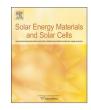Contents lists available at ScienceDirect

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Effects of a pre-annealing treatment (PAT) on Cu$_2$ZnSn(S,Se)$_4$ thin films prepared by rapid thermal processing (RTP) selenization

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ABSTRACT

In this study, CZTSSe precursors (Se/Cu/SnS/ZnS) were deposited by sputtering and evaporation and then annealed without added chalcogen substances in an argon-filled atmospheric chamber using rapid thermal processing (RTP). A low-temperature pre-annealing treatment (PAT) was applied to induce a pre-reaction between Se and Cu/SnS/ZnS. It was found that the PAT leads to the formation of CuSe and Cu$_{2-x}$Se and enhances Se incorporation during RTP chalcogenization. Scanning electron microscopy (SEM), X-ray diffractometry, Raman analysis and scanning transmission electron microscopy with energy dispersive spectroscopy (STEM-EDS) were applied to investigate the differences between the absorber with the PAT and the one without the PAT. Better morphologies on the surface and in the cross section were obtained for the CZTSSe absorber annealed using the PAT compared with the absorber annealed without the PAT. Both absorbers showed nearly pure kesterite phases in their upper regions, as confirmed by Raman analysis. However, STEM-EDS maps revealed that when the absorber was prepared without the PAT, Zn- and S-rich secondary phases and voids were easily formed near the back contact. The electrical characteristics and efficiencies of the CZTSSe thin films showed drastic changes; the CZTSSe solar cell without the PAT showed no diode response, but the cell with the PAT showed an efficiency of 6.77% with an open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) of 376 mV, 31.39 mA/cm^2 and 57%, respectively.

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1. Introduction

Thin-film solar cells based on Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) are currently some of the most promising solar cells. Their advantages compared with the more developed p-type semiconductors, such as CdTe and Cu(In,Ga)Se$_2$ (CIGS), are that the compounds used in CZTSSe solar cells are inexpensive, earth-abundant, and non-toxic [1]. CZTSSe is a p-type semiconductor that has a kesterite structure, which is derived from a chalcopyrite structure [2]. This thin-film semiconductor has a tunable bandgap in the range of 0.99 eV [3] to 1.51 eV [4], depending on the selenium and sulfur contents.

Furthermore, the CZTSSe thin-film absorber has an approximate absorption coefficient greater than 10^4 cm^{-1} in the visible range.

Many methods have been employed to fabricate CZTSSe absorbers, e.g., thermal co-evaporation [1,4–8], sputtering [9–12], co-sputtering [13,14], pulsed laser deposition [15], electrochemical deposition [16], chemical vapor deposition (CVD) [17], the sol–gel method [18–20] and nanoparticle synthesis [21–23]. An efficiency of 12.6% has been achieved in solar cells using a CZTSSe absorber layer fabricated using a non-vacuum process [24]. However, the best conversion efficiency for a vacuum-processed Cu$_2$ZnSnSe$_4$ (CZTSe) solar cell device achieved to date is 9.7% [25]. In addition, some critical limitations remain, including control of the secondary phase formation, a narrow range of homogeneous compounds, characterization of the absorber [1], and decomposition during thermal annealing [26]. To overcome these limitations, modification or improvement of the fabrication method is a useful approach for creating higher-quality absorber layers for CZTSSe-based solar cells. A higher-quality absorber layer may also improve the efficiency of CZTSSe thin-film solar cells.

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Although there are a variety of possible methods that could be used, a two-step process is a reasonable approach to produce a good-quality absorber and a high conversion efficiency in thin-film solar cells. A two-step process means that the precursors are made first using a specific fabrication method; then, thermal annealing is subsequently performed [3,9,27]. Guy Brammertz et al. reported the fabrication of a CZTSe absorber using pure H_2Se gas as the selenium source annealed at 450 °C [9]. Shin et al. and Ge et al. supplied H_2S gas in a furnace as the sulfur source to produce CZTS thin-film absorbers at various temperatures and annealing times [10,13]. Some research groups used sulfur powder as the sulfur source [14,28]. These two-step fabrication methods show reasonable quality and performance in solar cells and are profitable for commercialization and mass production. The rapid thermal processing (RTP) of stacked elemental layer precursors as another two-step fabrication method is very promising and has many advantages: RTP generally uses low cost Se films as the chalcogen reactant instead of toxic H_2Se gas, which requires high installation costs. Additionally, the processing time is relatively short compared with the common gas-based annealing process. Although many successful studies of the RTP selenization of Se/stacked elemental precursor structures have been reported in the traditional CIGS thin-film solar cell field, to the best of our knowledge, there has been only one report that addressed the RTP selenization of Se/stacked elemental precursor structures for the newly emerging CZTSSe [29].

In this study, selenization via RTP was studied, and a novel low-temperature pre-annealing process was proposed for CZTSSe thin-film solar cells. The production of CZTSSe absorption layers from precursors made by sputtering and evaporation and subsequent RTP under atmospheric pressure without any added chalcogen substances were demonstrated. The ability of a pre-annealing treatment (PAT) in the RTP system to provide a better morphology, clear phase formation, and improved electrical properties was investigated. The CZTSSe solar cell with the PAT process exhibited an open-circuit voltage (V_{oc}) of 376 mV, a short-circuit current (J_{sc}) of 31.38 mA/cm^2, a fill factor of 57.36% and a conversion efficiency of 6.77% with an active area of 0.185 cm^2, whereas the cell without the PAT showed no photovoltaic characteristics.

