Cu₂ZnSnS₄ solar cells prepared by sulfurization of sputtered ZnS/ Sn/ CuS precursors

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Abstract: Cu₂ZnSnS₄ (CZTS) thin films were grown on Mo-coated Soda-lime-glass (SLG) substrates by sulfurization of sputtered ZnS/Sn/CuS precursors at different temperatures i.e. 560 °C, 580 °C and 600 °C. The effects of sulfurization temperature on the quality of CZTS thin films and solar cells were investigated. The crystal structure, surface morphology, chemical composition, phase purity and surface roughness of CZTS thin films which were fabricated at different sulfurization temperatures were characterized by X Ray Diffraction (XRD), scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS), Raman spectroscopy and atomic force microscope (AFM), respectively. The results show that all CZTS thin films exhibit a polycrystalline kesterite structure and preferred (112) orientation. For the sulfurization temperature of 580 °C, the obtained CZTS thin films are dense and flat with larger grain size. Meanwhile **composition studying** indicates that the fabricated CZTS with single phase is copper poor and zinc rich. Furthermore, the surface roughness of CZTS film is the lowest. Finally, the CZTS solar cells with the structure of SLG/ Mo/ CZTS/ CdS/ i-ZnO/ ITO/Al were fabricated and demonstrated the best power conversion efficiency of 3.59 % when **used** sulfurization temperature was 580°C.

Key words: Cu₂ZnSnS₄ (CZTS) thin films; sputtering; sulfurization temperatures; power conversion efficiency

1. Introduction

Although Copper-indium-gallium-selenide (CIGS) and Cadmium Telluride (CdTe) were regarded as two prominent thin film solar cell materials which have already been commercialized, the element cadmium is toxic,

and tellurium is rare for CdTe^[1]. Besides, selenium is a toxic material, indium and gallium are not abundantly available^[2,3]. In contrast, the elemental constituents of Cu₂ZnSnS₄ (CZTS) are not only non-toxic, but also earth-abundant and inexpensive^[4,5]. Naturally, it is a p-type semiconductor with a high optical absorption coefficient of over 10⁴ cm⁻¹, and has a direct band-gap of 1.5 eV^[6,7] which is the optimal value for single-junction thin film solar cells leading to the detailed balance limiting efficiency of about 32.2 % ($J_{sc}=29.6\text{mA/cm}^2$, $V_{oc}=1.23\text{ V}$, $FF=90\%$)^[8-12]. To date, the reported highest power conversion efficiency (PCE) for pure sulfide CZTS, pure selenide Cu₂ZnSnSe₄ (CZTSe) and mixed sulfide-selenide Cu₂ZnSn(S,Se)₄ (CZTSSe) have reached 8.4 %^[13], 11.6 %^[14] and 12.6 %^[15] respectively. However, the PCE of CZTS solar cells is still lower than that of CIGS (21.7 %) and CdTe (21.0 %)^[16]. Su et al. fabricated Cu₂ZnCdSnS₄ (CZCTS) solar cell with a PCE of 9.24 % by adding Cd into CZTS thin films to form Cu₂Zn_{1-x}Cd_xSnS₄ (CZCTS) thin films with the tunable direct band gap^[17]. Although the PCE of pure CZTS solar cells are much lower than that of CZTSe, CZTSSe and CZCTS solar cells, the development of more environment friendly and large-scale production for CZTS solar cells are still essential because they do not have toxic Se and Cd elements.

Basically, the fabrication techniques of CZTS absorber layer can be classified into two categories: vacuum based and non-vacuum based methods. Vacuum-based fabrication techniques normally include sputtering^[18,19], pulsed laser deposition (PLD)^[20], and thermal evaporation^[21], while the non-vacuum based deposition techniques contain the sol-gel^[4,22], spray pyrolysis^[23], electrodeposition^[24,25] and so on. For the industrialization of solar cells, sputtering method currently is widely used in semiconductor preparation process because it is easy to transfer to large-scale industrial production and to control the composition of thin films. It is well known that the CZTS thin films fabricated by sulfurization of sputtered ZnS/ SnS/ Cu precursors^[26] have been widely investigated. However, the films which were fabricated by sputtering ZnS/ SnS/ Cu precursors peel off easily during the process of high temperature sulfurization due to the compactness of SnS. Besides, to our knowledge, the CZTS films prepared by

sputtering ZnS/ Sn/ CuS precursors have not been reported. In this work, we presented an effective method to produce high quality absorber layers by sulfurization of sputtered ZnS/ Sn/ CuS precursors and mainly investigated the effects of different sulfurization temperatures on the properties of CZTS thin films and the corresponding solar cell performance. Furthermore, the CZTS films prepared under different sulfurization temperatures have been used to fabricate CZTS solar cells with the structure of SLG/ Mo/ CZTS/ CdS/ i-ZnO/ ITO/ Al, and the best power conversion efficiency of 3.59 % was obtained at the optimized sulfurization temperature .

