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# Effect of the stacked structure on performance in CZTSSe thin film solar cells

Li-Ching Wang, Yi-Cheng Lin\*

Department of Mechatronics Engineering, National Changhua University of Education, No. 2, Shi-Da Road, Changhua 500, Taiwan

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## ABSTRACT

This study investigated the influence of stacked structures on the formation of secondary phases, as pertaining to the performance of  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe) thin film solar cells. Absorber layer precursors of  $\text{ZnS}/\text{Cu}/\text{Sn}$  (Sample A) and  $\text{ZnS}/\text{Cu}/\text{Sn}/\text{Cu}/\text{Sn}$  (Sample B) were prepared by sputtering and selenization. Secondary phases of  $\text{Cu}_2\text{SnSe}_3$ ,  $\text{Cu}_{2-x}\text{S}$  and  $\text{ZnS}$  were observed at the bottom of the absorber layer in Sample A, while only  $\text{ZnS}$  secondary phases appeared in the absorber layer of Sample B. The structure of stacked precursors was shown to have a significant influence on the formation of secondary phases as well as the crystal quality of the CZTSSe absorber layer. CZTSSe thin film solar cells were prepared from a structure of  $\text{glass}/\text{Mo}/\text{CZTSSe}/\text{CdS}/\text{ZnO}/\text{Al}/\text{Al}$ . Sample B demonstrated cell efficiency of 2.4%, which is far superior to the 0.75% efficiency of Sample A. The existence of  $\text{Cu}_{2-x}\text{S}$  and  $\text{Cu}_2\text{SnSe}_3$  secondary phases degraded the crystal quality of the absorber layer and increased the number of defects in the crystalline structure.

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## 1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  (CZTSSe) compounds are widely viewed as possible replacements for  $\text{Cu}(\text{In},\text{Ga})_2\text{Se}$  thin film solar cells, due to the non-toxicity and relative abundance of the constituent elements. CZTSSe compounds are direct band gap semiconductors with a high absorption coefficient ( $>10^4 \text{ cm}^{-1}$ ) and band gap similar to CIGS, ranging from 1 to 1.5 eV. Numerous researchers have demonstrated the efficacy of these materials in the fabrication of thin film solar cells. Unfortunately, secondary phases, such as CTS,  $\text{Cu}_x\text{Se}$ ,  $\text{Zn}_x\text{Se}$ ,  $\text{ZnS}$  and  $\text{SnS}$  are also produced during the growth of the CZTS absorber layer, which makes the preparation of single phase CZTSSe film very difficult.

Secondary phases distributed in the CZTSSe absorber layer affect the energy gap of the film as well as the type of conductivity [1,2]. This can limit the open circuit voltage of the resulting solar cell, if the energy gap of the secondary phase is below that of the actual absorber layer, as is the case with  $\text{Cu}_x\text{S}_2$ ,  $\text{SnS}$  and  $\text{Cu}_2\text{SnS}_3$  (CTS) [3]. Secondary phases with a high energy gap can also be problematic [4]. Determining the means to avoid the formation of secondary phases is crucial to the electrical properties and quality of CZTSSe thin films. One study reported that controlling the composition

ratio of the elements is the most effective means of avoiding the formation of secondary phases [5]. Another study reported that avoiding secondary phases depends largely on the ability to control the path of phase transition [5–7]. According to Katagiri and co-workers [8], the order in which pure metal layers of Cu, Zn and Sn are laminated can have a profound influence on cell efficiency, due to changes that occur in the phase sequence during annealing. This would explain why CTS and other secondary phases commonly form, even in cases where the elemental composition is correct.

This study investigated CZTSSe films with variously stacked layers of precursor elements: Sample A ( $\text{ZnS}/\text{Cu}/\text{Sn}$ ) and Sample B ( $\text{ZnS}/\text{Cu}/\text{Sn}/\text{Cu}/\text{Sn}$ ). The objective of this study was to elucidate the crystallization behavior of CZTSSe films and analyze the influence of secondary phases on the performance of CZTSSe thin film solar cells.

