

PREPARATION OF (Ag,Cu)₂ZnSn(S,SE)₄ FILMS BY DMSO-BASED METAL SALT METHOD

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A DMSO based metal salt method was used to prepare (Ag,Cu)₂ZnSn(S,Se)₄ (ACZTSSe) thin films, the influence of preparation condition on the properties of ACZTSSe films was investigated. It was found the selenization temperature for the annealing process and the drying temperature for the film formation process greatly influence the properties of the prepared films. By optimizing the preparation process, no obvious secondary phases were observed in the obtained ACZTSSe films. The films show uniform and compact morphology, the crystalline grains in the film are in the size of micro-meters. Based on the ACZTSSe absorber layers, solar cells were fabricated which achieved efficiencies of 6.3%.

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1. Introduction

Cu₂ZnSn(S,Se)₄ (CZTSSe) is a promising alternative to Cu(In,Ga)Se₂ (CIGS) photovoltaic material. Up till now, the efficiencies of CZTSSe solar cells achieved 12.6%, but still lower than the record efficiency of CIGS solar cell. It is proved the performance of CZTSSe is limited by the open-circuit voltage [1]. This low open-circuit voltage problem was believed caused by the low quality of the CZTSSe material and the mismatch of the properties between absorber layer and buffer layer.

For CZTSSe material, the electrical properties are determined by the intrinsic defects in the material. Due to the low formation energy, unfavorable intrinsic defects may exist in CZTSSe material [2]. For example, the formation of Cu/Zn antisites is relatively low (because Cu and Zn have similar ionic radius in the lattice of CZTSSe, thus large amount of [Cu_{Zn}+Zn_{Cu}] defect cluster can exist in the material. This defect cluster may further increase the band tailoring energy. According to a simulation for CZTSSe solar cell, the large band tailoring energy can direct result in the low open-circuit voltage.

Recently, researchers propose to replace Cu element by Ag element for CZTSSe material [2, 3]. A fully replacement of Cu element by Ag element can greatly increase the formation energy of Ag/Zn antisites, but the conductivity of the semiconductor change from p-type to n-type [4]. Alternatively, a partly replacement of Cu by Ag element can be used. Since the ionic radius of Ag is 16% larger than that of Cu, the element replacement may induce strains in the lattices, which may suppress the formation of [Cu_{Zn}+Zn_{Cu}]. It has been reported that a 10% replacement of Cu by Ag can increase the solar cell efficiency from 9.0% to 9.7% (open-circuit voltage increase from 369 mV to 406 mV) [5].

Currently most of the ACZTSSe films were prepared by co-evaporation [4, 5] or nano-ink based methods [3]. In this paper, we prepared ACZTSSe films by a DMSO-based solution method, which has the prospect to prepare high-efficient solar cells and the advantages of low toxicity, low cost and easy process. We investigated how the preparation conditions (e.g., selenization

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temperature) influence the properties of the ACZTSSe films. Based on the optimization, ACZTSSe films were prepared and solar cells were fabricated which show efficiencies up to 6.34%. The films and solar cells are characterized, and the result are discussed in this paper.

2. Experimental details

2.1. Preparation method

For the metal salt method, normally a precursor solution was firstly prepared and then precursor films were formed by using the solution. For the preparation of precursor solution, firstly 2 mL of DMSO was added to a vial containing a magnetic stirrer. Then copper(II)-acetate monohydrate (99.99%, 2.1 mmol), silver-nitrate (99.5%, 0.2 mmol), tin(II)-chloride dehydrate (99.99%, 1.6 mmol), zinc-chloride (99.99%, 1.6 mmol) and thiourea (99.0%, 5.5 mmol) were successively added into the DMSO solution with stirring. Finally, a clear and transparent solution was obtained.

By using the precursor solution, wet film was spin-coated on Mo/SLG substrate (by an Easy Coater 6 spin-coater). Then the wet film was dried at the drying temperature of 200/250/350°C for 2 min. This process was repeated on the same substrate for about 10 times to achieve the desired thickness (~1 μm) of the film.

