Effect of pre-annealing on $\text{Cu}_2\text{ZnSnSe}_4$ 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 $\text{Cu}_2\text{ZnSnSe}_4$ (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 ($\eta = 5.65\%$). This enhancement in solar cell performance was mainly attributed to an improvement in shunt resistance (R_{sh}) from 80 to $150 \Omega\text{cm}^2$, which resulted in improvements in open-circuit voltage and fill factor.

Keywords: $\text{Cu}_2\text{ZnSnSe}_4$, pre-annealing, thin film, solar cell

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1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (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 $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cells [11]. The annealing process is a crucial part of the two-stage formation of single-phase, highly crystalline $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe). The annealing conditions (e.g., annealing temperature, holding 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 ($\geq 550^\circ\text{C}$) 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 SnSe₂ 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 [SnSe₂ + Se] vapor under N₂ 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 K α radiation ($\lambda = 1.54 \text{ \AA}$) 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 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/cm²).

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 comparison, a CZTSe thin film with high crystalline quality exhibits four Raman peaks at 170, 192, 230, and 243 cm^{-1} [17, 18]. Thus, the XRD and Raman analyses indicate that pre-annealing the stacked metal precursor facilitated the formation of highly crystalline CZTSe.

Figure 2 shows the surface and cross-sectional SEM images of CZTSe samples with and without pre-annealing. Compared with the CZTSe sample without pre-annealing, the CZTSe sample with pre-annealing shows large, densely packed grains. The grain size of the absorbent layer can affect the performance of polycrystalline solar cells [19] because the recombination rate of photogenerated carriers can be reduced by increases in grain size. In this study, the thickness of MoSe_2 was increased after pre-annealing, and the main crystal phases in the precursor changed from binary alloy (Cu–Sn and Cu–Zn) to ternary chalcogenide CTSe after pre-annealing (Fig. 1(a)). In our previous study, we obtained CZTSe with large, densely packed grains when CTSe and ZnSe bilayers were used as precursors [5]. Therefore, we employed similar conditions in the present study. The improvement in the morphology of the CZTSe film may be related to the formation of an intermediate CTSe phase during pre-annealing.

Figure 3 shows the current density–voltage (J–V) curves (a) and external quantum efficiency (EQE) curves (b) of the CZTSe solar cells with and without pre-annealing. The cell parameters are summarized in Table 1. By the pre-annealing, the efficiency of CZTSe solar cell was significantly improved from 5.65% to 7.02%. The improvement in the solar cell performance can be attributed to the increases in an open-circuit voltage

(V_{oc}) from 0.317 to 0.343 V and in a fill factor (FF) from 49.9% to 56.9%, which in turn are mainly ascribed to the increase in shunt resistance (R_{sh}) from 80 to 150 Ωcm^2 (Table 1). The CZTSe device with pre-annealing exhibited a more densely packed morphology (Figs. 3(b) and (d)) than the device without pre-annealing, which led to the suppression of shunting [20]. In contrast, pre-annealing in ambient Se increased the series resistance (R_s) from 0.4 to 0.6 Ωcm^2 owing to an increase in the thickness of the MoSe₂ layer (from 150 to 300 nm); however, the value of R_s was still quite small compared with that of a CZTSe device with high conversion efficiency (>8%) reported in the literature [14, 17]. In our case, this implies that the performance of CZTSe solar cells with pre-annealing is virtually unaffected by the increased thickness of the MoSe₂ layer. The bandgaps of CZTSe with and without pre-annealing were estimated from the EQE curves to be 0.988 and 0.985 eV, respectively. The pre-annealing treatment did not result in any significant changes in the bandgaps. The EQE curves show low response in the long-wavelength region, indicating significant recombination loss in the bulk and at the back interface due to the small minority carrier diffusion length and/or a narrow space charge region [4].

4. Conclusion

We prepared CZTSe thin films using a stacked Zn/Cu/Sn metal precursor with and without pre-annealing (300°C) followed by post-annealing (500°C). The effects of pre-annealing the stacked metallic precursor on the crystalline quality and morphology of the resultant CZTSe thin films were investigated. The crystallinity and morphology of the CZTSe thin films were enhanced by pre-annealing. Consequently, the conversion efficiency of the CZTSe solar cells produced from the pre-annealed precursor was

improved from 5.65% to over 7%. This improvement in cell performance is related to the improvement in shunt resistance by the pre-annealing treatment.

