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Short communication

# Characterization of $Cu(In,Ga)Se_2$ thin films prepared via a sputtering route with a following selenization process

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**Abstract**

$Cu(In,Ga)Se_2$ films were prepared via a sputtering route with a following selenization process. In, CuIn, and $Cu_3Ga$ were observed in the precursor films. Selenization at 450 °C yielded monophasic $Cu(In,Ga)Se_2$ films. The diffraction angles of the (112) peaks shifted toward high angles, and a uniform morphology of the obtained films was observed with high-temperature selenization. The amount of gallium ions incorporated into indium ions increased with the temperature. The probable formation mechanism of the sputtering-derived $Cu(In,Ga)Se_2$ was proposed. Firstly, selenium species diffuse into the precursor films to form $Cu(In,Ga)Se_2$ and $Cu_{2-x}Se$ phases. Subsequently, the complete reaction of selenium with residual species leads to the formation reaction of single-phased $Cu(In,Ga)Se_2$. An efficiency of 8.34% was achieved for the fabricated solar cell.

*Keywords:* $Cu(In,Ga)Se_2$; Solar cells; Sputtering

## 1. Introduction

Thin-film solar cells have been developed as the second-generation solar cells owing to their low cost and low material consumption. Chalcopyrite semiconductors are among the important absorber layers utilized in the solar cells [1]. Recently, increasing attention is being paid to $Cu(In,Ga)Se_2$ owing to its direct band gap and high absorption coefficient [2–4]. Moreover, the photovoltaic conversion efficiency of $Cu(In,Ga)Se_2$ solar cells reaches a high value [5].

In previous studies, the co-evaporation method [6,7] is widely used for synthesizing $Cu(In,Ga)Se_2$ solar cells with a high conversion efficiency. However, it is usually difficult to control the chemical compositions of the as-prepared $Cu(In,Ga)Se_2$ properly [8] owing to the use of metal evaporation source sequentially via the three-stage process [9,10]. Another vacuum process such as the two-step process has been developed to prepare $Cu(In,Ga)Se_2$ films. The metallic films are deposited as the precursor films via the sputtering method, followed by the selenization process under a controlled atmosphere to yield $Cu(In,Ga)Se_2$ films. Heating at high temperature in a toxic atmosphere ($H_2Se$) is essential in the two-step process [11].

In this study, a simple selenization process using Se pellets as the selenium source was adopted to synthesize $Cu(In,Ga)Se_2$. The effects of selenization temperatures on the phase formation and the morphology of the obtained films were explored. The formation mechanism of $Cu(In,Ga)Se_2$ film was also proposed. Furthermore, the conversion efficiency of the fabricated solar cell was investigated.

## 2. Experimental

Copper/gallium (25 wt%) alloy targets and indium targets were sequentially used for depositing the precursor films on soda-lime glass (SLG) substrates via the sputtering route employing a DC magnetron sputtering system. After depositing the precursor films, the samples were selenized in a reducing atmosphere (5 vol% $H_2$ and 95 vol% $N_2$) in a tube furnace at temperatures ranging from 350 to 550 °C for 0.5 h. In the selenization process of specimens, Se pellets were used as the selenium source.

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Once Se pellets were heated, the selenium gas was formed and carried by the carrier gas ($H_2$ and $N_2$) to activate the selenization reactions.

A Cu(In,Ga)$Se_2$ solar cell device was fabricated with a structure consisting of glass/Mo/Cu(In,Ga)$Se_2$/CdS/i-ZnO/ITO. A CdS buffer layer was coated on Cu(In,Ga)$Se_2$ films via chemical bath deposition (CBD). Subsequently, i-ZnO (100 nm) and ITO (300 nm) were deposited employing a RF magnetron sputtering system.

Phase evolution of the precursor and selenized specimens was analyzed using an X-ray powder diffractometer (XRD, Philips X'Pert/PMD) and Cu Kα radiation at 45 kV and 40 mA. The microstructures were investigated employing scanning electron microscopy (SEM, Hitachi S-800). The current–voltage characteristic of the fabricated solar cell was measured via an AM1.5G (100 mW/cm$^2$) solar simulator (Hong-Ming Tech.).

