



## Cu<sub>2</sub>ZnSnSSe<sub>4</sub> solar cells with 9.6% efficiency via selenizing Cu-Zn-Sn-S precursor sputtered from a quaternary target



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### ABSTRACT

CZTSSe (sulfur around 1%) absorber was prepared by sputtering on a CZTS target followed by selenization under Ar carried H<sub>2</sub>Se gas. The mechanism of CZTSSe formation was investigated by Ar annealing and selenization of sputtered CZTS precursor. The apparent decomposition temperature of CZTS precursor annealed under Ar atmosphere was between 450 °C and 500 °C. While the temperature that CZTS precursor transformed into high-selenium CZTSSe film annealed under Ar carried H<sub>2</sub>Se gas was determined to be ≤ 400 °C. CZTSSe with single-grain layer was obtained when selenization temperature exceeded 520 °C. By supplying H<sub>2</sub>Se from suitable temperature, the metal components of precursor and resulting absorber were almost the same. The highest efficiency of 9.6% achieved at the optimal temperature of 560 °C.

### 1. Introduction

Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe)-based absorber has been proposed as a potential candidate to replace Cu(In,Ga)Se (CIGS) which is predicted to experience a supply shortage of indium and gallium for terawatt scale [1] or for a long run development. CZTSSe semiconductor shows abundant constituents, low cost as well as the potential excellent photovoltaic properties [2,3]. So far, the record efficiency of CZTSSe solar cells has reached to 12.6% [4].

The process of annealing CZTS precursors sputtered from a quaternary target is a promising approach which is favorable to ensure uniformity of both thickness and performances for large area CZTS absorbers. The precursor containing four constituent elements exhibits intermixed and uniform distribution of each element [5], reducing long-distance diffusion for homogenization. The element Sn bonded in weak kesterite phase is less likely to escape into atmosphere [6,7]. The surface of film is also smooth after annealing. Using this approach, several progresses have been made by optimizing composition and annealing parameters. Adopting the composition in Cu-poor and Zn-rich region, the CZTS solar cell with PCE of 6.48% has prepared by simple single sputtering followed by sulfurization [8]. By optimizing the sulfurization parameters, efficiency 4.04% for CZTS solar cell has gained [9]. Co-sputtering a CZTS quaternary target and ZnS target to adjust composition, efficiency 6% for CZTS solar cell can be achieved (with ZnO nanorod) [10]. By adjusting the relative content of

composition in CZTSe target, efficiency 4.16% for CZTSe solar cell has obtained [11]. Using CZTS target and various ratios of Se/S powder during annealing, CZTS<sub>0.46</sub>Se<sub>0.54</sub> solar cell has exhibited the highest efficiency of 6.9% [12].

Despite all this, large grains for polycrystalline absorber are also desired due to the reduction of potential defects at grain boundary [13]. Inspired by fabrication of CZTSe absorber by selenizing quaternary CZTS nanocrystals [14] and binary and ternary nanocrystals [15], a driven force from sulfide-to-selenide transition would enhance grain growth during selenization. This is also observed in the process of selenizing CZTS precursor using selenium powder. However, the appearance of Cu<sub>2-x</sub>Se and the increase of carrier concentration are observed after selenization, resulting in poor performance [16].

In this work, we adopted Ar carried H<sub>2</sub>Se gas as selenium source due to the advantages of highly active selenium atoms and easy control of Se partial pressure and when to supply H<sub>2</sub>Se. CZTSSe absorber was prepared by sputtering on a CZTS target followed by selenization under Ar carried H<sub>2</sub>Se gas. The mechanism of CZTSSe formation was systematically investigated by Ar annealing and selenization of sputtered CZTS precursor. By optimizing selenization temperature using a fixed composition, a highest efficiency of 9.6% for CZTSSe solar cells has achieved.

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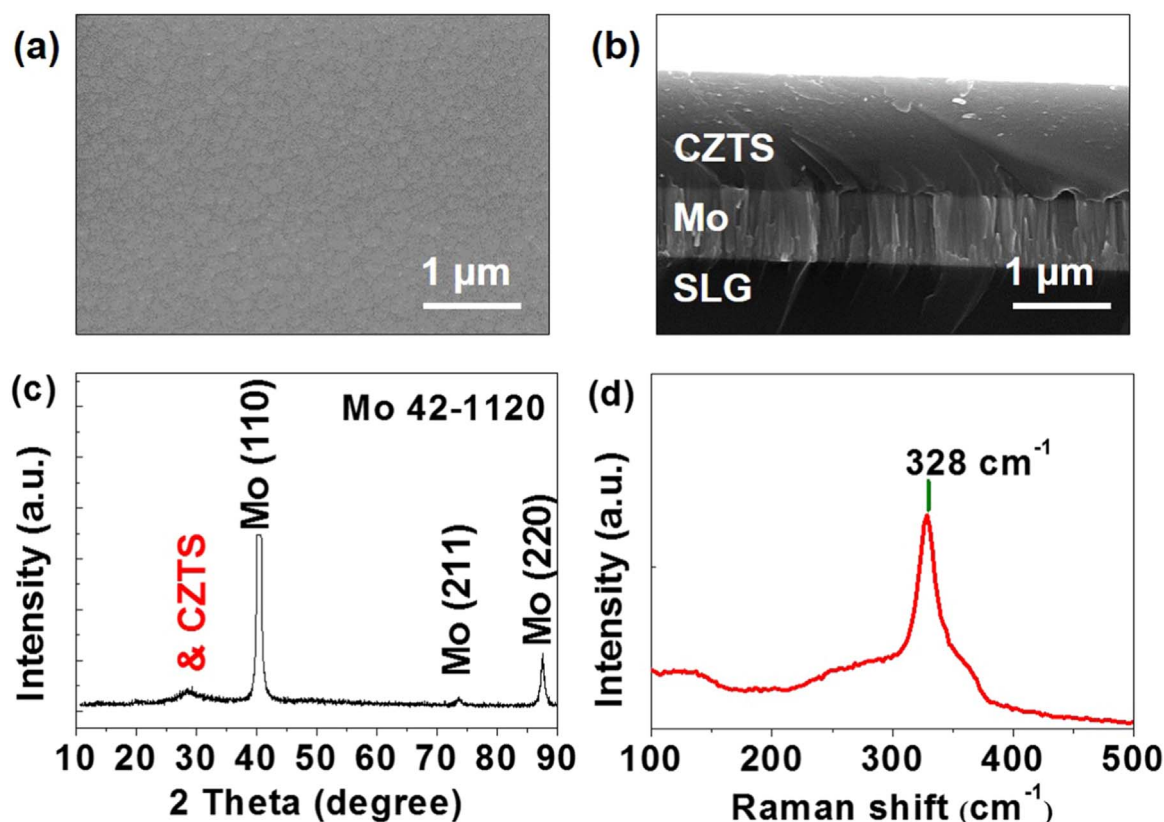