After the preparation of the precursor film, a selenization process was used to transform the precursor film to ACZTSSe film. The precursor film was firstly placed in a tube furnace (GSL-1600X) with Se pellets. Then the tube was evacuated and refilled with nitrogen to a pressure of around 100 Torr. Finally, the tube with the sample were heated up to the selenization temperature of 450/500/550/600°C for 15 min and then cooled naturally.

For solar cell fabrication, CdS buffer layer was deposited on ACZTSSe layers by chemical bath deposition. Then i-ZnO and AZO layers were successively deposited on CdS buffer layer by sputtering. After that, Ag grids were evaporated on top of AZO as top contact of the solar cell.

2.2. Characterization

The phases in the prepared films were analyzed by a Bruker D8 Advance X-ray diffractometer with Cu K_{α} radiation and a JY LabRAM HR Raman spectrometer equipped with 532 nm laser. Morphologies of the films were observed and recorded by a FEI Scanning Electron Microscopy (SEM). The compositions of the films were characterized by an energy dispersive spectrometer (EDS) setup that attached in SEM. The solar cell performances were measured using an Agilent B1500A semiconductor parametric analyzer under simulated AM 1.5 global solar irradiations. The quantum efficiencies (QE) of the solar cells were conducted using a QTesT 1000ADX setup.

3. Results and discussion

We firstly investigated the influence of selenization temperature on the preparation of ACZTSSe films. Different selenization temperature of 450 °C, 500 °C, 550 °C and 600 °C were used for the selenization while the drying temperature for the wet films was fixed at 250 °C. Fig.1 shows the SEM images of the films that selenized at different temperature. For the films selenized at 450 °C and 500 °C, there seems no crystallization process as the low temperature. Therefore, no obvious crystalline grains can be found in these films. When the selenization temperature increases to 550 °C, crystalline grains can be seen in the film, but the film is not compact. As the selenization temperature increases further to 600 °C, crystallized film with compact morphology was obtained. Fig. 2 shows the XRD patterns of the films that selenized at different temperature. Obvious secondary phases (especially the $\text{Sn}(\text{S},\text{Se})_2$ phase, which corresponding to the XRD peak at around 14°) can be seen in the XRD patterns for the selenization temperature of 450 °C, 500 °C and 550 °C. For the films selenized at 600 °C, all the peaks in the XRD pattern can be attributed to the ACZTSSe material, and no obvious secondary phases can be found from the XRD result. According to the experimental results mentioned above, the suitable temperature for the selenization would be 600 °C. Only at this temperature, the reaction of the elements in the films and the crystallization process of ACZTSSe can be finished.

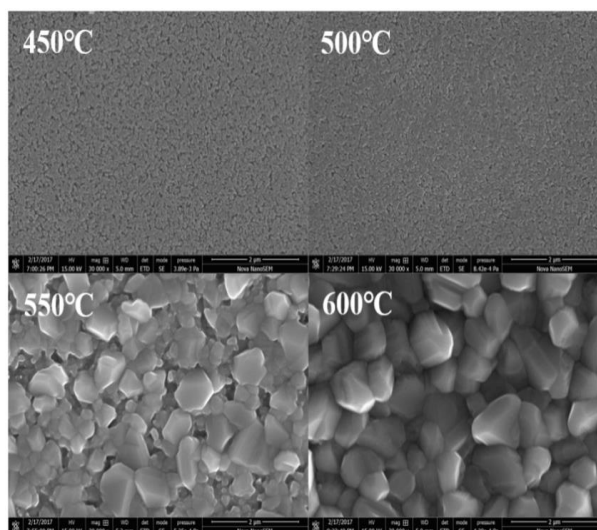


Fig. 1. SEM images of the films that selenized at different temperature.

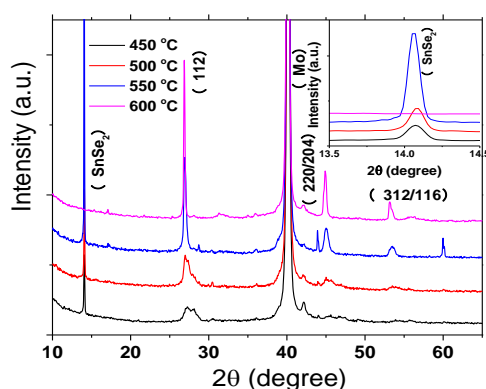


Fig. 2. XRD patterns of the films selenized at different temperature.