2. Experimental details

2.1. Sample preparation

CZTS thin films were grown on Mo-coated Soda-lime-glass (SLG) substrates by two-stage process: the precursors deposition and sequential sulfurization at different elevated temperatures. The CZTS precursors with 700-800 nm thickness were deposited by radio frequency (RF) magnetron sputtering using ZnS (4 N), Sn (4 N), and CuS (4 N) as the targets, and the sputtering powers were 50 W, 50 W and 50 W, respectively. The SLG/ Mo/ ZnS/ Sn/ CuS deposition order was adopted to fabricate the precursors. Before CZTS precursors deposition, the 1 μm thickness of bi-layer Mo electrode was deposited by DC magnetron sputtering under high work pressure to achieve better adhesion with SLG and then under low work pressure to get better conductivity. The base pressure in the sputtering chamber was evacuated to 5.0×10^{-4} Pa and the rotating speed of substrate was 7 rpm. The sputtering process was carried out at room temperature using Ar as the working gas and the sputtering pressure was 0.3 Pa for ZnS, Sn and CuS. The distance from the target to the substrate was 100 mm. Then, the CZTS absorber layers were formed by sulfurizing ZnS/ Sn/ CuS precursors. The sulfurization process was carried out using the graphite boat with 0.5 g S (5 N) powder and 0.05 g Sn powder, during which the heating rate was 25 $^{\circ}\text{C}/\text{min}$ and the pressure was maintained at 5000 Pa under Ar atmosphere. To study the effects of sulfurization

temperature on the quality of CZTS films, the precursors were heated to 560 °C, 580 °C, 600 °C and held for 15 min, respectively. Finally, the CZTS thin films were taken out when the temperature reached room temperature.

The CZTS film solar cells with the structure of SLG/ Mo/ CZTS/ CdS/ i-ZnO/ ITO/ Al were fabricated. Firstly, a CdS buffer layer (60 nm) was deposited onto CZTS films by chemical bath deposition (CBD) using CdSO₄ as Cd source and thiourea as S source. A solution of CdSO₄ (0.03 M 10 ml) and thiourea (1.5 M 10 ml) in a mixture of ammonia (25 % 40 ml) and deionized water (DIW 330 ml) was heated to 80 °C before dipping the absorber samples inside. During the chemical bath deposition process, the solution was stirred at a constant rate (400 r/min). The CdS thickness was controlled by changing the deposition time. After depositing the buffer layer, the samples were cleaned by ultrasonic cleaner to wipe out CdS colloidal particles with inferior adhesion on the surface, followed by the deposition of 60 nm i-ZnO and 220 nm ITO by RF sputtering. Finally, the cells were completed by evaporating 2 µm Al grid contact.

2.2. Characterization

The crystallographic phase of ZnS-Sn-CuS precursors and the prepared CZTS films was investigated by X-ray diffraction (XRD) using a Rigaku Ultima IV type Diffractometer at 40 KV and 40 mA with Cu-K α ($\lambda=1.5418$ Å) radiation and step size of 0.02° in the range of 2 θ from 20° to 80°. The Raman spectrum of the films was obtained at room temperature in air by using Leica microscopy $\times 200$ performed on a Renishaw inVia where back-scattering measurements were made by a CCD camera, the 514.5nm line of an Ar⁺ laser was used as the excitation source. The morphology of CZTS films was obtained by Supra 55-VP Zeiss field emission scanning electron microscope (SEM) with an operating voltage of 5 KV. The chemical composition of the CZTS films was analyzed by an energy dispersive X-ray analyzer (EDS) (Oxford instrument, Aztec) attached to the SEM, with an acceleration voltage, working distance and emission current of 15 KV, 8.5 mm and 10 µA, respectively. The current-voltage (I-V) characteristics of the solar cells were measured using a solar simulator under global AM1.5

(100 mW/cm² illumination) conditions.

3. Results and discussion

3.1. Structural characterization

Figure. 1. (a) shows the XRD pattern of ZnS/ Sn/ CuS precursors, and the major phases are Cu₆Sn₅, Cu₅Zn₈ and ZnS which are the main intermediates to form CZTS thin films. Figure. 1. (b) shows the XRD patterns of the CZTS thin films sulfurized at different temperatures. The XRD patterns of all CZTS thin films show the distinct (112), (200), (220) and (312) peaks for the kesterite structure (JCPDS 26-0575), and all of the samples have a preferential (112) orientation. In addition, two peaks at $2\theta = 26.5^\circ$ and 32° with low intensity are observed in the diffraction pattern of the films sulfurized at 560 °C and 600 °C which correspond to Cu_{2-x}S (JCPDS 23-0958), and a small peak at $2\theta = 40.5^\circ$ corresponds to Mo (JCPDS 01-1205). The appearance of two low intensity peaks of Cu_{2-x}S phase may be that the reaction is not complete at 560 °C while the CZTS will decompose at a high temperature of 600°C: $2\text{Cu}_2\text{ZnSnS}_4 \rightarrow 2\text{Cu}_2\text{S} + 2\text{SnS} + 2\text{ZnS} + \text{S}_2$.

