

CIGS THIN FILMS SPUTTERED BY USING CHALCOGENIDE CuSe_2 WITH MULTILAYER-STACK-STRUCTURE AND RAPID THERMAL ANNEALING

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$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) is the most promising material in solar cell industries owing to its special properties including controllable band gap energies by adjusting the chemical composition ratio of Ga / (In + Ga). The wide-spread manufacturing method of the CIGS thin film is either the selenization with selenium / sulfur containing gas after sputtering method or the three-stage evaporation process with four sources of the pure elements. In this study, to overcome the drawbacks of the selenization process, a novel non-selenization method was proposed to produce a multilayer-stack-structure by RF sputtering using a chalcogenide CuSe_2 target followed by the rapid thermal annealing at 400 °C. CIGS chalcopyrite (112), (220) / (204), and (312) / (116) phases were formed successfully using this non-selenization method. The crystal quality and grain size of the CIGS thin films increased with decreasing the Ga / (In + Ga) thickness ratio. The optical band gap energies, average absorbance in the range of 400 - 1500 nm, resistivity, carrier mobility and carrier concentration of the CIGS thin films were 1.73 - 1.88 eV, ~0.5, $6.15 \times 10^{-3} \Omega\text{-cm}$, 2.33 cm^2/Vs , and $5.07 \times 10^{16} \text{ cm}^{-3}$, respectively, which are acceptable for high quality CIGS thin film solar cells. Moreover, these properties could be controlled by adjusting the Ga / (In + Ga) thickness ratio.

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1. Introduction

In recent years, considerable attention has been paid to thin film solar cells including polycrystalline copper indium gallium diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, CIGS) thin films with a chalcopyrite lattice structure as an absorber layer owing to its suitable optical absorption ($> 10^5 \text{ cm}^{-1}$), long-term electrothermal stability, high tolerance to defects, no toxic or hazardous pollutants, such as arsenic and cadmium, and a tunable band gap (1.04 – 1.68 eV) by adjusting the chemical composition ratio of Ga / (In + Ga) [1, 2]. The highest conversion efficiency exceeding 20.3% has been achieved in heterostructured CIGS solar cells [3], which is approaching the highest efficiency of conventional polycrystalline silicon solar cells [4, 5]. A co-evaporation and post-selenization process is widely employed for achieving high conversion efficiency but this conventional method has several drawbacks impeding industrial production, such as process complexity, expensive equipment, slow deposition rate and poor reproducibility [6]. Against the conventional manufacturing processes, the selenization of sputtered Cu-In-Ga precursors using H_2Se vapor was proposed as a suitable method for preparing CIGS thin films at low cost [7]. On the other hand, critical problems in the selenization process still remain, such as highly toxic H_2Se , slow reaction rate and poor adhesion with back contact [1]. Therefore, a non-selenization process is needed to prepare CIGS thin films. Few studies have been performed. Of these AVANCIS GmbH and Co. KG formed an elemental precursor film by DC-magnetron sputtering of Cu-In-Ga and the thermal

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evaporation of Se followed by rapid thermal annealing (RTA) in a sulfur containing ambient [8,9]. Jheng *et al.* prepared CIGS thin films by co-sputtering with Cu-Ga alloy and In-Se alloy targets before a two-step annealing process without an additional selenium source under vacuum [1]. In a previous study, a novel method was proposed for preparing a chalcopyrite CIGS thin film without a selenization process by RF magnetron sputtering with In, Ga and CuSe₂ compound targets [10]. Chalcogenide CuSe₂ compound is one of deviations from stoichiometry of copper selenide, which has attracted considerable attention for use in electronics, optoelectronics and photovoltaics with semiconducting behavior [11]. The proposed method formed chalcopyrite (112), (220) / (204), and (312) / (116) phases by using either conventional annealing in a furnace or a RTA treatment at 400 °C without a selenium / sulfur containing gas. This process has many advantages including simplicity, large-area manufacturing for mass production, and excellent electrical and optical properties [10]. Another merit of this novel method is the ease of adjusting chemical composition ratio of Ga / (In + Ga) in CIGS thin films. In the present study, multilayer-stack-structured thin films with different thickness ratios were deposited.