We further investigated the influence of the drying temperature of the wet films on the properties of the obtained films. For this series of samples, different drying temperature of 200 °C, 250 °C and 300 °C were used and the selenization temperature was fixed at 600 °C. Fig. 3 shows the SEM images of the films that prepared with different drying temperature. As the drying temperature increases from 200 °C to 300 °C, the sizes of the crystalline grains in the films decreases gradually, and the crystalline grains change from the round shape to facet shape. For the films prepared with the drying temperature of 200 °C, voids can be seen in the film. While for the films prepared with the drying temperature of 250 °C and 300 °C, the films are rather compact.

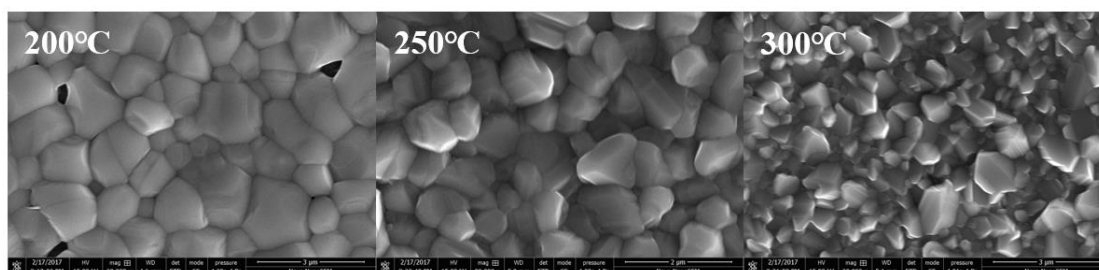


Fig. 3. SEM images of the films prepared at different drying temperature.

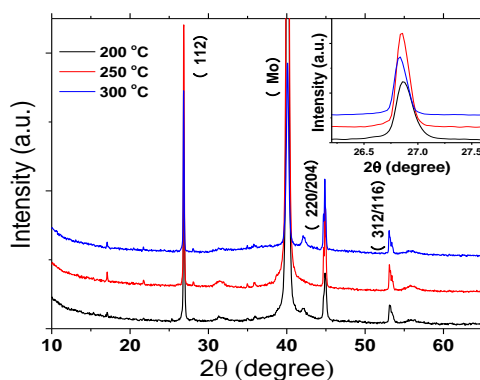


Fig. 4. XRD patterns of the films prepared at different drying temperature.

Fig. 4 shows the XRD patterns of the films prepared with different drying temperature. For all the films, no obvious secondary phases can be identified from the XRD patterns. As the drying temperature increases, the main peak of ACZTSSe shifts slightly to low angle. This could be caused by the different Se/S ratios of the films (i.e., high Se content at low drying temperature). Fig. 5 shows the Raman spectra of the films prepared with different drying temperature. The Raman results also prove that no obvious secondary phases are formed in the films. As the drying temperature increases, the main Raman peak shift slightly to low wavenumber. This would also be caused by the different Se/S ratios of the films. Besides, we observed that the height ratio between the Raman peaks at 173 cm^{-1} and 198 cm^{-1} are different for different films. For the film prepared with the drying temperature of $200\text{ }^{\circ}\text{C}$, this ratio is relatively high. As mentioned in the reference, the decrease of the height for the 173 cm^{-1} peak relative to the height for the 198 cm^{-1} peak indicates the increase of the concentration of the $[\text{V}_{\text{Cu}}+\text{Zn}_{\text{Cu}}]$ defect cluster in the CZTSSe material, and the $[\text{V}_{\text{Cu}}+\text{Zn}_{\text{Cu}}]$ defect cluster is believed beneficial to the performances of CZTSSe solar cells. Therefore, a drying temperature higher than $200\text{ }^{\circ}\text{C}$ would be suitable for the preparation of ACZTSSe films. As the films prepared with the drying temperature of $300\text{ }^{\circ}\text{C}$ shows small grain sizes, the suitable drying temperature for ACZTSSe films would be $250\text{ }^{\circ}\text{C}$.

