnSn(S, Se)_4$ (CZTSSe) thin film solar cells have received much attention due to abundant reserves and low expense of $Cu_2ZnSn(S, Se)_4$ compared with successfully industrialized CdTe and $Cu_2InGaSe4$ devices [1–4]. Among various methods for the preparation of CZTSSe thin film, solution-based method has attracted focus owing to its simple and low cost nature [5–14]. Recently, the highest efficiency of CZTSSe based thin film solar cells has been reported to be 12.6% based on hydrazine solution for dissolving metal sulfide [15]. However, hydrazine is high explosive and toxic solvent, which is hardly used for commercially viable products, thus urging developing new and environmental technology for CZTSSe based thin film solar cells. Therefore, massive simple solution based methods had been reported to fabricate the CZTSSe based thin film [16–20]. Haass et. al. reported an 11.2% efficient kesterite CZTSSe thin film solar cell which was fabricated using a solution of metal chlorides dissolved in DMSO [21]. By dissolving metallic oxide in 1-butylamine, thioglycolic acid and ethanol mixture, Pan's group reported a CZTSSe thin film solar cell with 6.03% efficiency [22]. However, the use of metal chloride or metallic oxide as the starting materials will introduce the impurity Cl and O into the film. Compared to these compounds, pure metallic elements do not introduce impurity into the film, and solar cells with higher efficiency can be expected. Pan's group reported an 8.02% efficiency kesterite CZTSSe thin film solar cell by using pure metallic elements as metal sources and the mixture of thioglycolic acid, ethanolamine and 2-methoxyethanol as solvent [23]. In our previously report, an 6.4% efficiency kesterite CZTSSe thin film solar cell was fabricated by using the mixture of 1,2-ethanedithiol and 1,2-ethylenediamine for pure metallic elements dissolving [24].

Generally, in order to achieve high solar cell efficiency, the CZTSSe thin film must need selenization process that always causes the Sn loss by the way of gaseous $SnSe_2$, which will relatively increase the content of Cu and Zn. Thus may increase secondary phase and defects, such as $Cu_{2-x}Se$, ZnSe, Cu_{Sn}, V_{Sn}, Zn_{Sn}, etc [25–32]. These secondary phase and defects are responsible for most recombination of photogenerated carriers in CZTSSe films, which are detrimental to the efficiency of CZTSSe based devices [33–37]. To prevent the loss of Sn, some groups supplement Sn in the form of $SnSe_2$ pellets with CZTSSe precursor films together during the selenization process [29,31,32]. However, this method may also cause unbalance of Sn in the bulk of CZTSSe thin films.

Here, we use 1,2-ethanedithiol and 1,2-ethylenediamine to dissolve the metal of Cu, Zn, Sn, S and Se powders to form CZTSSe precursor solution. The CZTSSe precursor films were fabricated

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using the above precursor solution by spin-coating method. After selenization at 550 °C, the obtained CZTSSe films were used to fabricate CZTSSe based solar cells. In order to investigate the effect of additional Sn complement on the performance of CZTSSe based solar cells, different amount of additional Sn were complemented to the precursor solution. The solar cell fabricated with 15% additional Sn complement shows the best conversion efficiency of 8.71% (V_{OC}=0.42 V, J_{SC}=32 mA cm^{-2}, FF=63.19%). To the best of our knowledge, it is the highest efficiency of CZTSSe based thin film solar cells fabricated from pure element solution.

2. Experimental section

2.1. Materials

Cu (99.9%, Aladdin), Zn (99.9%, Aladdin), Sn (99.8%, Alfa Aesar), S (99.9%, Aladdin) and Se (99%, Alfa Aesar) powders are used as received without further purification. 1,2-ethanedithiol ($HSCH_2CH_2SH$, AR), 1,2-ethylenediamine ($H_2NCH_2CH_2NH_2$, AR), thioglycolic acid ($HSCH_2COOH$, 99%), ethanolamine ($HOCH_2CH_2NH_2$, AR), 2-methoxyethanol (AR), ammonium hydroxide (NH_4OH, 25%), cadmium sulfate (AR) and thiourea (AR) were all purchased from Aladdin.

2.2. Preparation of precursor solution

Cu (1.24 mmol), Zn (0.76 mmol), Sn (0.62 mmol), S (2.7 mmol) and Se (0.3 mmol) powders were added into a 25 ml round flask. Then, 0.5 ml of 1,2-ethanedithiol and 5 ml of 1,2-ethylenediamine were injected into the flask. The mixture was magnetically stirred in a heating jacket at 70 °C for 1.5 h. After that, 1 ml of thioglycolic acid, ethanolamine and 2-methoxyethanol mixture (1:1:2) were injected into this round flask. This mixture underwent continuous stirring till the color turned into golden yellow. Here, the mixture of thioglycolic acid, ethanolamine and 2-methoxyethanol was used as thickening agent to improve the stability of solution and CZTSSe precursor film forming ability. This non-hydrazine solution method for dissolving pure metal brings convenience for commercial industry. To investigate the influence of Sn, different diadditional of Sn (0%, 5%, 10%, 15% and 20%) was added in the above solutions and used for the fabrication of different CZTSSe precursor films.