2. Material and methods

The metal precursor layers were deposited by sequentially sputtering 99.99% ZnS, SnS and pure Cu targets onto molybdenum-coated (0.5 μm) soda-lime glass substrates. The deposition of one pure metal and two metal compound target precursors was performed in three steps. The three precursors were deposited under sputtering powers of 150 W, 200 W, and 200 W for the Cu (DC power), SnS (RF power), and ZnS (RF power) targets, respectively, at a working pressure of 3 mTorr under an argon atmosphere. External heat was not provided during the metal deposition. Details of the sputtering processes are thoroughly described elsewhere [28]. Out of the many possible precursor stack orders, in this study, we chose Cu/SnS/ZnS/Mo-Glass, which showed good adhesion and reasonable photovoltaic characteristics in our previous report [30]. After the deposition by sputtering, a 4-μm layer of selenium was deposited by thermal evaporation onto the Cu/SnS/ZnS/Mo stack, which provided a final precursor structure of Se/Cu/SnS/ZnS/Mo-Glass. The 4-μm selenium layer was expected to be quantitatively sufficient to transform the precursor film into a CZTSSe film because the chalcogen element S already existed in the Cu/SnS/ZnS film.

These precursor films were then annealed at atmospheric pressure without any additional chalcogen substances in a small, Ar-filled RTP chamber. The main reaction temperature was set to 600 °C. The samples were heated to 600 °C at a ramping rate of 25 °C per second and then annealed for 20 min. To explore the effects of low-temperature pre-annealing, a pre-annealing treatment (PAT) was optionally applied before the main thermal annealing in the same RTP chamber. Based on preliminary experiments, the PAT was performed at 250 °C for 15 min with the same ramping rate, i.e., 25 °C per second. To determine the effects of the PAT, some samples were pre-annealed at 250 °C for 15 min. Then, the samples were annealed at 600 °C for 20 min, which is adequate for CZTSSe crystallization in the system. Other samples were annealed at 600 °C for 20 min only without the PAT. After annealing, the RTP heating zones were allowed to naturally cool to room temperature. The 4-μm-thick selenium layer and the thermal annealing conditions were selected based on preliminary experiments, which are shown in detail in the supplementary material.

Solar cell devices were fabricated on Mo-coated soda lime glass substrates with annealed CZTSSe films. After the CZTSSe film was formed, a 40-nm CdS film was deposited using the chemical bath deposition (CBD) method as a buffer layer. Then, a 50-nm intrinsic ZnO layer and a 300-nm Al-doped ZnO layer were deposited using RF sputtering. Finally, a 500-nm Al collection grid was deposited on the device using thermal evaporation. An antireflective layer was not added to the solar cells in this study.

The electrical characteristics were measured using a Keithley 2400 source meter unit and a solar simulator to provide simulated 1.5-AM irradiation. The structural properties were measured using an X-ray diffractometer (XRD, Model: Empyrean [Panalytical/Netherlands]) at 40 kV and 30 mA with a Cu source. The surface and cross-sectional morphologies of the thin-films were characterized using high-resolution field emission scanning electron microscopy (HR FE-SEM, Model: SU8020 [Hitachi/Japan]) at 3 kV and 10 μA. Macro-Raman measurements were performed in the quasi-backscattering geometry. To more efficiently detect the secondary phases using quasi-resonance Raman, three different lasers, i.e., the 632.8 nm line of a He–Ne laser, the 514.5 nm line of an Ar ion laser, and the 441.6 nm line of a He–Cd laser, were used as excitation sources. The penetration depths of the lasers are estimated to be less than 200 nm [31]. The laser beam was line-focused with a cylindrical lens to an area of ∼100 μm × 5 mm with a total power of ∼20 mW. The scattered light was filtered by a pair of holographic edge filters and then dispersed by a Triax 320 spectrometer (JY Horiba). Finally, the signal was detected with a thermoelectrically cooled back-illuminated charge-coupled-device detector array. The element concentration profiles of the thin films were analyzed by energy dispersive spectroscopy (EDS) using scanning transmission electron microscopy (STEM, Model: HF-3300 [Hitachi/Japan]).

3. Results and discussion

Generally, the thermal annealing process for thin-film absorbers is performed in one step in a furnace at high temperatures. A variety of reactions and secondary phases are produced while increasing the temperature or maintaining thermal annealing at high temperatures. In the case of our precursor system, i.e., Se/Cu/SnS/ZnS/Mo-Glass, selenium tends to be easily evaporated during the thermal annealing process because the melting temperature of selenium (221 °C) is significantly lower than that of the other substances involved. Severe selenium loss occurs when the temperature is increased. Selenium loss due to evaporation at high temperatures must be managed to obtain well-crystallized CZTSSe thin films. Therefore, a method to retard selenium evaporation might be very helpful for the production of CZTSSe absorbers. To transform Se into a relatively non-volatile species, we intentionally