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References

- [1] Katagiri H, Jimbo K, Yamada S, Kamimura T, Maw WS, Fukano T, et al. Appl Phys Express. 2008;1.
- [2] Buffiere M, Brammertz G, Batuk M, Verbist C, Mangin D, Koble C, et al. Appl Phys Lett. 2014;105.
- [3] Repins I, Beall C, Vora N, DeHart C, Kuciauskas D, Dippo P, et al. Sol Energ Mat Sol C. 2012;101:154-9.
- [4] Kim S, Kim KM, Tampo H, Shibata H, Matsubara K, Niki S. Sol Energ Mat Sol C. 2016;144:488-92.
- [5] Kim KM, Liao KH, Tampo H, Shibata H, Niki S. Appl Phys Express. 2015;8.
- [6] Sun L, He J, Kong H, Yue FY, Yang PX, Chu JH. Sol Energ Mat Sol C. 2011;95:2907-13.
- [7] Guo L, Zhu Y, Gunawan O, Gokmen T, Deline VR, Ahmed S, et al. Prog Photovoltaics. 2014;22:58-68.
- [8] Patel M, Mukhopadhyay I, Ray A. J Phys D Appl Phys. 2012;45.
- [9] Wang W, Winkler MT, Gunawan O, Gokmen T, Todorov TK, Zhu Y, et al. Adv Energy Mater. 2014;4.
- [10] Dun CC, Huang WX, Huang HH, Xu JW, Zhou N, Zheng Y, et al. J Phys Chem C. 2014;118:30302-8.

- [11] Rockett AA. Curr Opin Solid St M. 2010;14:143-8.
- [12] Nishiwaki S, Kohara N, Negami T, Wada T. Jpn J Appl Phys 2. 1998;37:L71-L3.
- [13] Shin B, Bojarczuk NA, Guha S. Appl Phys Lett. 2013;102.
- [14] Shin B, Zhu Y, Bojarczuk NA, Chey SJ, Guha S. Appl Phys Lett. 2012;101.
- [15] Kim KM, Tampo H, Shibata H, Niki S. Thin Solid Films. 2013;536:111-4.
- [16] Wibowo RA, Jung WH, Al-Faruqi MH, Amal I, Kim KH. Mater Chem Phys. 2010;124:1006-10.
- [17] Jeon JO, Lee KD, Oh LS, Seo SW, Lee DK, Kim H, et al. Chemsuschem. 2014;7:1073-7.
- [18] Yao LY, Ao JP, Jeng MJ, Bi JL, Gao SS, He Q, et al. Nanoscale Res Lett. 2014;9.
- [19] Sites JR, Granata JE, Hiltner JF. Sol Energ Mat Sol C. 1998;55:43-50.
- [20] Lin YX, Ikeda S, Septina W, Kawasaki Y, Harada T, Matsumura M. Sol Energ Mat Sol C. 2014;120:218-25.

Figure Captions

Figure 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).

Figure 2. SEM images of surfaces and cross-sections of CZTSe thin films (or devices) with (b, d) and without (a, c) pre-annealing.

Figure 3. (a) **Dark (dashed lines) and light (solid lines)** J–V curves and (b) EQE spectra of CZTSe solar cells with and without pre-annealing. **The inset in (b) shows the estimation of bandgaps of these two CZTSe absorbers from EQE.**

Figure1

Figure2

Figure3

Table

Table 1. Solar cell parameters of the CZTSe solar cells with and without pre-annealing (R_s , R_{sh} , J_0 , and A were calculated light J - V curve using the single diode model).

Sample	Eff. (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	R_s (Ω cm ²)	R_{sh} (Ω cm ²)	A	J_0 (A/cm ²)
w/ pre-annealing	7.02	0.343	35.99	0.569	0.6	150	1.91	2.74×10^{-5}
w/o pre-annealing	5.65	0.317	35.74	0.499	0.4	80	2.62	1.29×10^{-4}