Table. 1. Shows the full width at half-maximum (FWHM) of the main diffraction peak (112). The intensity of peak (112) increases and the FWHM decreases from 0.331 to 0.303 when sulfurization temperature varies from 560 °C to 580 °C. And the intensity of the (112) peak decreases and the FWHM increases from 0.303 to 0.355 with increasing sulfurization temperature from 580 °C to 600 °C. This indicates the crystalline nature of the CZTS thin films improves with increasing sulfurization temperature. However, when the sulfurization temperature is further increased to 600 °C, the intensity of diffraction peaks slightly weaken and the FWHM increases, implying that the crystalline quality of the sulfurized CZTS thin films is slightly degraded. This may be due to the decomposition of CZTS at high temperature.

Table 1 The relation of FWHM and sulfurization temperature

sulfurization temperature (°C)	560	580	600
FWHM (°)	0.331	0.303	0.355

General speaking, the XRD patterns of CZTS and some secondary phases like cubic ZnS and tetragonal Cu_2SnS_3 are difficult to distinguish due to their similar structure^[27]. So, the CZTS main diffraction peak is easy to overlap with ZnS and Cu_2SnS_3 . In order to identify the phase purity of CZTS, the Raman scattering measurements were performed, as described in Fig. 2. It can be observed that the major peaks at 287 cm^{-1} , 338 cm^{-1} , 374 cm^{-1} are in good agreement with the Raman peaks of the CZTS thin films near $256\text{--}257\text{ cm}^{-1}$, $287\text{--}288\text{ cm}^{-1}$ and $337\text{--}389\text{ cm}^{-1}$ reported by other groups^[28]. No other peaks corresponding to ZnS (350 cm^{-1}), Cu_{2-x}S (473 cm^{-1}) and Cu_2SnS_3 (303 cm^{-1}) are observed at sulfurization temperature of $580\text{ }^\circ\text{C}$, which indicates that the CZTS presents a good quality with single phase^[29]. However, for the CZTS films sulfurized at $560\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$, the corresponding Raman spectra present the weak peak of Cu_{2-x}S (473 cm^{-1}), which is in good agreement with the XRD patterns above. Besides, Raman spectra reveal the presence of MoS_2 with a weak peak at around 410 cm^{-1} when the sulfurization temperature is $580\text{ }^\circ\text{C}$ or $600\text{ }^\circ\text{C}$, because a high sulfurization temperature can promote S diffusing to the bottom and reacting with Mo to form thick MoS_2 .

3.2. Morphological and compositional analysis

Figure.3. Shows the surface morphology and cross-section SEM images of the CZTS thin films fabricated at different sulfurization temperatures. It can be seen that the grain size of the CZTS films becomes larger with the increasing of the sulfurization temperature from $560\text{ }^\circ\text{C}$ to $580\text{ }^\circ\text{C}$, and the CZTS film shows more smooth, uniform and dense surface without pinholes. Besides, it is clear that the CZTS absorber layer which was sulfurized at $560\text{ }^\circ\text{C}$ has some pinholes and consists of bi-layers: a large-grain top layer and a small-grain bottom layer. This may be because the sulfurization temperature $560\text{ }^\circ\text{C}$ is not enough for CuS, Sn and ZnS to react with S completely

to synthesize the CZTS. In contrast, with the sulfurization temperature increasing to 580 °C, the grains of the CZTS film are intact from top of the film to the surface of the substrate and the diameter of grains is almost equal to the thickness of the film, which is good for fabricating high efficiency solar cells. However, when the sulfurization temperature increases to 600 °C, the CZTS film presents rough surface with some agglomerations and pinholes, Especially, some voids present between absorber and Mo substrate. So, it can be conclude that the sulfurization temperature can not be too high nor too low, if the temperature is too high, the CZTS films will decompose into Cu_{2-x}S , SnS , ZnS and S , which causes some pinholes because of Sn loss. On the contrary, too low sulfurization temperature is unfavorable to the complete reaction. In this study, the best CZTS thin film could be obtained when sulfurization temperature was 580°C.

