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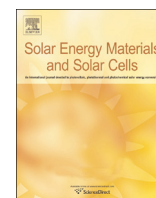
Phase segregations and thickness of the Mo(S,Se)$_2$ layer in Cu$_2$ZnSn(S,Se)$_4$ solar cells at different sulfurization temperatures

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ABSTRACT

The appearance of phase segregations in the kesterite Cu$_2$ZnSn(S$_x$,S$_{1-x}$)$_4$ (CZTSSe) absorber layer and formation of the interfacial Mo(S,Se)$_2$ layer during the annealing process is a challenge and limitation for the inderstrization of highly efficiency and low-cost thin film solar cells (TFSCs). These two factors are effectively controlled by sulfurization temperature. In this study, kesterite CZTSSe thin films were successfully prepared via the sulfurization of co-evaporated Cu–Zn–Sn–Se precursor, which was deposited on Mo-coated glass substrates at sulfurization temperatures ranging from 520 °C to 580 °C. The structure and phase of the sulfurized CZTSSe films were characterized by conventional XRD and Raman analyses. The thickness of the Mo(S,Se)$_2$ layer was estimated based on cross-sectional FE-SEM images. Advanced characterizations, such as STEM images and STEM EDS analyses of the sulfurized CZTSSe films were performed to detect the sulfurization temperature dependent phase segregation and localized fluctuations in the elemental composition of the sulfurized CZTSSe films. The formation of secondary phases was clearly evident at the bottom region in the CZTSSe absorber thin films prepared over sulfurization temperature of 540 °C. The performances of the devices were strongly related to the sulfurization temperature, thickness of the interfacial Mo(S,Se)$_2$ layer and proportion of secondary phases in the kesterite CZTSSe absorber layers. The highest power conversion efficiency was 5.52% and was achieved by the CZTSSe absorber layer prepared at 540 °C (V_{oc}:0.575 V, J_{sc}:18.14 mA/cm^2 and *FF*: 52.94%).

1. Introduction

Kesterite Cu$_2$ZnSn(S$_x$,Se$_{1-x}$)$_4$ (CZTSSe)-based compounds have recenlty attracted interest for photovoltaic (PV) applications in industry fields beacuse these materials feature a suitable and direct optical band gap energy (E_g), high absorption coefficient that exceeds 10^4 cm^{-1} in the visible wavelength region, low cost and non-toxic elements unlike CdTe- and Cu(In,Ga)Se$_2$(CIGS)-based thin film solar cells (TFSCs), which have already been commercialied [1–6]. Many reports of CZTSSe-based TFSCs using vacuum and non-vacuum techniques have been published. The highest recorded efficiency of CZTSSe based TFSCs was 12.6% (E_g=1.15 eV) and was achieved using a hybrid chemical approach [7]. Vacuum-based processes yielded a relatively lower efficiency of 11.6% (E_g=1.0 eV) for CZTSe absorber layers prepared via the selenization of co-evaporation techniques at 590 °C under mixture of Se and N$_2$ atmosphere [8]. In addition, pure sulfide CZTS TFSCs, which feature a relatively wide E_g of 1.5 eV yielded an efficiency of 8.4% when prepared via the sulfurization of a thermal evaporation deposited precursor [9]. Even though the efficiency of CZTSSe-based TFSCs has rapidly improved in recent years, this efficiency significantly lags behind the theoretical efficiency of these materials (Cu$_2$ZnSnS$_4$:32.4% and Cu$_2$ZnSnSe$_4$:31.0% for the single junction condition) [10]. Among the factors that reduce performance of CZTSSe TFSCs, the phase segregation and formation of an interfacial Mo(S,Se)$_2$ layer during the annealing process are critical factors [3,11]. The phase segregation and formation of an interfacial Mo(S,Se)$_2$ layer frequently occur during the annealing
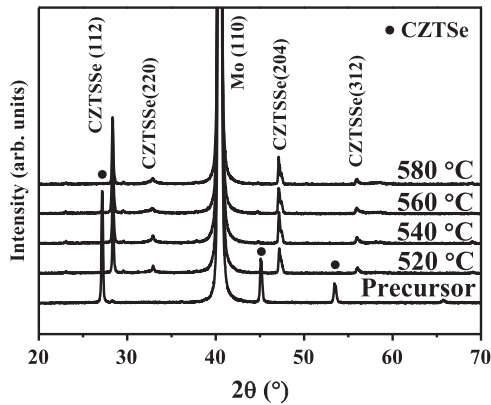
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Fig. 1. X-ray diffraction patterns of the precursor and annealed thin films prepared at different sulfurization temperatures.

Fig. 2. Raman spectra of the precursor and annealed thin films prepared at different sulfurization temperatures.

process of kesterite CZTSSe thin films under S or Se atmospheres. These phenomena arise because the formation energy of secondary phase and $Mo(S,Se)_2$ compounds is lower than that of CZTSSe-based compounds [3]. Reportedly, CZTSSe-based thin films were previously reported to easily undergo the secondary phase segregation of $Zn(S,Se)$ or $Sn(S,Se)_x$ located at the bottom region between the Mo and CZTSSe layers, which severely reduces the efficiency of the device [9,12,13]. In addition, the volatility that arises upon the heating of Sn and Zn materials presents a challenge for the compositional control of CZTSSe films during sulfurization process [14]. Scragg et al. have reported that the Sn in the surface region is unstable (Sn loss) and that back contact occurred during sulfurization process due to the decomposition of CZTS into secondary phases, such as $Cu_{(1-x)}S_x$, ZnS, and $Sn_{(1-y}S_y)$ (gas phase) during sulfurization process [14,15]. In addition, they have demonstrated an efficiency of 7.9% for a device utilizing a CZTS absorber layer that was prepared via the sulfurization of co-sputtering-deposited metallic precursor thin films from Cu, Zn, and Sn targets under H_2S gas atmosphere and they introduced a thin TiN barrier layer between the Mo and Cu–Zn–Sn–S precursor layers, which improved the back contact stability [13].

