Correlation between soft annealing conditions and structural, microstructural, morphological, and optical properties of CuInS$_2$ thin films prepared by sulfurization of stacked precursor films

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**Abstract**

CuIn$_2$S$_2$ (CIS) thin films were prepared by sulfurization of In/Cu stacked precursor films. Prior to sulfurization the stacked metallic precursors were subjected to the soft annealing in Ar atmosphere at different time (10, 30, and 60 min) and temperature (100 °C and 300 °C). The effect of soft annealing condition on the structural, morphological and optical properties of CIS films was investigated. X-ray diffraction, Raman, and X-ray photoelectron spectroscopy studies showed that the sulfurized thin films exhibited a CIS tetragonal structure with minor secondary phases such as Cu$_2$S and CuIn$_2$S$_4$. The secondary phases were minimized by introducing soft annealed process in the CIS thin films. Void free CIS microstructures have been observed for soft annealed CIS films. The band gap energy of CIS films were increased from 1.37 to 1.5 eV depending on the soft annealing conditions.

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1. Introduction

Chalcopyrite Cu(InGa)$_2$Se$_2$ (CIGS) is touted as being one of the most promising absorber materials for thin film solar cells due to its high absorption coefficient ($\sim 10^4$ cm$^{-1}$), tunable band gap energy, and long-term stability [1–3]. Cu(InGa)$_2$Se$_2$ (CIGS)-based thin film solar cells (TFSCs) have demonstrated over 20% power conversion efficiency (PCE) at laboratory scale (0.5 cm$^2$) using the three stages co-evaporation technique [4]. Intensive efforts have been carried out to achieve the $> 25\%$ PCE for CIGS TFSCs for commercialization process [5]. Among these efforts, the most promising solution has been the realization of tandem structured TFSCs, which have one cell stacked on top of another [6,7]. Each absorber layers in the solar cells have its own band gap energy from 1.0 eV to 1.7 eV [8]. Garcia et al. reported that the theoretical PCE of tandem structured CIGS TFSCs with two series junction cells with different band gap energies under ideal conditions can be achieved up to 42% [9]. Generally, the optical band gap energy of the bottom cell in a tandem structured TFSC is 1.0–1.3 eV, while that of the top cell is 1.4–1.7 eV [7]. From previous literature surveys, the bottom cells in tandem structured TFSCs with a narrow-band gap energy such as CIGS (1.2 eV, ZSW) and CuInS$_2$ (CIS) (1.0 eV, NREL) have already achieved high PCEs of about 20.3% and 14.8%, respectively [4,10]. However, the PCEs of the top cells in tandem structured TFSCs have been much lower than those of the bottom cells because the photo current density resulting from incident light reduced when the band gap energy was wider.

Different materials have shown their potential use as an absorber layer for top cells in tandem structured TFSCs such as CuAlS$_2$, CuGaS$_2$, CuGaSe$_2$, and CuInS$_2$ (CIS). However, these absorber materials have some drawbacks; Al (CuAlS$_2$) oxidizes easily, Ga (CuGaS$_2$ and CuGaSe$_2$) is expensive, and Se (CuGaSe$_2$) is...
toxic that limits their practical use in tandem structured TFSCs [6,11–18]. Among these, CuInS2 (CIS) is much stable and less toxic chalcopyrite, that can be used potentially as absorber for top cell in a tandem structured TFSCs [19,20]. The CIS-based absorber layers can be easily prepared by two-step processes; (i) preparation of metallic precursor and (ii) sulfurization of the metallic precursor in H2S or in Sulfur powder. Although CIS and CIS-based TFSCs indicated good characteristics as top cells in tandem solar cells, CIS-based TFSCs provides the highest practical PCE of 11.4% by the rapid thermal sulfurization of the Cu-In stacked metallic precursor [21]. Recent report demonstrates formation of CIS films with secondary phases and void formation at the substrate interface [22]. Therefore, it is necessary to study the sulfurization conditions such as: sulfurization temperature and time, ramp rate, and source of S to improve the PCE of CIS-based TFSCs.

![X-ray diffraction patterns](image)

**Fig. 1.** X-ray diffraction patterns ((a) 100°C and (b) 300°C) and FWHM value (c) of the CIS absorber thin films prepared at different soft annealing conditions.

