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Effect of pre-annealing on $Cu_2ZnSnSe_4$ thin-film solar cells prepared from stacked Zn/Cu/Sn metal precursors

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ABSTRACT

The effects of pre-annealing the stacked metallic precursor (Zn/Cu/Sn/Mo/glass) on the structural and morphological properties of the resultant $Cu_2ZnSnSe_4$ (CZTSe) thin films and their device properties were investigated. The crystalline quality and morphology of the CZTSe thin films were enhanced by the pre-annealing treatment. The pre-annealed CZTSe solar cells showed an improved conversion efficiency η of 7.02% compared with those that were not pre-annealed (η=5.65%). This enhancement in solar cell performance was mainly attributed to an improvement in shunt resistance (R_{sh}) from 80 to 150 Ω cm^2, which resulted in improvements in open-circuit voltage and fill factor.

1. Introduction

$Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe)-based chalcogenides are promising absorbent materials for low-cost, low-toxicity, and high-performance thin-film solar cells. CZTSSe thin films have been fabricated using different methods [1–9]. CZTSSe thin-film solar cells showing a high conversion efficiency of 12.6% were recently prepared by hydrazine-based solution processing [9]. However, the hydrazine-based preparation process is explosive, significantly hindering its industrial application [10]. Thus, a two-stage process comprising the deposition of a metallic precursor followed by annealing (selenization and/or sulfurization) is still the preferred method for fabricating CZTSSe thin films because it offers a feasible and cost-effective approach for large-scale production, which has been employed in the manufacturing of Cu(In,Ga)Se_2-based solar cells [11]. The annealing process is a crucial part of the two-stage formation of single-phase, highly crystalline $Cu_2ZnSnSe_4$ (CZTSe). The annealing conditions (e.g., annealing temperature, holing time, and Se pressure) are known to influence the formation of interfacial $MoSe_2$ layers, which is important because the thickness of the $MoSe_2$ layer affects the properties of the resultant device [12,13]. Therefore, a barrier layer is often used between the precursor and Mo electrode to suppress the formation of thick $MoSe_2$ layers under high-temperature (≥550 °C) annealing conditions [14].

In this work, CZTSe thin films were prepared via a two-stage process that first involved selecting a stacked metallic precursor (Zn/Cu/Sn/Mo) without a barrier layer and then followed by post-annealing treatment at low temperature (500 °C). We also pre-annealed the precursor material to improve the crystalline quality and morphology of the resulting CZTSe thin films. The effects of pre-annealing on the CZTSe thin films and their device properties were investigated.

2. Experiments

CZTSe thin films were prepared from a stacked Zn/Cu/Sn/Mo metal (ZCT) precursor followed by annealing treatment in Se and $SnSe_2$ environment. The pure metal precursors were deposited on Mo-coated soda-lime glass substrates at 100 °C using an evaporation method. To investigate the effects of pre-annealing, we prepared the precursors both with and without low-temperature (300 °C) pre-annealing for 10 min in a selenium environment. The both precursor samples were annealed at 500 °C for 15 min in [$SnSe_2$+Se] vapor under N_2 flow to form the CZTSe thin films. The compositions of the annealed CZTSe thin films were determined by electron probe microanalysis (EPMA) using an acceleration voltage of 15 kV (Cu/Zn+Sn=1.03, Zn/Sn=0.99). The crystal structures of the samples were studied by X-ray diffraction (XRD) and Raman spectroscopy. The morphological properties were also investigated by scanning electron microscopy (SEM). XRD measurements were carried out using a PANalytical X'pert XRD system with Cu Kα radiation (λ=1.54 Å) at 45 kV and 300 mA. Raman spectra were measured at room temperature using a Reinshaw inVia Raman microprobe with a laser excitation of 532 nm. SEM