In addition, the thickness of the interfacial $Mo(S,Se)_2$ layer in a CZTSSe-based solar cell can affect the device efficiency [16]. The interfacial $Mo(S,Se)_2$ layer results from the sulfurization or selenization process, and the formation of this layer can be avoided by controlling the partial S or Se pressure during the annealing process or inserting a thin metal nitride barrier layer. Shin et al. have demonstrated the effect of the thickness of the interfacial $MoSe_2$ layer on the performance of CZTSe solar cells and the grain size. They showed that the thickness of the $MoSe_2$ layer of CZTSe TFSCs positively correlated and the performance negatively correlated with the selenization temperature [17]. They introduced a very thin TiN barrier layer between the CZTSe and Mo layers to serve as the Se diffusion barrier layer. They could control the thickness of the $MoSe_2$ layer despite the high selenization temperature to reach an efficiency of 8.9% [17]. More recently, one possible solution for these difficulties in the CZTSSe TFSC has been reported by Li et al. They demonstrated the controllable thickness of $MoSe_2$ in CZTSe absorber layer though alloying process in the metallic precursor (so called soft annealing), which acts a temporary Se diffusion barrier and they fabricated the 8.7% efficient CZTSe TFSCs [18]. These findings collectively contribute to the improved efficiency of kesterite-based TFSCs. However, the most of abovementioned researches have characterized by X-ray diffraction, Raman spectroscopy, Auger electron spectroscopy, and energy-dispersive spectroscopy characterization tools have been used to check the secondary phases in the CZTSSe absorber thin films [19]. The results of these analyses are controversial because of the
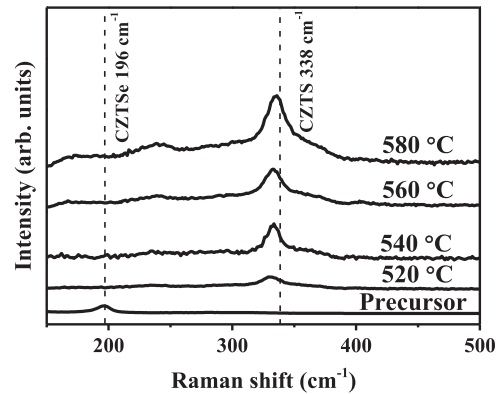
crystallographic similarity of the kesterite and secondary phase and overlapping of their EDS peaks between Mo and S elements at large area. One strong analysis method to solve above-mentioned problems is transmission electron microscopy (TEM) characterization. In particular, the scanning TEM (STEM) characterization method have merits such as easy detection of location of the segregated secondary phase in the absorber layer and information about microstructures, location of each element, chemical, interface, and grain boundaries characterization [19].

We have firstly reported the detailed systematic study on the phase segregation, grain growth, void formation and thickness of $Mo(SSe)_2$ layer though STEM characterization in the CZTSSe solar cells under different sulfurization temperatures and relationship between solar cell parameters and both of secondary phases and thickness of $Mo(SSe)_2$. Kesterite CZTSSe thin films were prepared via the sulfurization of co-evaporation-deposited Cu–Zn–Sn–Se precursor thin films using a rapid thermal annealing (RTA) process. The sulfurization temperature was systematically varied from 520 °C to 580 °C to assess the phase segregation, the interfacial $Mo(S,Se)_2$ layer, and the performance of kesterite CZTSSe TFSCs. A STEM analysis was conducted to clearly distinguish the secondary phase and CZTSSe compounds and precisely observe the thickness of the interfacial $Mo(S,Se)_2$ layers. The collective contribution of all of these parameters to the CZTSSe device performance is further discussed.

2. Experimental details

The Cu–Zn–Sn–Se precursor thin films were prepared on Mo-coated glass substrates using the co-evaporation technique at a substrate temperature of 100 °C. Mo thin films with 1 μm thick were prepared using the DC sputtering technique at room temperature. Four sources of elemental Cu, Zn, Sn, and Se from effusion cells were co-evaporated on substrates for 1 h at a substrate temperature of 100 °C. The S powder (0.04 g) and precursor thin films were placed in a graphite box (volume ~12.3 cm³), which was then placed in a tubular RTA system. The co-evaporated Cu–Zn–Sn–Se precursor thin films were annealed under an Ar+S vapor atmosphere. The sulfurization temperatures were varied from 520 °C to 580 °C at an interval of 20 °C for 20 min. The ramping rate of RTA process is 10 °C per second. After the annealing process, the annealed thin films were cooled naturally for 30 min.

The CZTSSe TFSCs were fabricated to have an SLG/Mo/CZTSSe/CdS/i-ZnO/AZO/Al structure. Per our standard protocols, we prepared a 60 nm thick CdS buffer layer using the typical chemical bath deposition method, and 50 nm thick i-ZnO/400 nm thick AZO