It is well known that the microstructure of the absorber layer in a TFSC is strongly related to the PCE [6]. The voids in the interface between the CIS absorber layer and Mo back contact lead to a disturbance in the movement of the carriers generated from light energy, finally photo current reduced in the TFSCs device [6]. On the other hand, the secondary phase, such as CuIn5S8 or CIS–CuAu, in the CIS absorber layer was also strongly related to the PCE because of its meta-stable and inferior structure. There was a lattice mismatch between CIS-chalcopyrite and CuIn5S8 or CIS–CuAu. These lattice mismatches led to a significant distortion of CIS compounds, which caused high series resistance and scattering factors in the absorber films [22]. In addition, the decrease of grain size and increase of grain defect density were observed in the CIS thin film containing CIS–CuAu or CuIn5S8 phase [22]. This secondary of CIS–CuAu phase in CIS thin films interrupt the carrier transport to both electrodes, reducing the current density of CIS-based TFSCs [23]. Recently, several researchers have varied preparative parameters and sulfurization process to prepare phase pure CIS absorber layer with compact morphology. [23,24]. Yan et al. have reported the effect of different metallic stacking types such as Cu/In, Cu/In/In, and In/Cu/In on the properties of CIS thin films and observed that CIS TFSCs prepared by sulfurization of In/Cu/In metallic stack shows the improved performance [25]. Joswig et al. reported the synthesis and characterization of CIS thin films prepared by sulfurization of single phase Cu11In9 metallic precursor. The Cu11In9 metallic precursor was transferred to the Cu16In9 at 307°C due to the In-loss to the volatile In2S compounds [26]. Tsai et al. reported the effects of different sulfurization conditions and precursor stacking types on the properties of CIS thin films and discussed the sulfurization mechanism [27]; (i) Cu-In stacked metallic precursor, (ii) Cu-In alloys, (iii) Cu–CIS–Cu–In alloys structure, and (iv) CuS–CIS structure. However, their study stated the need for a detailed study on

![Raman Spectra](image)

**Fig. 2.** Raman Spectra of the CIS absorber thin films prepared at soft annealing temperatures of 100°C (a) and 300°C (b), respectively.
the microstructure of the absorber layer, which may affect the improvement of the PCE of TFSCs. One promising solution is the sulfurization of CuInS2 and CuInSe2 alloy formatted by annealing of Cu-In stacked precursor because they require less energy to form CIS compounds than the individual Cu and In metallic precursors [27]. This behavior indicates that voids and secondary phases in CIS thin films can be reduced by the sulfurization of soft annealed Cu/In stacked precursors.

The aim of this article is to synthesize the high quality CIS thin film by sulfurization of sputtered Cu/In stacked precursor. The soft-annealing of the metallic stacks have been carried out at different annealing times and temperatures. The relation between soft annealing parameters and the properties of sulfurized CIS films have studied in details. The soft annealing parameters have been optimized to prepare phase pure CIS films with compact morphology.

2. Experimental details

Prior to the stacked precursor thin films deposition, glass substrates were cleaned ultrasonically using acetone, methanol, isopropyl alcohol, and deionized water for 10 min, consecutively. The cleaned substrates were blow-dried using N2 (99.99%) gas, before they were introduced into the sputtering chamber. CIS absorber thin films were prepared by a two step process. In the first step, In/Cu stacked precursor thin films were deposited sequentially on the glass substrates by the DC magnetron sputtering technique using In (99.99%) and Cu (99.99%) metallic targets at room temperature. Before sulfurization, the stacked Cu/In metallic precursors were soft-annealed in Ar atmosphere at 100, 300 °C for 10, 30, and 60 min to improve the adhesion and intermetallic Cu-In alloy. In the second step, the soft-annealed precursor thin films were sulfurized using a commercial furnace by X-ray photoelectron spectroscopy (JMS-7500F, JEOL, Japan) with an Olympus microscope equipped with a 100 × magnification lens in the backscattering configuration. The excitation source was an Ar ion laser, which could operate at 520 nm and 220 mW output powers. The surface morphologies of the thin films were characterized by field emission scanning electron microscopy (FE-SEM, Model: JSM-6701F, Japan). The chemical binding energies of the films were examined by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, ThermoVG Scientific, UK) operated at room temperature. The binding energy in the spectrometer was calibrated using the carbon 1 s line at 285.0 eV. The compositional ratios of the thin films were analyzed by energy dispersive spectroscopy (EDS) attached to the FE-SEM (JMS-7500F, JEOL, Japan). The optical properties of the thin films were measured by UV–visible spectroscopy (Cary 100, Varian, Mulgrave, Australia) operated at room temperature.

