

# An investigation on phase transition for as-sputtered $\text{Cu}_2\text{ZnSnSe}_4$ absorbers during selenization

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## ABSTRACT

The pure kesterite CZTSe absorbers are vital for CZTSe solar cells. However, the secondary phases such as Zn-Se, Cu-Se, Sn-Se and Cu-Sn-Se, which are almost harmful to CZTSe solar cells, often appear in the CZTSe absorbers. To investigate the phase transition pathways of as-sputtered Cu-Zn-Sn-Se precursors during selenization can provide a basis for the reduction of secondary phases and the preparation of high-performance CZTSe solar cells. In the work, the sputtered Cu-Zn-Sn-Se precursors were annealed in a selenium-containing atmosphere at temperatures from 200 to 580 °C for 30 min. The phase transition pathways were analyzed and presented. Low or high selenization temperatures were unfavorable for CZTSe growth. When the temperature were below 530 °C, the crystallization would be insufficient. Meanwhile, when the selenization temperature were above 560 °C, the CZTSe films would decompose during selenization and degrade rapidly. 530 °C seemed to be a relatively appropriate selenization temperature although the grain size was still not large enough at this temperature. By continuously inletting  $\text{H}_2\text{Se}$  gas during the whole selenization process, CZTSe decomposition could be suppressed even at high temperature of 550 °C. And thus the grain size was improved and CZTSe solar cell with the efficiency of 6.78% was obtained.

## 1. Introduction

Kesterite  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  (CZTSSe) has been considered to be the promising photovoltaic absorber material for thin film solar cells due to the advantages of its high absorption coefficient, earth-abundant, and low-toxicity (Wu et al., 2017; Yang et al., 2012; Feng et al., 2017). To date, the highest power conversion efficiencies (PCEs) for the  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) and CZTSSe solar cells are 11.6% (Lee et al., 2015) and 12.6% (Wang et al., 2014), respectively, which are obviously lower than that of 22.8% (Kamada et al., 2016) for CIGS solar cells. Compared with the parameters of CIGS solar cells, one of the key limiting factors for the CZTSSe solar cells is the large deficit in open circuit voltage ( $E_g/q-V_{oc}$ ). Several possible causes for the  $V_{oc}$  deficit have been proposed, such as the high recombination rate (Haass et al., 2015), the cliff-like conduction band offset (CBO) (Haight et al., 2011), the short minority-carrier lifetime (Repins et al., 2013), and the electrostatic potential fluctuations (Gokmen et al., 2013). High recombination rate has been believed to be related to the secondary phases in absorbers and p-n junction (Jung et al., 2017; Kumar et al., 2015). To figure out the formation of secondary phases during selenization would be helpful to

reduce or eliminate the secondary phases and achieve the pure kesterite CZTSe phase, which is meaningful for the preparation of high-efficiency CZTSe solar cells.

There have been some investigations on the phase evolution pathways from the different precursors of co-electrodeposited (He et al., 2013; Zhang et al., 2013) or sputtered (Jung et al., 2017) metallic Cu-Zn-Sn and Cu-Zn-Sn-S (Mainz et al., 2013) to secondary phases containing kesterite phases. However, there have been few reports about the phase transition process from sputtered Cu-Zn-Sn-Se precursor to kesterite CZTSe absorber during selenization (Jo et al., 2015). The binary and ternary secondary phases such as Zn-Se, Cu-Se, Sn-Se and Cu-Sn-Se are generally temperature dependent during selenization. The secondary phases are very detrimental for the devices. The phase transition pathways have not been thoroughly investigated, and the formation temperatures of secondary phases and the methods of avoiding secondary phases have not been clearly proposed. So the study of phase transition is helpful to improve the quality of absorber and the performance of CZTSe device.

In the work, the effects of selenization temperature on morphologies and phases of CZTSe absorbers were investigated. A Cu-poor and Zn-

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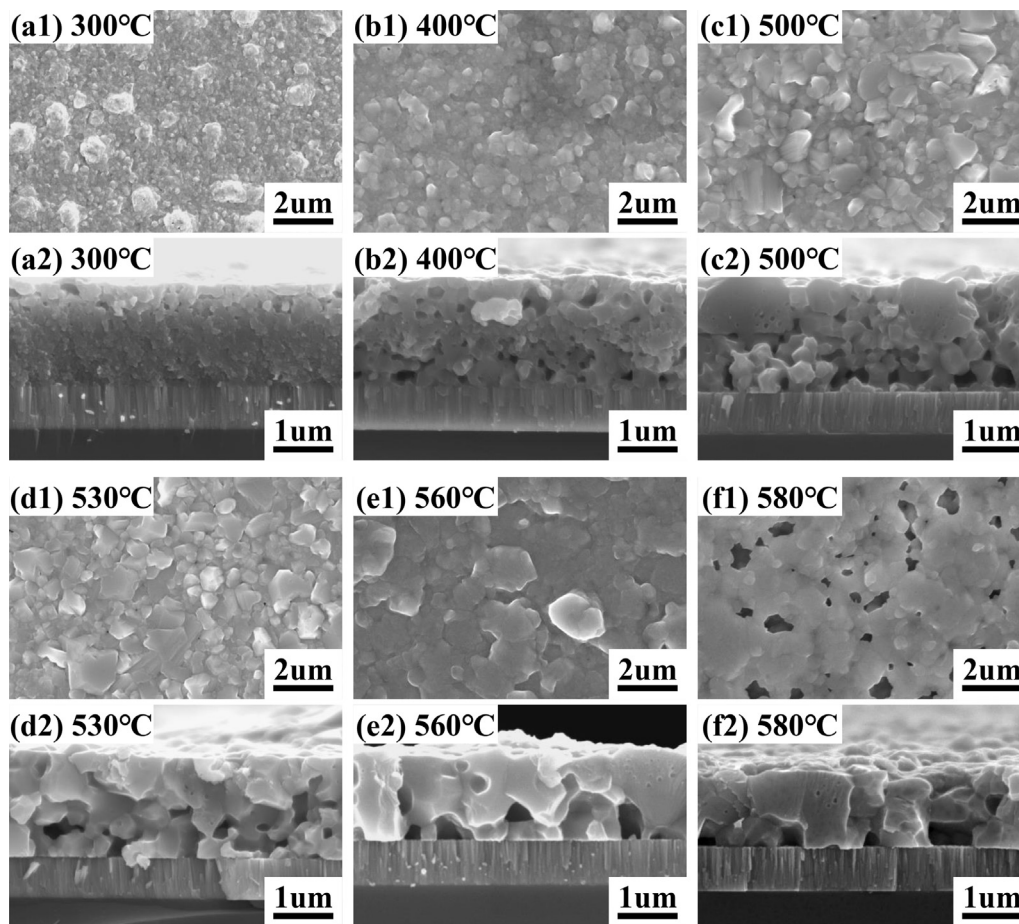