2. Experimental details

A commercial CuSe₂ alloy target (TASCO, 99.99% purity, 2 inches-diameter) was used for the preparation of CuSe₂ thin film on 2×2 cm Corning glass substrates [11]. The thin films were deposited by RF magnetron sputtering (Vacuum Science Co.) using the following fixed set of process parameters after pre-sputtering for 5 minutes: An Ar gas flux of 20 sccm, base pressure of 1.0×10^{-6} Torr, substrate to distance of 5.0 cm, RF sputtering power of 35 W, and vacuum pressure of 7.5×10^{-3} Torr during sputtering for 82 seconds at room temperature. An identical process was performed for subsequent sputter deposition of Ga and In layers on 137-nm-thick CuSe₂ thin films at RF sputtering powers of 35 and 20 W, respectively. Commercial In (MTI Co. Inc., 99.99% purity, 2-inch diameter) and Ga (MTI Co. Inc., 99.99% purity, 2-inch diameter) targets were used to produce the Ga / In / CuSe₂ multilayer-stack-structure. The total thickness of the Ga and In thin films was approximately 125 nm, as measured by X-ray reflectometry (XRR). The Ga / (In + Ga) thickness ratio was varied from 0.2 to 0.5 with an interval of 0.1. The deposition rates of Ga and In were 10 and 300 nm/minute, respectively. Subsequently, 138-nm-thickness CuSe₂ thin films were deposited on the stacked thin films using the above fixed set of process parameters for 83 seconds dissimilarly to our previous study [10]. Annealing of the stacked samples resulted in the formation of CIGS chalcopyrite (112), (220) / (204), and (312) / (116) phases in either a conventional furnace or by RTA at 400 °C without a selenium / sulfur containing gas, as reported elsewhere [10]. The RTA (Modular Process Technology Co., RTP-600S) treatment of the 400-nm-thick CuSe₂ / Ga / In / CuSe₂ stacked samples was performed to improve the temperature uniformity over conventional furnace heating at 400 °C for 10 seconds in N₂ gas ambient. The crystalline structure of the thin films was analyzed by X-ray diffraction (XRD, Philips, X'pert-PRO-MRD, Cu K α = 0.15405 nm, 40 kV, 30 mA). The optical properties of the thin films were measured using an ultraviolet-visible spectrophotometer (Varian Techtron, Cary500scan) in the range of 400 – 1500 nm. The electrical properties of the thin films, including the carrier concentration, resistivity and the mobility, were characterized using a Hall Effect measurement system (Accent Optical Technologies, HL5500PC) at room temperature. X-ray photoelectron spectroscopy (XPS, Multilab 2000, Thermo VG Scientific) surface analyses of the RTA-treated samples were performed using a monochromatic Al K α X-ray source (1486.6 eV). A take-off angle of 90° was used for all analyses. For the high-resolution spectra, the binding energies were referenced to the C 1s peak at 285.0 eV.

3. Results and discussion

Fig. 1 shows XRD patterns of the RTA-treated CuSe₂ / Ga / In / CuSe₂ stacked specimens with different Ga / (In + Ga) thickness ratios; (a) 0.2, (b) 0.3, (c) 0.4, and (d) 0.5. The XRD patterns were obtained by scanning 2θ in the range of 15 – 75°. All the RTA-treated stacked thin films showed the major diffraction peaks corresponding to CIGS chalcopyrite phases with a preferred orientation: (112), (220) / (204) and (312) / (116) at $2\theta = 26.63^\circ$, 44.47° and 52.47° [1, 6,