## 3. Results and discussion

Fig. 1 illustrates the X-ray diffraction patterns of sputtering-derived Cu(In,Ga)$Se_2$ films selenized at various temperatures for 0.5 h. The XRD peaks belonging to In, CuIn, and $Cu_3Ga$ were observed in the precursor films. After selenization at 350 °C, Cu(In,Ga)$Se_2$ was formed and $Cu_3Ga$ still remained. When the selenization temperature was increased to 400 °C, copper selenide was found to coexist with Cu(In,Ga)$Se_2$ in the prepared film. Monophasic Cu(In,Ga)$Se_2$ was obtained by increasing the selenization temperature to 450 °C. The XRD patterns are well consistent with the reported data (ICDD card no. 35-1102). The crystallinity of the obtained film was further enhanced by increasing the selenization temperature. According to the XRD results, the formation reactions were proposed. CuIn, In, and $Cu_3Ga$ started to react with Se vapor when the reaction temperature reached 350 °C. However, $Cu_3Ga$ still remained and this suggested incomplete selenization of $Cu_3Ga$ in the precursor films. As the selenization temperature reached over 400 °C, alloys were selenized to form selenide compounds. Copper selenide was found to be the second major phase during the formation of Cu(In,Ga)$Se_2$ in the selenization process employing Se vapors [12]. Cu(In,Ga)$Se_2$ films were successfully formed at the selenization temperature of 450 °C.

The relation between $2\theta$ of (112) diffraction peaks of Cu(In,Ga)$Se_2$ films and the selenization temperatures is shown in Fig. 2. It was observed that increasing the selenization temperature from 400 to 500 °C resulted in a shift of the (112) diffraction peak toward higher angles. When increasing the selenization temperature further to 550 °C, the diffraction angle of the (112) diffraction peak shifted insignificantly. It was due to the fact that $Ga^{3+}$ ions were incorporated into Cu(In,Ga)$Se_2$ to substitute indium ions, so that the lattice constants decreased due to the substitution of large $In^{3+}$ (0.062 nm, CN=4) by small $Ga^{3+}$ (0.047 nm, CN=4) [13]. Further increasing the temperatures led to increased amounts of $Ga^{3+}$ in Cu(In,Ga)$Se_2$ films and thereby the decreased lattice constants and eventually the shift in the (112) peak towards higher angles.

Fig. 3 depicts the scanning electron micrographs of the sputtering-derived Cu(In,Ga)$Se_2$ films that were selenized at various temperatures. It was found that the 350 °C-heated film with a small grain size was obtained (Fig. 3(a)) Once the selenization temperature was increased to 400 °C (Fig. 3(b)),

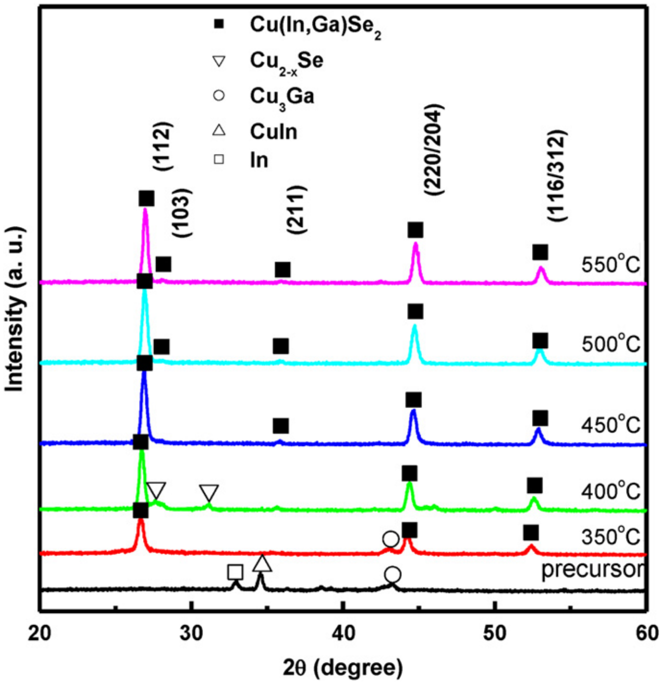

Fig. 1. X-ray diffraction patterns of the sputtering-derived precursor film and Cu(In,Ga)$Se_2$ films selenized at various temperatures for 0.5 h.