Fig. 1. SEM images of the surface (a), cross-section (b), XRD pattern (c) and Raman spectrum (d) of CZTS precursor.

## 2. Experimental

### 2.1. Preparation of films and solar cells

CZTS precursors were deposited on  $1'' \times 3''$  Mo-coated soda lime glass by sputtering a quaternary CZTS target with purity of 99.99% (Cu:Zn:Sn: S = 1.8:1.1:0.9:3 at%). The power density and deposition rate during sputtering were  $0.85 \text{ W/cm}^2$  and  $15 \text{ nm/min}$ , respectively. The substrate was not heated during deposition.

The CZTS precursors were then annealed in the following process. (a) Annealing under pure Ar gas. Temperatures of  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $450^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $560^\circ\text{C}$  were selected. (b) Annealing under Ar carried  $\text{H}_2\text{Se}$  gas. Temperatures of  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $480^\circ\text{C}$ ,  $520^\circ\text{C}$  and  $560^\circ\text{C}$  were selected. The CZTS precursors were placed in a quartz box ( $30 \text{ cm} \times 30 \text{ cm}$ ) that was in a sealed vacuum chamber. In both processes of (a) and (b), pure Ar gas with pressure of 100 mbar at room temperature ( $\sim 25^\circ\text{C}$ ) was first flowed into chamber before heating to slow the loss of possible volatile species. The heating rate of substrates was  $10^\circ\text{C/min}$ . For annealing processing (b), additional supply of selenium would begin from  $300^\circ\text{C}$  by inletting 30 vol%  $\text{H}_2\text{Se}$  in Ar gas with a flow rate of 20 sccm without outlet. Samples were kept at the selected temperature for 30 min. Afterwards, the supply of selenium would stop and the samples would cool down naturally with the annealing chamber.

After selenization, samples were followed by 50 nm CdS by chemical-bath deposition and 50 nm i-ZnO/400 nm AZO layer from sputtering, using our standard processing [5]. Total area of devices was  $0.30 \text{ cm}^2$  defined by mechanical scribing, which was also the active area due to no metallic grids. No antireflective coating was used.

### 2.2. Characterization

The microstructures of CZTSSe films were characterized by x-ray diffraction (XRD, DMAX 2500 V) with Cu K $\alpha$  irradiation ( $\lambda = 0.15418 \text{ nm}$ ) and Raman scattering spectroscopy (Raman, LabRAM HR

Evolution) with laser wavelength of 532 nm. The morphologies were observed by field emission scanning electron microscopy (FE-SEM, MERLIN VP Compact). The chemical compositions were measured by x-ray fluorescence (XRF-1800, SHIMADZU). The detection area of XRF was about  $1 \text{ cm}^2$ . Current-voltage characterization was performed using a  $6'' \times 6''$  solar simulator from Newport (with simulated AM 1.5 G illumination, calibrated by Si standard solar cell) and a Keithley 2400 source meter. External quantum efficiency (EQE) was performed using a QT500 AD quantum efficiency testing system (Crow Tech Corp.) with a xenon light source, a monochromator and lock-in amplifier.

## 3. Results and discussion

### 3.1. Characterization of CZTS precursor

As a reference for annealing sample, CZTS precursor is analyzed. The CZTS precursor is of a flat and uniform surface and a dense packing in the cross section without void and particles in the film as shown in Fig. 1(a) and (b). Fig. 1(c) and (d) show the XRD pattern and Raman spectrum, respectively. In the XRD pattern, a weak peak of diffraction locates at  $28.66^\circ$ . A main Raman peak at  $328 \text{ cm}^{-1}$  is observed in Raman spectrum. These two features slightly deviate from the standard pattern of CZTS phase. XPS data in our previous work supports that these two features are from CZTS phase [6]. Such features of weak and broad peak, and a slight shift of peak position are suspected to be caused by weak crystallization.

### 3.2. CZTS precursor annealed under Ar atmosphere

$\text{H}_2\text{Se}$  is highly toxic and active (corrosive) when it is using during selenization. A principle is to minimize total amount of  $\text{H}_2\text{Se}$ . For this issue, the temperature starting to supply  $\text{H}_2\text{Se}$  is important as well as volume percent. When  $\text{H}_2\text{Se}$  is continuously supplied from room temperature, the total  $\text{H}_2\text{Se}$  amount would increase. While it is supplied

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