2.3. Fabrication of CZTSSe thin film and solar cells

The CZTSSe precursor thin films were prepared by spin-coating of metal precursor solutions on molybdenum sputtered soda lime glass (SLG) substrate and then heating on hot plate at 310 °C in nitrogen atmosphere for 1 min. A thickness of about 1.7 μm thin film was obtained by repeating this procedure several times. Finally, the thin film was annealed at 550 °C in a graphite box containing 200 mg of Se powder for 15 min. CZTSSe thin film solar cells were fabricated using the selenized CZTSSe thin films by successively depositing the following additional layers: chemical bath deposition (CBD) of 60 nm cadmium sulfide (CdS), sputtering of 70 nm intrinsic zinc oxide (ZnO) and 200 nm indium-doped tin oxide (ITO). On the top of the device, Ag collection grid electrodes were deposited by thermal evaporation. No antireflection coating was utilized.

2.4. Characterizations

The Raman spectra were measured by a Renishaw inVia Raman microscope using an excitation laser with a wavelength of 532 nm. The powder X-ray diffraction (XRD) patterns were taken with a Bruker D8 Advance X-ray diffractometer. The scanning electron microscope (SEM) images were collected using a Nova NanoSEM 450 field emission scanning electron microscope (FESEM). Photocurrent density-voltage curves were recorded under the standard AM1.5 illumination (100 mW cm^{-2}) with a Keithley 2400 source meter. The external quantum efficiency (EQE) spectrum was measured using a Zolix SCS100 QE system equipped with a 150-W xenon light source and a lock-in amplifier. The electrochemical impedance spectroscopy analysis was performed on a CHI 660E workstation (ChenHua Instruments Co., Shanghai, China) with a conventional three electrode system.

3. Results and discussion

Fig. 1 shows the XRD pattern and Raman spectra of CZTSSe films prepared from precursor solutions with different amount of additional Sn after selenization. As shown in Fig. 1(a), the main peaks of different CZTSSe films are located at the degree of 27.91, 46.08, 54.45 and 73.62, corresponding the lattice plane of (112), (204), (312) and (316), respectively. The peak located at 40.36 degree is belonged to molybdenum sputtered on soda lime glass. Compared with the standard JCPDS card of CZTSe (No.52-0868), the XRD peaks of CZTSSe thin films move to higher degree, which are caused by remnant of S in the CZTSSe thin films. This phenomenon can be explained by smaller atom of S compared with Se, which cause decrease of the lattice. CZTSSe film prepared with no additional Sn shown a weak peak at about 30 degree, which is caused by CuS_2 (No.32-0348) and/or $CuSe_2$ (No.26-1115) [38,39]. The loss of Sn during selenization caused the relatively increase of Cu content in the CZTSSe film, which lead to the formation of $Cu(S,Se)_2$. With additional Sn complement, the weak peak belonged to $Cu(S,Se)_2$ disappeared gradually, which indicated the additional Sn complement suppressed the formation of $Cu(S,Se)_2$. As we all know, $Cu(S,Se)_2$ is narrow band gap compound, which often cause voltage loss and cell cutting-out [40–42]. When 20% additional Sn was added to the precursor solutions, the CZTSSe film after selenization shown a weak peak located at 14.87 degree. This weak peak is corresponded to $Sn(S,Se)_2$ or SnS_2 (No.23-0677) and $SnSe_2$ (No.23-0602) [43]. When the additional Sn (20%) is beyond the loss of Sn during selenization, the redundant Sn will react with S and Se to form $Sn(S,Se)_2$. Due to the n-type nature of $Sn(S,Se)_2$, it will reduce the parallel resistance, which is detrimental to the final devices [43]. Due to the similarity of the XRD pattern between CZTS/CZTSe and some second phases, such as Cu_2SnS_3, CuS, ZnS and Cu_2SnSe_3, CuSe, ZnSe, Raman spectra was used to further study the composition of CZTSSe films fabricated with different amount of additional Sn. As shown in Fig. 1(b), the peaks located at 174, 196 and 236 cm^{-1} are corresponding to CZTSe, and the peak located at 333 cm^{-1} is homologous with CZTS. CZTSSe film prepared with no additional Sn shown a weak peak at 250 cm^{-1}, which can be identified as ZnSe [2]. With the increase of additional Sn complement, this weak peak located at 250 cm^{-1} disappeared gradually and only weak peak at 236 cm^{-1} was observed. This result indicated that, additional Sn complement could suppress the formation of impurity ZnSe. Through XRD and Raman analysis, we can confirm there are no secondary phases such as Zn(S,Se), $Cu(S,Se)_2$ and $Sn(S,Se)_2$ in the CZTSSe film prepared with moderate additional Sn complement (10–15%).

To further study the effect of additional Sn complement on elemental composition of different CZTSSe films, energy-dispersive X-ray (EDX) spectrometry was used to analyse the elemental composition of different CZTSSe films after selenization. As shown in the Table 1, the content of Sn varied from 7.93% to 9.35% when the amount of additional Sn varied 0% from 20%. This change suggested that the additional Sn can enter the final CZTSSe films