7, 10, 12]. This confirms that this method can achieve excellent crystallization quality and grain growth. Sufficient electrical properties including the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) can be obtained by reducing the carrier recombination and structural defect-originated leakage current in the thin films by the densely packed (112), (220) / (204), and (312) / (116)-oriented grains [1]. Weak diffraction peaks of (323) / (305) and (332) / (316) were observed at $2\theta = 64.15^\circ$ and 70.91° corresponding to a CIGS chalcopyrite phase [6, 7, 10, 13]. The XRD pattern of all specimens did not indicate the presence of noticeable peaks except for the CIGS-based chalcopyrite peaks, as shown in Fig. 1. The intensities of the major (112), (220) / (204), and (312) / (116) peaks increased with decreasing Ga / (In + Ga) thickness ratio from 0.5 to 0.3, and then decreased slightly at a thickness ratio of 0.2, as shown in the inset in Fig. 1 indicating the normalized intensity. A similar trend of intensity was observed for each case of all the CIGS-based peaks and only (112) peak. This means that the crystallinity of CIGS films increased with decreasing Ga / (In + Ga) thickness ratio from 0.5 to 0.3. The full width at half maximum (FWHM) of (220) / (204) and (312) / (116) peaks decreased with decreasing Ga / (In + Ga) thickness ratio from 0.5 to 0.3, as shown in Fig. 2, whereas the sharp and strong (112) peak showed no significant difference in the FWHM with decreasing thickness ratio, which indicates an increase in grain size of the CIGS thin films. The FWHM is affected directly by the Ga concentration due to a distortion of the chalcopyrite lattice structure resulting from the incorporation of Ga into the In sites [14, 15]. Moreover, both peaks corresponding to the (220) / (204) and (312) / (116) orientations shifted to lower 2θ values with decreasing Ga / (In + Ga) thickness ratio (Fig. 2), which is consistent with the well-known shift in the diffraction peaks to a higher angle with increasing Ga content due to the decrease in the 'a' and 'c' lattice constants. Hence, the d spacing increases with the replacement of the larger In atoms with smaller Ga atoms [13–16]. Therefore, XRD suggests that polycrystalline CIGS was rebuilt on the substrate, and the crystallinity could be modified by changing the thickness ratio of the multilayer-stack-structured thin films.

The optical band gap energy of the RTA-treated samples was estimated by a linear extrapolation of each curve back to the energy axis from the Tauc plot of $(\alpha h\nu)^2$ vs. the photon energy ($h\nu$), as shown in Fig. 3, where α is the absorption coefficient, h is Plank's constant and ν is the frequency of the incident photon. All the estimated optical band gap energies ($E_g = 1.73 - 1.88$ eV) were higher than the reported values ($E_g = 1.04 - 1.68$ eV) [1]. XPS surface analyses attributed this phenomenon to the Cu-poor ($\text{Cu} / (\text{In} + \text{Ga}) < 0.8$) and Ga-rich ($\text{Ga} / (\text{In} + \text{Ga}) > 0.8$) compositions of all the RTA-treated thin films (*not shown*). Note that the highest conversion efficiency was acquired by varying the composition: $0.80 < \text{Cu} / (\text{In} + \text{Ga}) < 0.92$ and $0.30 < \text{Ga} / (\text{In} + \text{Ga}) < 0.35$ [3].

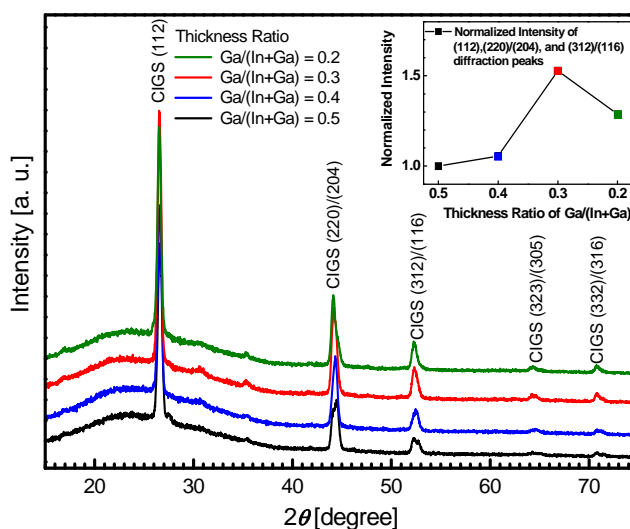


Fig. 1. XRD patterns of the RTA-treated specimens with different Ga / (In + Ga) thickness ratios from 0.5 to 0.2. The inset shows the normalized XRD intensity of (112), (220) / (204), and (312) / (116) phases in the RTA-treated specimens as the same change in thickness ratios.