Based on the experimental results above, we obtained the optimized preparation parameters for the ACZTSSe films. The composition of the ACZTSSe film prepared with the optimized preparation process was measured by EDS. The result reveals that the prepared ACZTSSe film has the composition of $(\text{Cu}+\text{Ag})/(\text{Zn}+\text{Sn})=0.87$, $\text{Zn}/\text{Sn}=1.25$ and $\text{Ag}/(\text{Ag}+\text{Cu})=0.84$. This composition is close to the optimum composition for kesterite photovoltaic material.

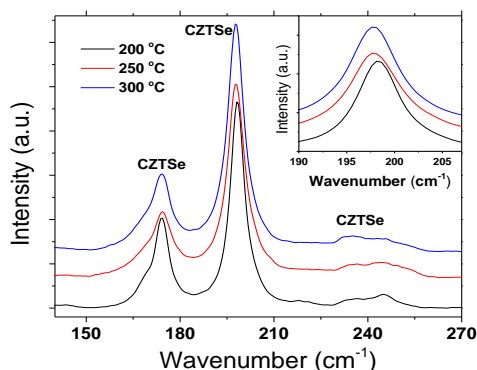


Fig. 5. Raman spectra of the films prepared with different drying temperature.

Based on the ACZTSSe films prepared with the optimized preparation parameters, we fabricated solar cells by depositing CdS buffer layer, i-ZnO layer and Al-doped ZnO layer successively.

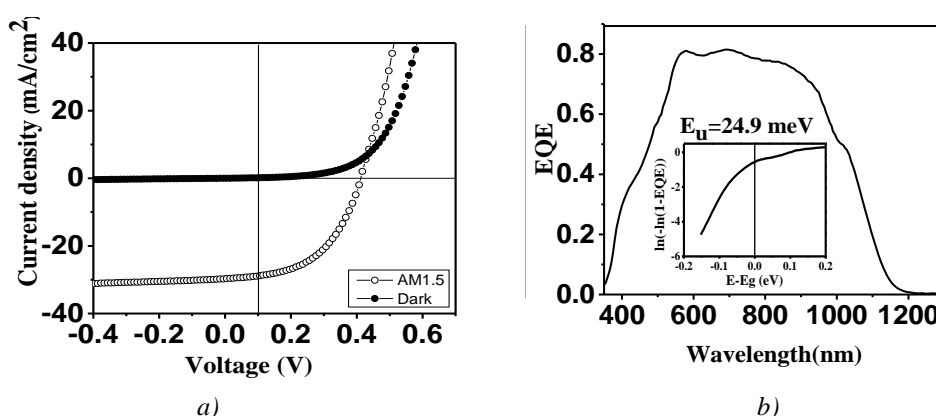


Fig. 6. (a) J-V curves of ACZTSSe solar cell (b) External quantum efficiency (EQE) of ACZTSSe solar cell and the Urbach energy (E_u energy) plotting (insert).

Fig. 6 presents the J-V and EQE results for the ACZTSSe solar cell we prepared. The ACZTSSe solar cells exhibited the best efficiency of 6.3% (on an effective area of 0.43 cm^2 , without antireflection layer) with the open-circuit voltage (V_{oc}) of 407 mV, short-circuit current density (J_{sc}) of 29.7 mA/cm^2 and fill factor (FF) of 52.5%. From Fig. 5(b) we can see the EQE value in the wavelength region between 600 nm to 900 nm is around 80%, indicating the collection of the photo-carrier in the solar cell is well. The E_u energy of the absorber material is extracted from the EQE result as shown in insert image. The result reveals the E_u energy of the ACZTSSe film is 24.9 meV, which is smaller than the reported value in literature [8].

4. Conclusions

In this paper, we used a non-vacuum DMSO-based metal salt method to prepare ACZTSSe thin films. The influence of preparation parameters (selenization temperature and drying temperature) on the morphologies and structures of the films were investigated. It was found the best selenization temperature and drying temperature was $600 \text{ }^\circ\text{C}$ and $250 \text{ }^\circ\text{C}$, separately. The ACZTSSe film prepared with the optimized process was mainly consisted of kesterite phase, no obvious secondary phases were detected. The ACZTSSe film showed uniform and compact morphology, the crystalline grains in the film were in the size of micro-meters. Based on the ACZTSSe films we prepared, solar cells were fabricated which shows efficiencies up to 6.3%.

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