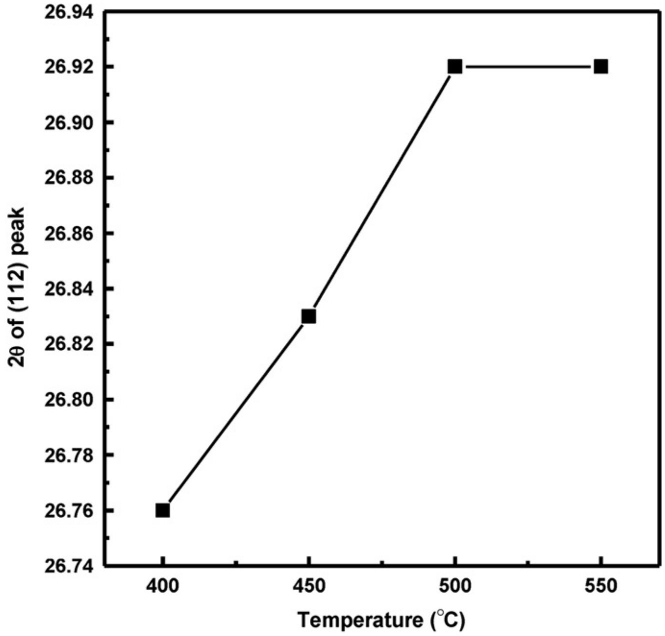

Fig. 2. Variation of $2\theta$ of the (112) diffraction peak of Cu(In,Ga)$Se_2$ films versus the selenization temperature.

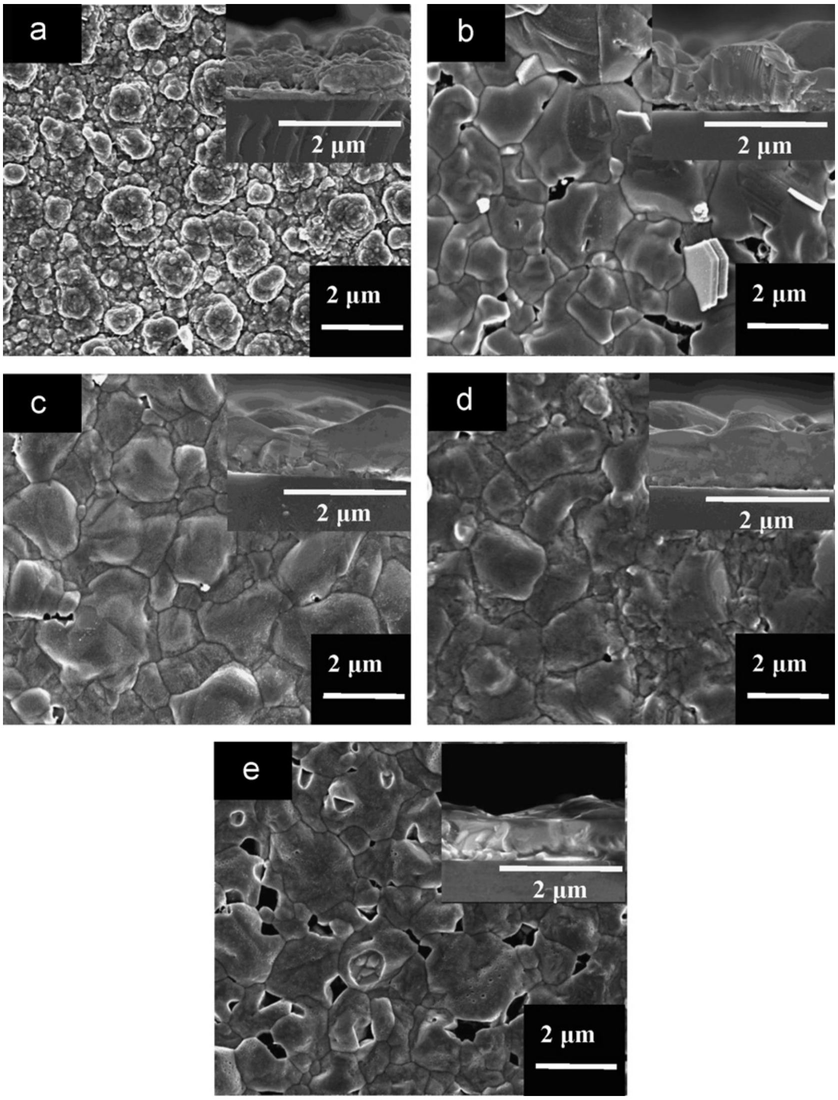

Fig. 3. Scanning electron micrographs of the sputtering-derived $Cu(In,Ga)Se_2$ films selenized at (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C and (e) 550 °C for 0.5 h. Inset: the cross-section micrographs of corresponding films.

the grain size of the prepared films was increased to 1 μm and the hexagonal-shaped particles were formed. Based on the energy dispersive X-ray (EDX) results and Fig. 1(c), the major elements of the small particles were copper and selenium. It was confirmed that the small particles were $Cu_{2-x}Se$. When the selenization temperatures were increased to 450 °C and 500 °C (Fig. 3(c) and (d)), the densified and uniform films with the grain size increasing to about 2 μm were obtained. As the selenization temperature reached 550 °C (Fig. 3(d)), the grain size was decreased and some pores were observed in the prepared $Cu(In,Ga)Se_2$ film. It is suggested that selenium would evaporate at high temperatures [14], thereby resulting in the porous film morphology.