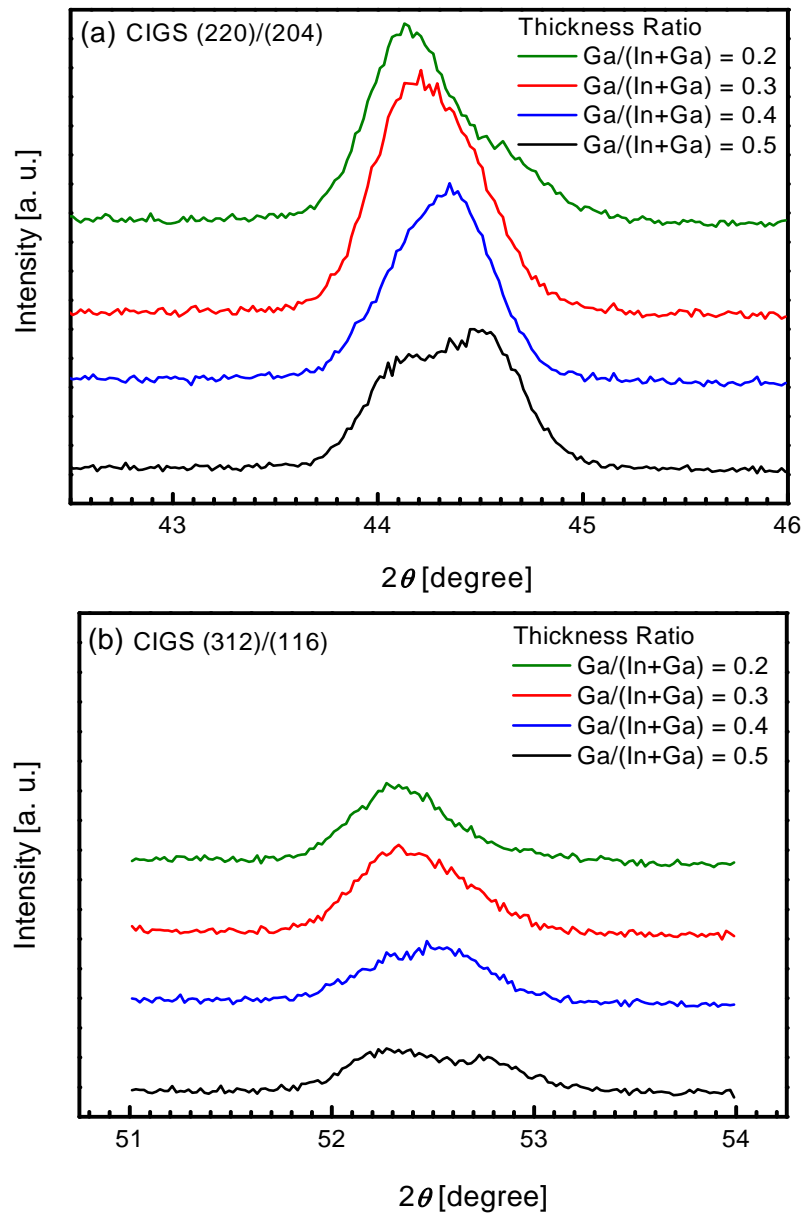


Fig. 2. Magnification of the (a) CIGS (220) / (204) and (b) CIGS (312) / (116) XRD peaks in the RTA-treated specimens with different Ga / (In + Ga) thickness ratios.

The optical band gap energy of Cu-poor ($\text{Cu} / (\text{In} + \text{Ga}) < 1$) thin films is generally higher than that of the stoichiometric ($\text{Cu} / (\text{In} + \text{Ga}) = 1$) thin films [16, 17]. Because the optical band gap energy of CIGS thin films can be controlled by adjusting the chemical composition ratio of Ga / (In + Ga), the larger chemical composition ratio of Ga / (In + Ga) results in a higher optical band gap energy [16, 18]. This innovatively devised method is still unable to control the chemical composition ratio of Ga / (In + Ga) completely by quantifying the thickness ratio. Nevertheless, further studies will overcome this problem with the optimum annealing process [6]. The well-known tendency to increase in the optical band gap energy was observed with increasing Ga / (In + Ga) thickness ratio, which confirmed that the thickness ratio can be used to control the chemical composition ratio of Ga / (In + Ga) in CIGS thin films [19, 20]. The absorbance at a certain wavelength of light can be calculated using the formula: $A = -\log T = \log I_0 / I$, where A is the absorbance, T is the transmittance, I_0 is the intensity of incident radiation, and I is the intensity of transmitted radiation. The average absorbance in the range of 400 – 1500 nm was approximately 0.5, as shown in the inset in Fig. 3, which means that approximately 70% of

incident radiation can be absorbed by 400-nm-thick thin films because the absorbance can be enhanced by adjusting the chemical composition ratio of Ga / (In + Ga) [21].