3. Results and discussion

The X-ray diffraction patterns of stacked metallic precursor exhibits several peaks due to the Cu, In, and Cu–In alloy phases [JCPDS data file nos.: 89-2838 (Cu/Cub.), 85-1409 (In, Cub.), and 65-0704 (CuIn/Hex.)] without oxidation compounds. The soft annealing of the metallic precursor at 100 °C has shown diffraction peaks corresponding to Cu11In90 and Cu16In11 phases. Further increase soft annealing temperature (300 °C) leads to form only Cu16In11 phase. The stacked metallic precursor were soft annealed at 100 and 300 °C for different times (10, 30, and 60 min) followed by sulfurization at 550 °C. Fig. 1(a) and (b) shows the XRD patterns of sulfurized films soft annealed at 100 °C and 300 °C for different times. Form figure it is clearly observed that, all the samples have shown polycrystalline nature. The peaks can be assigned to (112), (200), (220), (312), and (224) planes of the tetragonal crystal structure of CuInS2 [JCPDS data file no.: 89-6095] without secondary phases. It is noteworthy that, CIS films without soft annealing have preferred orientation along (112) plane. For the films soft annealed at 100 °C, the intensity of (112) plane is increased for CIS film soft annealed at 10 min. With further increase in soft annealing time the intensity of (112) plane decreases [shown in Fig. 1(a)]. On the other hand, the films soft annealed at 300 °C have shown decrement in the intensity of (112) plane with increase in soft annealing time [shown in Fig. 1(b)]. The results clearly indicates the no oxidation and pure metal compounds while those with soft-annealed at 300 °C showed the only CuInS2 phase (shown not here). However, the sulfurized films showed a strong diffraction peak corresponding to (112) plane from the tetragonal CIS structure, regardless of soft-annealing conditions. All the sulfurized CIS thin films prepared at different soft-annealed conditions showed the several diffraction peaks corresponding to the (112), (200), (220), (312), and (224) planes of the tetragonal CIS structure [JCPDS data file no.: 89-6095 (CuInS2/Tet.)], which indicated that the sulfurized CIS thin films were polycrystalline and phase-pure, without secondary phases such as Cu, In, Cu–In alloys, CuInS2, Cu2–xS, 932.1 eV

CIS, 932.9 eV

Without soft-annealed

Without soft-annealed

S, In2S3, In3S2,
and oxidation compounds. The X-ray diffraction analysis of the sulfurized CIS thin films prepared at 100 °C for 10 min showed that the peak intensity for the (112) plane is enhanced as compared to the films without soft-annealing. The intensity decreased with increasing soft-annealed time. On the other hand, the intensities for sulfurized CIS thin films prepared at 300 °C decreased as compared to the films without soft-annealing. They decreased with increasing soft-annealed time. In order to confirm crystallinity of sulfurized CIS thin films, the value of full with at half maximum (FWHM) were calculated using Gaussian fitting. Fig. 1(c) shows the value of FWHM in the sulfurized CIS thin films prepared at different soft annealing conditions. The FWHM value of sulfurized CIS thin films prepared with soft annealing are lower value than that without soft annealing (0.166°). The FWHM value of sulfurized CIS thin films prepared with soft annealing decreased with increasing soft annealing time and temperature. These results indicate the improved crystallinity in the CIS thin films when soft annealing process is carried out. Although the XRD patterns indicated the crystal structures of the sulfurized thin films, they could not be defined because the position of diffraction angle was similar between the tetragonal CIS structure and secondary phase structures such as Cu2−xS, In2S3, and CuIn2S8. Therefore, the crystal structures of the sulfurized thin films were analyzed by Raman and XPS analyses.

