



Controlled post-sulfurization process for higher efficiency nontoxic solution-deposited $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ absorber thin films with graded bandgaps



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ABSTRACT

A practical way of adjusting post-sulfurization process with variable durations is proposed to improve the cell-conversion efficiency of non-toxic solution driven $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ absorber thin films. The degree of bandgap grading was controllable by changing the sulfurization time from 2 min to 30 min due to the dissimilar distribution of sulfur across the absorber layer. Deeper intensified distributions of Ga and S were responsible for enhancements in the open-circuit voltage and cell-conversion efficiency. A competitive efficiency of ~8.81% for the 10 min-sulfurized CIGSse cell was achieved with other promising parameters, i.e., short-circuit current density of 33.17 mA/cm², open-circuit voltage of 0.496 V, and fill factor of 53.5%, resulting from the improved carrier collection and reduced recombination by the bandgap grading. This improved efficiency corresponds to a ~15.6% enhancement compared to the unsulfurized sample.

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1. Introduction

Thin film solar cells have been extensively investigated as cost-effective alternatives to Si-based solar cells. Among the materials explored, $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe) is considered one of the most promising light absorbers because of its high absorption coefficient of $\sim 10^5 \text{ cm}^{-1}$ and tunable bandgap energy (approximately 1.0–1.6 eV) as a function of the In/Ga ratio [1–3]. These characteristics enable the fabrication of thinner CIGSe solar cells with a thickness of 1–2 μm , compared to $\sim 300 \mu\text{m}$ for crystalline Si solar cells [4]. Recently, a record conversion efficiency of $\sim 22.3\%$ was reported for solar cells with a CIGSe absorber layer [5]. However, the CIGSe layer requires a complex vacuum deposition process, i.e., co-evaporation or subsequent evaporation of CIGSe constituents. Therefore, a simple solution-based approach has been regarded as a promising strategy to avoid processing-related cost issues.

To date, a considerable number of technical approaches using a variety of chemical solutions have been reported for the successful preparation of CIGSe thin films [6–17]. The processing of a hydrazine solution that incorporates dissolved Cu_2S , In_2Se_3 , and Ga_2S_3 has resulted in a high efficiency of 15.2% [11]. However, because of

the toxicity and explosive nature of hydrazine, many research groups have made efforts to replace the solution with nontoxic precursors, but they have had limited success with the conversion efficiency. The nontoxic processes often use pre-synthesized nanoparticles [6–10] or common solutions with dissolved metal salts [11–16] or hybrid solution using both of dissolved precursor and nanocrystals [17]. For example, a high conversion efficiency of 8.6% was reported for $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGSse) absorbers that were fabricated using thioacetic acid as an effective solvent with a suitable sulfur source [13]. Park et al. reported solar cells with a wide-bandgap $\text{Cu}(\text{In,Ga})\text{S}_2$ (CIGS) absorber layer prepared by spin coating of a nitrate-based solution, with a conversion efficiency of 8.28% and a relatively high open-circuit voltage (V_{oc}) of $\sim 0.787 \text{ V}$ [14]. Recently, CIGSse thin films prepared by aqueous spray-pyrolysis using halide-based solutions demonstrated a conversion efficiency of 10.5% [15].

Sulfurization of CIGSe films is known to be an effective way to increase V_{oc} by lowering the valence-band maximum (VBM) [18]. Various techniques of intentional incorporation of sulfur, such as annealing under H_2S flow [18,19], sequential evaporation of In_2S_3 and sulfur after CIGSe deposition [20], and use of ditertiarybutylsulfide [(t-C₄H₉)₂S] vapor with nitrogen gas [21], have been reported with performance benefits. The widening of bandgap energy also reduces carrier recombination in the space-charge

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region (SCR) owing to the formation of deep trap states [22]. The bandgap of a CIGSSe-based absorber film depends on changes in the S/(Se + S) ratio as a result of sulfurization [23]. Solar cells fabricated with a graded bandgap structure, obtained by changing the elemental ratio in the film, are expected to have high efficiency because of effective carrier collection [15,23]. For example, Park et al. successfully obtained an efficiency of ~11.7% for a CIGSSe-based solar cell prepared by simple paste coating and subsequent selenization–sulfurization [24].

This work intends to pursue the enhancement of cell performance by using simple spin coating of non-toxic precursor solutions combined with rapid post-selenization sulfurization of the absorber layer. The uniqueness of this work is to reveal the importance of holding time at the peak temperature of sulfurization, which results in different profiles of graded bandgaps across the absorber layer. The careful control of sulfurization with temperature and soaking time yields a promising absorption state through bandgap engineering. As a result, we demonstrated a ~15.6% increase in conversion efficiency in the resultant solar cells. We assume that this successful example can be applicable to other process-driven systems as an easier solution for better photo-conversion efficiency.