Fig. 1. The surface and cross sectional morphologies of the CZTSe thin films selenized at different temperatures of 300 °C (a1 and a2), 400 °C (b1 and b2), 500 °C (c1 and c2), 530 °C (d1 and d2), 560 °C (e1 and e2), and 580 °C (f1 and f2).

rich CZTSe quaternary ceramic target was fabricated by hot pressing sintering of mixed binary selenide powders. The Cu-Zn-Sn-Se absorbers were prepared by sputtering with the CZTSe target and subsequently annealing in a selenium-containing atmosphere at different temperatures. The CZTSe films were investigated on morphologies, elemental compositions, phase compositions, electrical properties, and optical properties. Based on the obtained results and related analyses, the phase transition pathways of the as-sputtered CZTSe thin films during selenization were proposed. The method of suppressing the decomposition of CZTSe films and reducing secondary phase during selenization was investigated. Finally, a CZTSe solar cell with the efficiency of 6.78% was obtained by suppressing the generation of secondary phase.

## 2. Experimental

### 2.1. Preparation of CZTSe target

The  $\text{Cu}_2\text{Se}$ , ZnSe and  $\text{SnSe}_2$  raw powders of about 100 meshes with purity above 99.99% were mixed with the mole ratio of 0.8:1.1:0.9. Then the mixed powders were put into a nylon jar with  $\text{ZrO}_2$  grinding balls and ball-grinded in a planetary ball mill (QM-3SP4, Nanjing NanDa Instrument Plant) for 2.5 h at a rotating speed of 400 rpm to make the powders thoroughly blended. Subsequently, the mixed powders were put into a mould and applied for hot pressing sintering process. The sintering process was performed at temperature of 600 °C to 700 °C for 3 h, and the pressure was above 30 MPa for 25 min. The size of obtained CZTSe target was  $360 \times 80 \times 5 \text{ mm}^3$ , and the mole compositions of Cu, Zn, Sn and Se were 21.9%, 15.1%, 12.3% and 50.7%, respectively.

### 2.2. Preparation of CZTSe thin films

The clean soda-lime glass (SLG) substrates with the size of  $76 \times 25 \text{ mm}^2$  and a base pressure of  $2 \times 10^{-3} \text{ Pa}$  for sputtering were used. About 800-nm-thick molybdenum (Mo) layer was deposited by middle-frequency magnetron sputtering from Mo target with the power density of  $1.09 \text{ W/cm}^2$ . The CZTSe precursors were deposited onto Mo-coated SLG substrates by sputtering from the Cu-poor and Zn-rich quaternary CZTSe target at room temperature. The working pressure of 0.7 Pa argon (Ar, 99.999%), and the power density of  $0.70 \text{ W/cm}^2$  were selected for CZTSe deposition. Subsequently, the fabricated SLG/Mo/CZTSe samples were annealed in a selenization chamber for 30 min at 200, 300, 400, 450, 500, 530, 560, and 580 °C separately. The related parameters were as follows. The annealing chamber was evacuated to a pressure of  $2 \times 10^{-3} \text{ Pa}$  and heated to the setting temperatures with a heating rate of  $10 \text{ °C/min}$ . Then the chamber was added by inletting Ar diluted  $\text{H}_2\text{Se}$  (1 vol.%) gas for 10 min with a gas flow rate of 600 sccm. After a duration time of 30 min, the samples were cooled down with the chamber naturally. Supplementary experiments were conducted to suppress the possible decomposition of CZTSe phase by continuously inletting the  $\text{H}_2\text{Se}$  gas during the whole heating process. The CdS layer was deposited by CBD. The CBD-CdS process was carried out with 5 mM sulfate cadmium ( $\text{CdSO}_4$ ), 125 mM thiourea ( $\text{CS}(\text{NH}_2)_2$ ) and 1.27 M aqueous ammonia at the bath temperature of 70 °C. Thereafter a 50 nm i-ZnO layer and a 450 nm AZO layer were deposited on all the samples at 200 °C by mid-frequency magnetron sputtering with similar process reported previously (Sun et al., 2018).

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