Fig. 2(a and b) shows the Raman spectra of the CIS films prepared at soft annealed at 100 °C and 300 °C, respectively. The strong peaks located at 292 cm⁻¹ corresponds to the tetragonal CIS phase, regardless of the soft-annealed condition. The Cu and In based oxidation compounds were not observed regardless of the soft-annealed condition. The sulfurized CIS films prepared without soft-annealing exhibits both CIS–CH peaks at 295 cm⁻¹ with secondary peaks located at 342 cm⁻¹, 360 cm⁻¹, 415 cm⁻¹, 445 cm⁻¹, and 477 cm⁻¹ corresponding to the CuInS2x, Cu1−xS, and Cu2−xS phases, respectively. The weak peak located at 305 cm⁻¹ for the CIS–CuAu(CA) phase was observed from thin film prepared without soft-annealing [22]. The sulfurized CIS films prepared with soft-annealing at 100 °C and 300 °C have shown reduced peak intensities of the secondary and CIS–CA phases, compared to the films prepared without soft-annealing except for the sulfurized thin film that was prepared with soft-annealing at 300 °C for 60 min The sulfurized thin films prepared with soft-annealing at 300 °C for 60 min showed the relatively enhanced peaks due to the CuInS2x and Cu1−xS compounds. The secondary phase peaks from CuInS2x, In2S3, and Cu2−xS for the sulfurized thin films prepared with soft-annealing at 300 °C were relatively reduced, as compared to those for the sulfurized thin films prepared with soft-annealing at 100 °C [6,18].

Fig. 3 shows the high resolution XPS spectra of the Cu 2p core level for the sulfurized thin films prepared at soft-annealing temperatures of 100 °C (a) and 300 °C (b), respectively. A typical survey spectrum of all the sulfurized thin films confirmed the presence of Cu, In, and S from the CIS thin film as well as C from the reference. No formation for metal-oxide binding with Cu–O and In–O compounds was observed regardless of the soft-annealing condition. The CIS films without soft annealing have shown broad binding energy peaks around 932.5 eV corresponding to the Cu 2p3/2 core levels in the Cu2−xS (932.1 eV) and CIS (932.9 eV) compounds, indicating formation of mixed phases [28]. The sulfurized thin films prepared with soft-annealing at 100 °C for 10 min exhibits a strong peak at 932.9 eV corresponding to the

![Cross-sectional view FE-SEM images of the CIS absorber thin films prepared without soft-annealing (a), with soft-annealing at 100 °C for 10 min (b), 100 °C for 30 min (c), 100 °C for 60 min (d), 300 °C for 10 min (e), 300 °C for 30 min (f), 300 °C for 60 min and (g), respectively.](image-url)
Cu $2p_{3/2}$ core level in CIS compounds with no other peaks [28]. However, the sulfurized thin films prepared with soft-annealing at 100 °C for 30 min and 60 min have shown broad peaks corresponding to Cu$_{2-x}$S and CIS compounds. On the other hand, for the films soft annealed at 300 °C have shown decreased intensity of peaks form Cu$_{2-x}$S compound with increase in soft annealing time, shows significant impact of soft annealing for the formation of phase pure CIS. In addition, the binding energy peaks corresponding to In 3d and S 2p core levels were similar, regardless of the soft-annealed condition. The above mentioned XRD, Raman and XPS results indicated that the secondary phases in CIS films were significantly reduced by soft annealing process.

Fig. 4 shows cross-sectional view of FE-SEM images of the CIS thin films prepared without soft-annealing (a), with soft-annealing at 100 °C for 10 min (b), 30 min (c), and 60 min (d), at 300 °C for 10 min (e), 30 min (f), and 60 min (g), respectively. The FE-SEM images of the sulfurized CIS thin films have shown sharp interface between the glass substrate and CIS absorber layer without any indication of an interfacial reaction or formation of any interfacial compounds. The sulfurized CIS thin film prepared without soft-annealing has shown rough morphology with many voids between the glass substrate and the CIS thin films. However, the sulfurized CIS thin films prepared with soft-annealing have shown less voids than that prepared without soft-annealing. The surface morphologies of the sulfurized CIS thin films prepared with soft-annealing at 100 °C were rougher than that prepared without soft-annealing. In particular, 3 μm sized grains have been observed in the sulfurized CIS thin film prepared with soft-annealing at 100 °C for 30 min. The sulfurized CIS thin films prepared with soft-annealing at 300 °C have shown better morphologies than those prepared without soft-annealing and with soft-annealing at 100 °C.