## 2. Material and methods

The CZTSSe thin film was deposited using metallic and sulfide precursors. Two sputtering sources were used to grow precursors: RF-sputtering system for  $\text{ZnS}$  and DC sputtering for the growth of metallic layers of Cu and Sn. The CZTS precursor layer was deposited from  $\text{ZnS}$  (99.99%), Cu (99.99%) and Sn (99.99%) at sputtering powers of 150, 70 and 40 W, respectively, at a working pressure of 4 mtorr under ambient Ar. The thin film precursors were prepared on Mo-coated substrates of soda lime glass (SLG). The Mo back

\* Corresponding author. Tel.: +886 4 7232105; fax: +886 4 7211149.  
E-mail address: [ielinyc@cc.ncue.edu.tw](mailto:ielinyc@cc.ncue.edu.tw) (Y.-C. Lin).

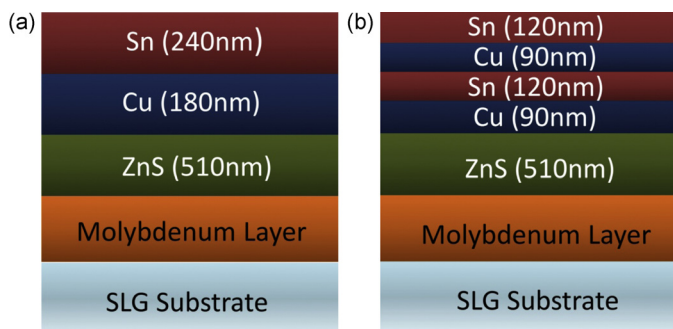


Fig. 1. Illustration of precursor elements in a stacked structure: (a) Sample A (ZnS/Cu/Sn) and (b) Sample B (ZnS/Cu/Sn/Cu/Sn).

contact was prepared by DC sputtering. We investigated two stacks of precursors: Sample A comprising ZnS (510 nm)/Cu (180 nm)/Sn (240 nm) and Sample B comprising ZnS (510 nm)/Cu (90 nm)/Sn (120 nm)/Cu (90 nm)/Sn (120 nm). The thicknesses of the two precursor CZTS layers are approximately 930 nm. Illustrations of the two stacks are presented in Fig. 1. The selenization of precursors for the synthesis of the CZTSSe layers was performed in a tube furnace under an inert atmosphere of Ar. Selenium was provided in the form of selenium pellets disposed with the samples on a graphite box beneath the quartz tube. Annealing was performed at 848 K for 30 min at a ramping rate of 10 K/min.

A field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) was used to observe the microstructure and measure the thickness of the films. We also employed energy-dispersive X-ray spectroscopy (EDX, Hitachi S3000N) attached to the SEM in order to measure the elemental composition at the surface and perform a cross-sectional mapping of the element distribution. X-ray diffraction (XRD, Cu  $K\alpha$ ,  $\lambda = 1.54052 \text{ \AA}$ , BRUKER, D8 Discover SSS) was used to investigate the crystalline structure of the CZTSSe absorber layer. However, the secondary phases of ZnS and CTS have a crystal structure similar to that of CZTSSe, such that the diffraction peaks overlap. Assessing the quality of the film by XRD proved difficult; therefore, further analysis of the secondary phases in the film was performed by Raman spectroscopy (Ramboss 500i Micro-Raman System) using a green laser with a wavelength of 532 nm as the light source. X-ray Photoelectron spectroscopy (XPS, XPS: PHI Quantera, SXM/Auger: AES 650, ULVAC-PHI) was used to provide the depth profiles of the thin film elements.

The solar cell devices were processed by KCN etching (10 wt%) for 10 min followed by chemical bath deposition of an n-type CdS layer. Highly resistive layers of intrinsic ZnO and conductive ZnO:Al were then deposited by sputtering. The structure of the resulting device was SLG/Mo/CZTSSe/CdS/ZnO:Al/Al without  $\text{MgF}_2$  anti-reflection film. Cell efficiency was measured at 100 mW/cm<sup>2</sup> using an AM 1.5 solar simulator.