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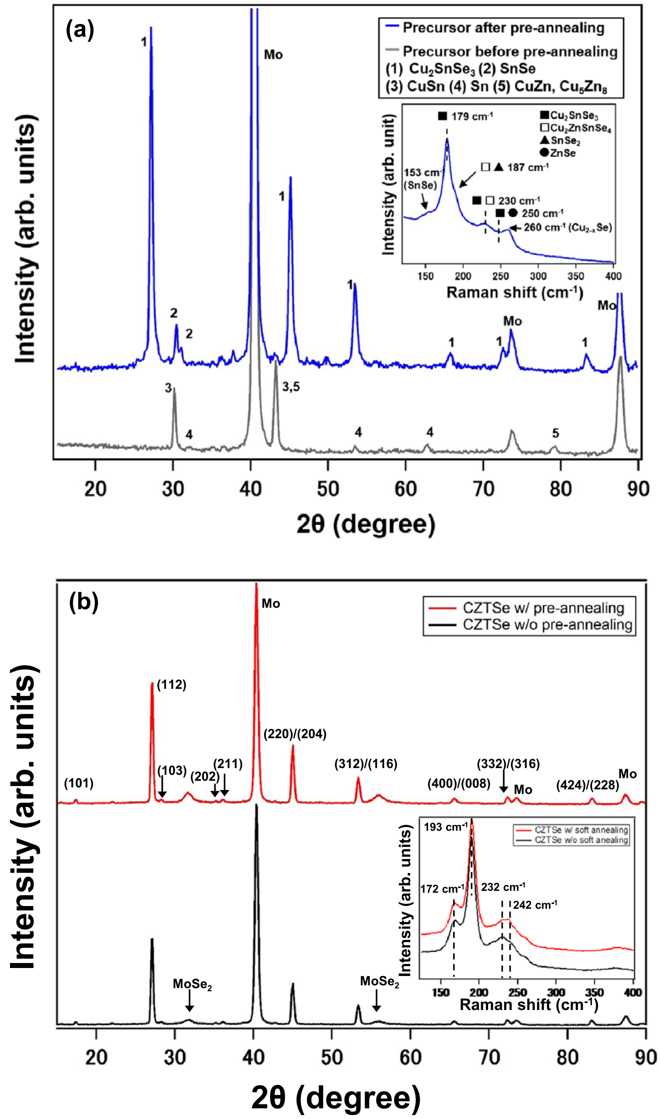

Fig. 1. XRD patterns of (a) the precursor before and after pre-annealing and (b) CZTSe thin films with and without pre-annealing. The inset shows Raman spectra of the precursor after pre-annealing in (a) and CZTSe thin film with and without pre-annealing in (b).

measurements were conducted at an electron beam acceleration of 5 kV (Hitachi S-4800II). CZTSe solar cells with glass/Mo/CZTSe/CdS/i-ZnO/ZnO:Al/Al-grid structures were fabricated without the use of an antireflection coating. The photovoltaic parameters of the solar cells were measured under AM 1.5 G illumination (100 mW/cm^2).

3. Results and discussion

The XRD patterns of the ZCT precursors before and after pre-annealing (Fig. 1(a)) indicate significant differences between the crystal phases in the two precursors. The as-grown precursor consisted of a metal element (Sn) and binary Cu–Sn and Cu–Zn alloy phases. The diffraction pattern of the pre-annealed precursor shows peaks of Cu_2SnSe_3 (CTSe, ICDD no. 01-089-2879) and SnSe (ICDD no. 01-075-1843). It is difficult to distinguish between the diffraction patterns of CTSe and those of related selenides such as CZTSe, ZnSe, and $Cu_{2-x}Se$ since their peak positions are similar. Thus, to confirm the phase composition of the pre-annealed precursor, Raman spectroscopy was used as complementary method. The Raman spectra of the pre-annealed precursor (inset of Fig. 1(a)) shows an intense peak at 179 cm^{-1} along with a shoulder at 187 cm^{-1}, corresponding to CTSe and CZTSe phases, respectively [5,15]. Weak peaks at 153 cm^{-1}, 230 cm^{-1}, 250 cm^{-1}, and 260 cm^{-1} are also observed, which are assignable to SnSe, CTSe (and/or CZTSe), CTSe (and/or ZnSe), and $Cu_{2-x}Se$ phases, respectively. These results indicate that CTSe (main phase) coexisted with CZTSe, SnSe, and ZnSe (minor phases) in the precursor pre-annealed at 300 °C, which is in good agreement with previous reports [16].

The XRD patterns of the annealed CZTSe thin films prepared from precursors with and without pre-annealing are shown in Fig. 1(b). The prominent diffraction peaks in both patterns can be well indexed to the tetragonal CZTSe phase (ICDD no. 00-052-868). Compared with the pattern of CZTSe without pre-annealing, the pattern of CZTSe with pre-annealing exhibits increased peak intensity and narrower peak widths. The Raman peaks of both samples indicate the pure CZTSe phase without any secondary phases such as SnSe, ZnSe, $Cu_{2-x}Se$, and CTSe (inset of Fig. 1(b)). Moreover, the Raman spectrum of the CZTSe thin film with pre-annealing shows four characteristic Raman peaks at 172, 193, 232, and 242 cm^{-1}, whereas the spectrum of CZTSe without pre-annealing has only three Raman peaks at 172, 193, and 232 cm^{-1}. For