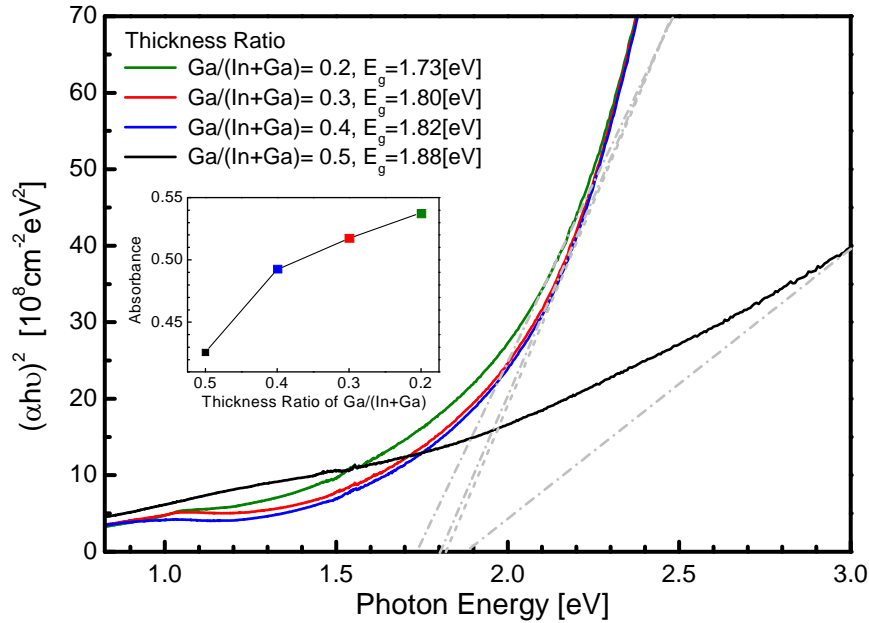


Fig. 3. Tauc plot of $(\alpha h\nu)^2$ vs. the photon energy ($h\nu$) for the the RTA-treated CIGS thin films with decreasing Ga / (In + Ga) thickness ratio from 0.5 to 0.2. The optical band gap energies were estimated through a linear extrapolation of each curve back to the energy axis. The inset shows the average absorbance in the range of 400 -1500 nm with the same change.

Fig. 4 shows the effects of the Ga / (In + Ga) thickness ratio on the electrical properties of the RTA-treated thin films including resistivity (ρ), carrier mobility (μ) and carrier concentration (n) determined by Hall Effect measurements. All the RTA-treated thin films in this experiment exhibited p -type conductivity according to Hall Effect measurements. The resistivity decreased and the carrier concentration increased with decreasing Ga / (In + Ga) thickness ratio. The resistivity of the RTA-treated thin film was $3.72 \times 10^2 \Omega\text{-cm}$ at a Ga / (In + Ga) thickness ratio of 0.5. The resistivity reached a minimum value of $6.15 \times 10^{-3} \Omega\text{-cm}$ at a Ga / (In + Ga) thickness ratio of 0.2. The carrier mobility decreased rapidly with decreasing Ga / (In + Ga) thickness ratio from 0.5 to 0.4 due to the considerable increase in carrier concentration. The carrier mobility increased with decreasing Ga / (In + Ga) thickness ratio from 0.4 to 0.3. The decrease in carrier scattering and increase in carrier mobility related to the decrease in resistivity was attributed to the better crystallinity and larger grains on the thin film surface [6], which also agrees with the FWHM results from XRD analysis. The reduced resistivity would improve the short circuit current density and fill factor (FF) in the solar cell due to the decreased series resistance of the thin films [15]. The required carrier concentration of CIGS thin films is more than $2 \times 10^{16} \text{ cm}^{-3}$, which is the relevant property of the NREL 19.9%-efficient device [22, 23]. The carrier concentration of the RTA-treated thin film was in the order of 10^{14} cm^{-3} at a Ga / (In + Ga) thickness ratio of 0.5, which is insufficient for the suggested value. On the other hand, the carrier concentration increased significantly to the order of 10^{20} cm^{-3} at Ga / (In + Ga) thickness ratio < 0.4 . The decreased grain boundaries, which act as recombination centers [24], resulted in an increase in carrier concentration in the RTA-treated thin film at a Ga / (In + Ga) thickness ratio < 0.4 due to the decreased recombination of photogenerated electrons [25, 26]. The maximum value was $5.07 \times 10^{20} \text{ cm}^{-3}$, which exceeds the requireds.