### 3. Results and discussion

#### 3.1. Influence of structural stacking on microstructure and compositions

SEM images show that the morphology of the CZTSSe absorber films depends strongly on the stacked structure of the precursor elements. Fig. 2(a) and (b) presents SEM cross-section images of the variously stacked layers in the CZTSSe absorber films, represented as Sample A and Sample B. The total thickness of the precursor film was approximately 930 nm. Under the same selenization conditions, the precursor films were grown to thicknesses of 2  $\mu\text{m}$  (Sample A) and 1.8  $\mu\text{m}$  (Sample B). Meanwhile the thickness of the Mo back contact increased during selenization from 800 nm to

1.1  $\mu\text{m}$ . Phase separation was observed in the microstructure of the CZTSSe layers in both samples with incomplete grain growth occurring at the interface between CZTSSe and Mo layers. This resulted in bi-modal size distribution involving equiaxed grains coupled with incomplete grain growth at the bottom of the absorber layer [9]. In terms of overall microstructure, we observed that the grains in the CZTSSe layer of Sample B were larger than those in Sample A when viewed in cross-sections as well as at the interface.

A summary of the elemental composition of the CZTSSe films by EDS analysis is provided in Table 1. The total thicknesses of the stacked precursor layers are same in both samples; however, significant differences were observed in the composition ratios following selenization. The proportion of Zn/Sn in Sample B is lower than that of Sample A and the Cu/(Zn + Sn) ratio is higher. Moreover, Sample A has a lower Sn content and higher Cu/(Zn + Sn) ratio than Sample B. This suggests that the escape of Sn during selenization caused this change in the elemental ratio [5]. According to a previous study, the optimal ratio of elements in a high performance solar cells is  $\text{Cu}/(\text{Zn} + \text{Sn}) = 0.8\text{--}0.9$  or  $\text{Zn}/\text{Sn} = 1.1\text{--}1.3$  [10]. In this study, the structure of Sample B approached this ideal value.

Fig. 3 presents depth profiles illustrating the chemical composition of samples selenized at a temperature of 848 K for 30 min, as measured by XPS. The concentration of Sn is low at the surface of Sample A. According to Weber et al. [5], Sn evaporates at temperatures exceeding 627 K. In the vicinity of the molybdenum interface, we observed a considerable increase in the Zn and S content. We speculate that this may be due to the presence of secondary phase ZnS, which has been observed at the molybdenum interface in high efficiency CZTS cells [11]. The content of Cu was approximately 26% at the surface and approximately 30% in the center of the film. This Cu-rich state may be related to the presence of secondary phases containing copper. In Sample B, we observed a significant increase in the Zn and S contents near the molybdenum interface, with Cu and Sn uniformly distributed throughout the film. The concentration of Se was also shown to decrease from the surface to the bottom of Sample B.

#### 3.2. Effect of stacked structure on crystalline structure

To gain a more complete understanding of the phase distribution in CZTSSe films, we performed cross-sectional mapping of each element using EDS, the results of which are presented in Fig. 4. Molybdenum signals are superimposed with sulfur and selenium near the interface. The interfacial layer was identified as  $\text{Mo}(\text{S,Se})_x$  with a thickness of approximately 200 nm. Sample A presented rich Zn and S signals at the bottom of the film, indicating the presence of secondary phase ZnS. The Cu signal in the center and at the surface of the film was less pronounced. We conjecture that Cu compounds exist in the center and at the surface of the film. No differences were observed in the luminance signals of Cu, Sn and Se in any part of the film. In Sample B, signals of zinc and sulfur were observed at the bottom of the film, except that ZnS indicates the absence of other secondary phases. As observed in the SEM images, the small grains at the bottom of the film near the molybdenum interface are comprised of ZnS. It is generally believed that when secondary phases of ZnS exist at the CZTSSe layers, due to it has a wide band gap and usually not a very high conductivity, thus it would not harm the open-circuit voltage of the solar cell [9,12].

Fig. 5 presents XRD results of CZTSSe films in samples selenized at 848 K. The XRD peaks are indexed accordingly to the maximum intensity of (1 1 2), (2 2 0) and (3 1 2) phases positioned at  $2\theta = 27.3^\circ$ ,  $45.7^\circ$  and  $54.2^\circ$ , respectively. These findings are in good agreement with the CZTS and CZTSe in figures provided by the Joint Committee on Powder Diffraction Standards. The diffraction peaks of ZnS,  $\text{Cu}_2\text{SnS}_3$ , and other secondary phase overlap those of CZTSSe and cannot therefore be differentiated by XRD [13]. Nonetheless, we

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