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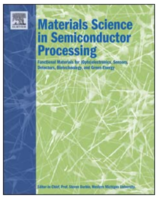

Improving the efficiency of a $Cu_2ZnSn(S,Se)_4$ solar cell using a non-toxic simultaneous selenization/sulfurization process

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ABSTRACT

This paper proposes a simple non-toxic simultaneous selenization/sulfurization process to improve cell efficiency in $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells with the aim of modulating the S/(S + Se) ratio. Experiment results show that the S content in the thin film increases with the S/(S + Se) ratio, and the S content on the surface is higher than inside the device when S/(S + Se) ratio ≧ 0.55. Higher S content on the surface results in a V-shaped energy gap profile. The simultaneous selenization/sulfurization process was shown to inhibit the formation of an excessively thick interfacial $MoSe_2$ /$Mo(S,Se)_x$ layer, while enhancing the uniformity of Cu, Zn and Sn distribution in the absorber layer. The Zn/Sn ratio of the CZTSSe absorber layer was shown to decrease with an increase in the S/(S + Se) ratio, thereby increasing the likelihood that secondary phases of $SnSe_2$, CuSn(S,Se), ZnS, SnS and Cu_2SnS_3 will form in the absorber layer. Conductive atomic force microscopy (C-AFM) results revealed that secondary phases of $SnSe_2$ and $Cu_2Sn(S,Se)_3$ on the surface of the film increased the number of leakage current pathways along the grains of secondary phases. The proposed simultaneous selenization/sulfurization method increases device efficiency from 5.2% (conventional non-toxic selenization) to 6.3% when S/(S + Se) = 0.55.

1. Introduction

The constituent materials in CZTS-based solar cells are abundant, and these devices achieve excellent optoelectronic performance [1–5], with power conversion efficiencies reaching 12.6% [6]. Todorov *et al.* [7] achieved efficiency of 9.7% for CZTSSe; however, this required significant quantities of Se + S using a hydrazine-based solution deposition technique, which can be highly toxic and unstable. Performing selenization before sulfurization during the fabrication of ZTS-based solar cells has been shown to increase the energy gap of the absorber layer, thereby increasing the Voc and overall efficiency of the device [8]. The active nature of sulfur makes it difficult to control the phase purity and composition of the absorber layer through the addition of sulfur. Nonetheless, secondary phases of $SnSe_2$, ZnS, SnS and Cu_2SnS_3 are easily formed [9,10]. Duanet et al. [11] reported a hydrazine-based solution deposition technique using a Cu-Zn-Sn precursor followed by selenization and sulfurization; however, the resulting S/(S + Se) ratio was too high. This altered the defect energy level and concentration, thereby reducing carrier collection efficiency. The S/(S + Se) ratio plays an important role in the performance of CZTS-based solar cells with effects on the material structure and energy gap of the resulting CZTSSe thin film [11,12]. Using a sol-gel process to prepare the CZTSSe absorber layer, Su et al. [13] achieved device efficiency of 5.1%. Huang et al.[14] outlined a simultaneous selenization/sulfurization process for use in the fabrication of $Cu(In,Ga)(Se,S)_2$ thin films using a $H_2S/H_2Se/N_2$ hybrid gas. They studied the energy gap of $Cu(In,Ga)(Se,S)_2$ thin film by varying the concentration ratios of H_2S/H_2Se.

No previous study has presented a non-toxic simultaneous selenization/sulfurization sputtering process using Cu-Zn-Sn precursors to enhance the performance of CZTS-based solar cells. Furthermore, no studies have elucidated the influence of the S/(S + Se) ratio on secondary phase leakage in the CZTSSe absorber layer. Our objective in this study was to develop a simultaneous selenization/sulfurization process to enhance the performance of CZTS-based solar cells. Transmission electron microscopy (TEM) and C-AFM were used to analyze the influence of the S/(S + Se) ratio on secondary phase leakage in the CZTSSe absorber layer.

2. Experiment details

In this experiment, a Cu-Zn-Sn metal precursor was deposited on a $2 \times 2\ cm^2$ soda glass substrate with the back contact coated with Mo

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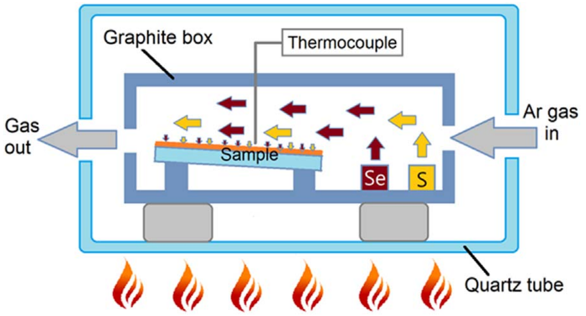

Fig. 1. Schematic diagram showing simultaneous selenization/sulfurization of Cu-Zn-Sn metal precursors with non-toxic Se and S vapors in graphite box within quartz furnace tube.