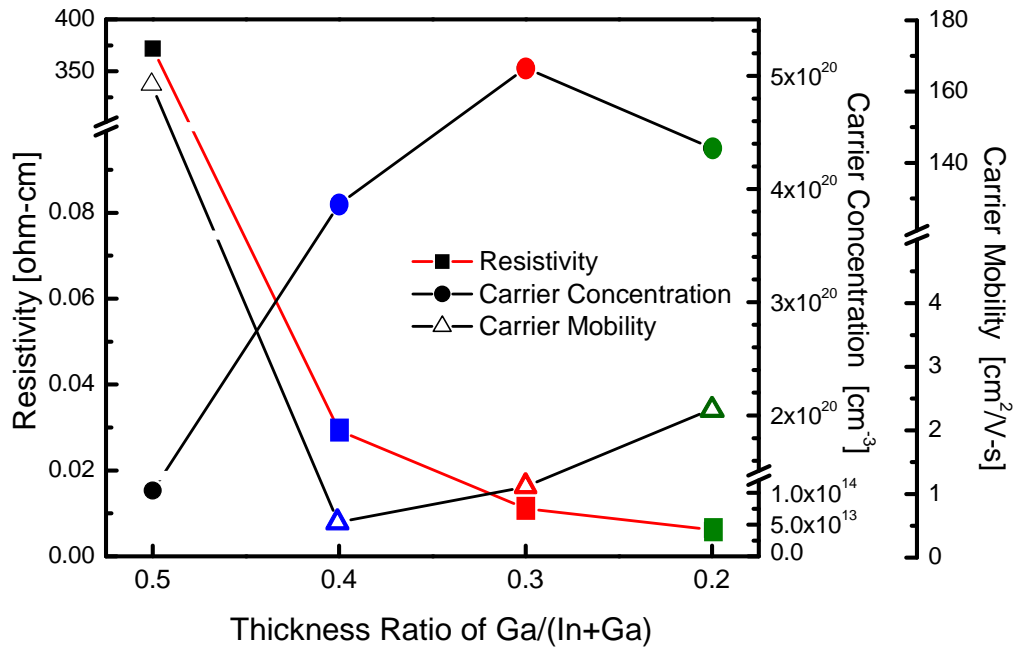


Fig. 4. Resistivity (ρ), carrier concentration (n), and carrier mobility (μ) of the RTA-treated CIGS thin films with decreasing Ga / (In + Ga) thickness ratio.

4. Conclusions

This study reported a new non-selenization method for preparing CIGS thin films by the sputtering deposition of multilayer-stack-structured thin films using a CuSe₂ alloy target followed by a RTA treatment. The CIGS chalcopyrite (112), (220) / (204), and (312) / (116) phases were formed by the RTA treatment at 400 °C for 10 seconds without a selenium / sulfur containing gas. The XRD peaks of the RTA-treated CIGS thin films became stronger, narrower, and shifted to lower 2θ values with decreasing Ga / (In + Ga) thickness ratio, which confirmed the enhanced crystallinity and grain size of the RTA-treated CIGS thin films. The optical band gap energy was in the high range of 1.73 – 1.88 eV and the average absorbance was approximately 0.5 in the range of 400 – 1500 nm due to the Cu-poor and Ga-rich compositions of the thin films. Nevertheless, more study will be needed because these values could be controlled by adjusting the Ga / (In + Ga) thickness ratio. The resistivity, carrier mobility and carrier concentration of the CIGS thin films were $6.15 \times 10^{-3} \Omega\text{-cm}$, $2.33 \text{ cm}^2/\text{Vs}$ and $5.07 \times 10^{16} \text{ cm}^{-3}$, respectively, which are good or acceptable values for high quality CIGS thin film solar cells. The Hall Effect measurements were also affected by the proportion of Ga in the total thickness of In and Ga. Overall, this novel non-selenization process can be used to prepare the CIGS thin films, and the film characteristics can be controlled by adjusting the thickness ratio.

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