Table 2 Shows the results of chemical composition analysis using EDS. The EDS analysis of the films sulfurized at 560 °C, 580 °C and 600 °C revealed the changes of elemental content. The chemical composition was affected by sulfurization temperature, the Zn and Sn content decreased with increasing temperature, so the Cu compositional ratio increased slightly. Moreover, the amount of sulfur also increased with increasing sulfurization temperature. All CZTS films were non-stoichiometric. The atomic composition ratios of Cu/ (Zn+Sn) and Zn/ Sn were around 0.82 and 1.18, respectively, when sulfurization temperature at 580 °C. It is in good agreement with the optimum compositional ratios of high-efficiency CZTS solar cells reported to be Cu-poor and Zn-rich (Cu/ (Zn+Sn)=0.85, Zn/ Sn=1.2) ^[30] by others.

Table 2 Sample composition as determined by EDS for the CZTS thin films sulfurized at different temperatures.

sulfurization temperature	560 °C	580 °C	600 °C
Cu (at%)	23.60	21.92	23.65
Zn (at%)	13.89	13.63	12.96
Sn (at%)	10.07	12.56	8.98

S (at%)	52.44	51.89	54.41
Cu/(Zn+Sn)	0.98	0.84	1.07
Zn/Sn	1.38	1.09	1.44
S/(Cu+Zn+Sn)	1.10	1.08	1.19

Figure. 4. Shows the atomic force micrograph of the CZTS films prepared at different sulfurization temperatures. The root mean squared (RMS) roughness of films were 21.5 nm (560 °C), 16.8 nm (580 °C), and 25.7 nm (600 °C), respectively, which indicates that the film sulfurized at 580 °C was smooth and also good for the performance of the solar cells, because it just needs a very thin CdS buffer layer to completely cover the surface of the absorber layer to form a good quality heterojunction.

3.3. The J-V characteristics of CZTS thin-film solar cells

The current density-voltage characteristics of three devices based on the structure of SLG/ Mo/ CZTS/ CdS/ i-ZnO/ ITO/ Al are presented in Fig. 5 and the device parameters are listed in Table 3. It should be mentioned that the active area of all devices is 0.12 cm². It can be observed that all device parameters dramatically improved when the sulfurization temperature was 580 °C, and the corresponding PCE reaches to 3.59 %. However, for CZTS thin film solar cells sulfurized at 560 °C and 600 °C, the open-circuit voltages of them are far lower than that of solar cells sulfurized at 580 °C. The reason is that in both CZTS films annealed at 560 °C and 600 °C there exist some second phases and pinholes which are some leakage paths to limit the voltages. It should be noted that the short-circuit current density of CZTS thin film solar cell sulfurized at 600 °C is also the lowest due to some voids between CZTS and Mo layer. However the short-circuit current density (J_{sc}) and fill factor (FF) of the CZTS (sulfurized at 580 °C) solar cell with the best efficiency of 3.59 % is quite low compared with the champion cell efficiency of 8.4 % in the world. This may be due to a thick MoS₂ layer between CZTS absorber and Mo layer which will cause a high series resistance, and there are some defects in the CZTS and interface, that are bad for

the carrier collection.

Table 3 Photovoltaic parameters of the CZTS solar cells with different sulfurization temperatures.

Cells	PCE(%)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF(%)
CZTS(560 °C)	1.86	560	10.1	33.0
CZTS(580 °C)	3.59	635	13.6	41.9
CZTS(600 °C)	1.19	546	7.32	29.8

4. Conclusions

In this work, we successfully fabricated CZTS films by sputtering ZnS/ Sn/ CuS precursors for the first time, and mainly investigated the effect of different sulfurization temperature on the quality of CZTS thin films, the results revealed that an appropriate annealing temperature is very important to fabricate single phase CZTS thin films with good crystallinity. Too low sulfurization temperature is unfavorable to the complete reaction and too high temperature will make CZTS films decompose into Cu_{2-x}S, SnS, ZnS and S, which causes some pinholes and voids. Finally, the CZTS films prepared under different sulfurization temperatures have been used to fabricate CZTS solar cells. And the obtained highest power conversion efficiencies (PCEs) is 3.59 % corresponding to sulfurization temperature of 580 °C. In a word, the CZTS films prepared by sputtering ZnS/ Sn/ CuS precursors are also hopeful to develop high efficiency of CZTS solar cells by further optimization of fabrication process in the future.

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Figure captions:

Figure. 1. X-ray diffraction (XRD) patterns of (a) precursor and (b) CZTS thin films sulfurized at different temperatures.

Figure. 2. Raman spectra of CZTS thin films sulfurized at different temperatures.

Figure. 3. Surface morphologies and cross-sectional SEM image of the CZTS films sulfurized at different temperatures.

Figure. 4. Atomic force microscope (AFM) of CZTS thin films sulfurized at different temperatures.

Figure. 5. I-V characteristics of the CZTS solar cells with structure of SLG/ Mo/ CZTS/ CdS/ i-ZnO/ ITO/ Al.

The absorber of CZTS thin films sulfurized at different temperatures.