via direct current magnetron sputtering. The thickness of the Cu-Zn-Sn film was 750 nm. The proportion of the ternary target was Cu:Zn:Sn = 1.8:1.2:1. We used Cu-Zn-Sn ternary target to prepare the CZTSSe absorption layer. Simultaneous selenization/sulfurization was subsequently implemented using non-toxic Se and S vapors in the same graphite box within a quartz tube (as shown in Fig. 1). The concentrations of the Se and S vapors were used to modulate the Se-S weight ratio in the graphite box in order to modulate the S/(S+Se) ratio in the absorber layer, the weight of Se was fixed at 0.25 g, and the parameters were set as shown in Table 1. The temperature was maintained at 500 °C for 20 min until the formation of the CZTSSe absorber layer was complete. The heating rate was 20 °C/min. After absorber layer deposition, the samples were immersed into reaction solution consisting 0.003 M $CdSO_4$, 0.03 M thiourea, 1.6 M NH_4OH at room temperature. Then the bath was heated to 83 ℃ for 17 min by plate stirrer and the CdS thin films were deposited on CZTSSe. Whereupon transparent conductive films of i-ZnO (50 nm) and SnO_2:In (ITO) (350 nm) were deposited by sputtering. Finally, an Al electrode was deposited by sputtering. The structure of the resulting device was as follows: glass/Mo/CZTSSe/CdS/i-ZnO/ITO/Al.

A field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) was used to characterize the morphology of the secondary phases and $MoSe_2$ layer. X-ray diffraction (XRD, JEOL TF-SEM JSM7000F, CuKα, $\lambda = 1.54052$ Å) with $\theta-2\theta$ scanning, and Raman analysis (Jobin Yvon T64000 at an excitation wavelength of 532 nm) were used to analyze the secondary phases that formed on the surface of the CZTSSe films. Grazing incident XRD (GIXRD) revealed a grazing incidence angle of 0.5–10°. A TEM specimen was fabricated using focused ion beam micromachining. Micro-regions were analyzed using a scanning transmission electron microscope (STEM, JEOL ARM200F) with accelerating voltage of 200 kV. Quantitative analysis of the elements in micro-regions (i.e., secondary phases within the CZTSSe absorber layer and their locations) was conducted using an X-ray energy dispersive analyzer (EDS). Current profiles of secondary phases on the surface of CZTSSe film were obtained using C-AFM (NT-MDT Solver P47-SP47) with bias voltage from +500 mV to −500 mV and a scanning area of 10 μm × 10 μm. SIMS (TOF-SIMS IV) was used to investigate the depth profiles of the thin film elements. Extraction voltages were set at 10 and 12.5 keV, respectively. The current of the O^{2+} ions was set to 80 and 120 nA, which impacted the surface of the samples with energies of 5.5 and 8 kV, respectively.

3. Results and discussion

3.1. CZTSSe thin film composition and morphology

Table 2 illustrates the influence of the S/(S+Se) ratios on the composition and morphology of the thin films, including the energy gap as measured using EDS. We controlled the S/(S+Se) ratios at 0, 0.55, 0.70, and 1, respectively, which are used as sample codes for this study. The Zn/Sn ratio decreased with an increase in S content. Cai et al. [15] outlined efficiency enhancement by adding SnS powder during selenization for $Cu_2ZnSn(S,Se)_4$ thin film solar cells and indicated that the tin loss can be restrained by adding S content during post-annealing. Therefore, The Zn/Sn ratio decreased with an increase in S content. Using the HSE (Heyd-Scuseria-Ernzerhof) functional [16], the energy gap in the absorber layer was calculated according to the S and Se content, as follows: 1.0, 1.2, 1.3 and 1.5 eV, respectively.

Fig. 2 presents topographic and cross-section SEM images of the of CZTSSe thin films with various S/(S+Se) ratios. The grain size decreased with an increase in S content due to the inhibition of grain growth by S. As shown in Fig. 2(a) and (d), no obvious signs of secondary phase grains were observed on the surface or in cross-sections of the CZTSe and CZTS samples. Some plate-like grains were observed in some surface regions of CZTSSe 0.55 and CZTSSe 0.70 samples. EDS

Table 1
The details about the Se-S weight ratio in graphite box to modulate the S/(S+Se) ratio in the absorbers.

Sample code	Selenium (g)	Sulfur (g)
CZTSe	0.25	0
CZTSSe 0.55	0.25	0.025
CZTSSe 0.70	0.25	0.05
CZTS	0	0.25

Table 2
Composition, energy gap and $Mo(S,Se)_x$ thickness of CZT(Se,S) thin films with various S/(S+Se) ratios.

Sample code	Zn/Sn	Cu/(Zn+Sn)	(S+Se)/Metals	**S/(S+Se)**	Energy gap (eV)	$MoSe_2$ /$Mo(S,Se)_x$ thickness (μm)
CZTSe	1.21	0.77	1.04	**0**	1.0	1
CZTSSe 0.55	1.04	0.81	1.12	**0.55**	1.2	0.2
CZTSSe 0.70	1.02	0.78	1.07	**0.70**	1.3	0.2
CZTS	0.95	0.67	1.22	**1**	1.5	0.1