The impact of soft annealing on the composition of CIS films has been evaluated in terms of Cu/In and $S/(Cu+In)$ ratios. Fig. 5 shows the compositional ratios of the sulfurized CIS thin films prepared without and with soft-annealing at 100 °C (a) and 300 °C (b). The compositional ratio of the CIS thin film prepared without soft-annealing deviated from stoichiometry and exhibits Cu-poor (Cu/In=0.78) and metal rich composition ($S/(Cu+In)=0.94$). This behavior was attributed to the high portions of Cu- and In-based secondary phases. The $S/(Cu+In)$ compositional ratio for the sulfurized CIS thin films prepared with soft-annealing at 100 °C increased from 0.94 to 1.01 with increasing soft-annealing time and the Cu/In compositional ratio for the same films were constant ~0.78. On the other hand, the Cu/In and $S/(Cu+In)$ compositional ratios for the sulfurized CIS thin films prepared with soft-annealing at 300 °C increased from 0.78 to 0.85 and from 0.94 to 1.18, respectively, with increasing soft-annealing time. These increases in Cu/In compositional ratio of sulfurized CIS thin films is attributed to the difference in the vapor pressures of the constituent elements of the compounds [18].

Fig. 6 shows the optical absorption coefficients ((a) 100 °C and (b) 300 °C) and the plots of $(ahv)^2$ vs photon energy ($hν$) ((c) 100 °C and (d) 300 °C) of the CIS thin films prepared without and with soft-annealing. The absorption coefficients of the sulfurized CIS thin films were over 10$^4$ cm$^{-1}$ in the visible region, regardless of soft-annealed condition. The absorption coefficient of the sulfurized CIS thin film prepared without soft-annealing showed the highest value in the visible region. This optical behavior was attributed to the roughness of sulfurized CIS absorber thin films. Although the FE-SEM images for sulfurized CIS thin films prepared with soft annealing showed the more rough morphologies than that without soft-annealing. The rough morphologies of sulfurized CIS thin films could be scattered light and then finally absorption reduced. All the sulfurized CIS thin films showed a very sharp absorption edge, attributed to the good homogeneity and size of the grains and low defects such as point defect, stacking fault, and vacancy in the films [18]. The optical band gap energies ($E_g$) of the sulfurized CIS thin films were determined by extrapolating the straight line portion at $α=0$. The $E_g$ in the sulfurized CIS thin film prepared without soft-annealing was ~1.3 eV. The relatively narrow $E_g$ compared to the literature value of ~1.5 eV was attributed to the presence of a secondary phase in the sulfurized CIS thin film. From literature surveys, $E_g$ values of Cu$_{2-x}$S and CuIn$_2$S$_3$ were estimated ~to be 1.2 eV and 1.25 eV, respectively [29,30]. The above mentioned XRD (Fig. 1), Raman (Fig. 2) and XPS (Fig. 3) results indicated that the sulfurized CIS thin film prepared without soft-annealing exhibits secondary phases such as Cu$_{2-x}$S and CuIn$_2$S$_3$. Thus, the narrow $E_g$ was attributed to a secondary phase in the sulfurized CIS thin film. The range of the $E_g$ of the sulfurized CIS thin films prepared with soft-annealing was wider than that of the sulfurized CIS thin films prepared without soft-annealing. The $E_g$ values of the sulfurized CIS thin films prepared with soft-annealing increased with soft-annealing time regardless of the soft-annealed temperature. In particular, the $E_g$ of the sulfurized CIS thin film prepared with soft-annealing at 300 °C for 60 min was ~1.5 eV.

4. Conclusion

CIS absorber thin films were prepared by sulfurization of In/Cu stacked metallic precursors at 500 °C for 1 h. Prior to sulfurization the stacked metallic precursor films were soft annealed at 100 and 300 °C for different annealing time. The soft annealing processes have shown significant impact on the properties of CIS films. The sulfurized CIS thin film prepared without soft-annealing showed the existence of many secondary phases, relatively narrow band
gap energy, and voids between the glass substrate and the CIS absorber layer in the film. The microstructure, secondary phase, and optical properties of the sulfurized CIS thin films were improved after soft-annealing. At the soft-annealing condition of 300 °C for 60 min, the sulfurized CIS thin film showed the best absorption characteristic, no secondary phase, no voids, and suitable optical band gap energy.

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