2. Experimental

A common non-toxic solution of $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$ was first prepared for spin coating. The precursors of 1 mmol copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}$; 98% purity, Aldrich, Milwaukee, WI, USA), 0.7 mmol indium acetate ($\text{In}(\text{CH}_3\text{COO})_3$; 99.9% purity, Aldrich, Milwaukee, WI, USA), and 0.3 mmol gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3\text{xH}_2\text{O}$; 99.9% purity, Aldrich, Milwaukee, WI) were completely dissolved in 2-methoxyethanol (99.9% purity, Aldrich, Milwaukee, WI), which was modified with propylene glycol (99%, Duksan, Gyungkido, Korea) as a stabilizer. Monoethanolamine (MEA; 99%, Duksan, Gyungkido, Korea) and diethanolamine (DEA; 99%, Duksan, Gyungkido, Korea) were added to the solution as chelating agents. The precursor solution was stirred using a magnetic bar at 80 °C for 1 h on a hot plate. Spin coating of the solution was carried out on a Mo-coated soda-lime silicate (SLS) glass substrate (thickness: ~1.5 μm) at a speed of 2000 rpm for 25 s. The coated film was dried at 300 °C for 10 min. The coating and drying procedure was repeated 12 times to obtain a target thickness of ~1 μm . The as-deposited precursor layer was selenized at 530 °C for 30 min under a N_2 flow in a quartz tube furnace, where Se pellets were placed in the front of the film sample. Multiple samples were prepared. Finally, the selenized thin films were sulfurized at different temperatures of 450, 475 and 500 °C under a N_2 - H_2S flow. The heating rate to the target temperature was 10 °C/min. The soaking time varied from 2 min to 30 min at the peak sulfurization temperature.

Solar cells with a typical layered structure of Al/ZnO:Al/i-ZnO/CdS/CIGSSe/Mo/SLS substrate and an active area of ~0.25 cm^2 were fabricated without an antireflection layer; the fabrication procedure is described in detail in our earlier work [25]. A CdS buffer layer with thickness of ~30 nm was deposited on the CIGSSe layer by a chemical bath method. The intrinsic ZnO (i-ZnO; 50 nm) and Al-doped ZnO (ZnO:Al; 500 nm) layers were deposited by radio frequency (RF) magnetron sputtering. An Al grid pattern was deposited as a current collector by thermal evaporation.

The crystalline phase was identified by an X-ray diffractometer (XRD: Rigaku B/Max-2500/PC, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation at a wavelength of 0.154 nm in Bragg–Brentano (θ – 2θ) geometry. Raman scattering spectra were measured at room temperature using an Ar-ion 532-nm emission line in backscattering geometry fitted with a liquid-nitrogen-cooled charge-coupled device (CCD)

detector (LabRam Aramis, Horiba Jobin Yvon, France). Cross-sectional microstructure was obtained by a field-emission scanning electron microscope (FESEM; JSM 6510, JEOL, Japan). The depth profile of the CIGSSe layer was examined by X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Scientific, UK) using an Al $\text{K}\alpha$ (1486.6 eV) radiation source. Ar ion-beam sputter etching was accomplished at 1 keV at a pressure of 4.8×10^{-9} mbar. The current-density–voltage (J – V) characteristics were recorded at room temperature under AM 1.5 illumination using a current–voltage curve analyzer (IviumStat, Ivium Technology, USA) and a solar simulator (Sun 2000, ABET Technology, USA). The external quantum efficiency (EQE) was measured by an incident-photon conversion-efficiency (IPCE) measurement unit (QEX 10, PV Measurements, Inc., Boulder, CO, USA).

3. Results and discussion

Prior to investigate the effects of soaking time upon sulfurization, the optimal sulfurization temperature was examined by the phase analysis and light absorption in conjunction with the level of sulfurization in the CIGSe absorber films. The XRD patterns and Raman spectra of the absorber films sulfurized at 450, 475 and 500 °C for 10 min are seen in Figs. S1 and S2 of the Supporting Information, respectively. The results indicate the gradual substitution of S into Se with increasing sulfurization temperature as we confirm the XRD peak shifts of the CIGSe phase toward the higher 2θ angle (Fig. S1) and the appearance of the CIGS Raman peak at higher temperatures (Fig. S2). From the EQE spectra of the corresponding cells as shown in Fig. S3, lower quantum efficiencies at longer wavelengths were observed for the 500 °C sample, indicating the effective sulfurization and thus bandgap-widening. Accordingly, the sulfurization temperature was fixed at 500 °C for the subsequent work.

Fig. 1 shows XRD patterns of the CIGSSe thin films prepared on Mo-coated SLS substrates. The films were sulfurized at the temperature of 500 °C for different durations of 2, 10 and 30 min after selenization at 530 °C. For comparison, the pattern of only the selenized sample without sulfurization is included. The patterns of all samples show three main peaks corresponding to the (112), (220/204), and (312/116) planes of the chalcopyrite structure (JCPDS# 35–1102). With the progress of sulfurization with prolonged time, the intensity of the main peaks slightly decreases while the peaks shift toward higher 2θ values. For example, the (112) peak in Fig. 1(b) clearly shifts to the higher 2θ region with increasing sulfurization time. This shift of XRD peaks of CIGSSe films after sulfurization is likely to be associated with the further substitution of S for Se owing to the smaller atomic size of sulfur

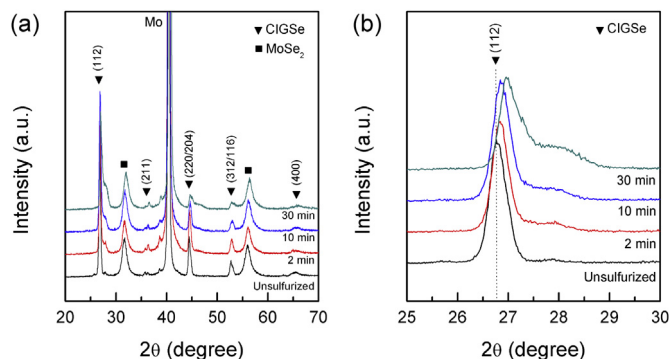


Fig. 1. (a) XRD patterns of CIGSSe thin films sulfurized at 500 °C for different durations, and (b) the highlighted (112) peak in the 2θ range of 25°–30°.

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