The cross-sectional micrographs of the sputtering-derived $Cu(In,Ga)Se_2$ films prepared at various temperatures are also shown in the inset in Fig. 3. The prepared films were found to exhibit a double-layered structure when the selenization temperatures were 350 °C and 400 °C as shown in the inset in Fig. 3(a)–(c). Upon elevating the selenization temperatures, densified and uniform films were obtained (Fig. 3(c)–(e)). According to the XRD results (Fig. 1), $Cu_3Ga$ still remained in the prepared films when the selenization temperature was 350 °C. The precursor films were deposited with a Cu–Ga/In bi-layered structure. During the selenization process, selenium species diffused into the precursor films and reacted with the metal species to form $Cu_{2-x}Se$ [15]. Upon heating at a low selenization temperature, some $Cu_3Ga$ still remained in the bottom layer owing to the incomplete diffusion of selenium across the prepared film. Furthermore, the top layer with a large grain size and the bottom layer with a small grain size were observed as the selenization temperatures were 400 and 450 °C. It is suggested that the bottom layer contained more gallium ions in $Cu(In,Ga)Se_2$ than the top layer, leading to the variation of the grain size of the prepared films. Nevertheless, the morphology of the selenized films became uniform as the selenization temperature reached over 500 °C because of the complete interdiffusion of gallium species in $Cu(In,Ga)Se_2$ films at high temperatures.

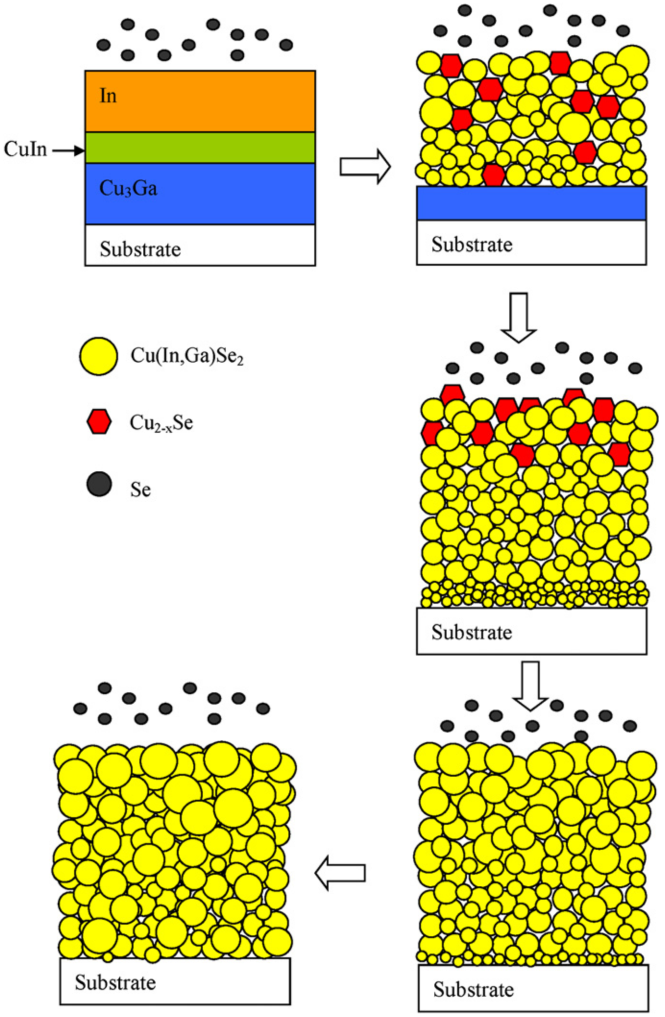

Fig. 4. Formation mechanism of the sputtering-derived $Cu(In,Ga)Se_2$ films obtained via the selenization process.

Fig. 4 illustrates the formation mechanism of the sputtering-derived $Cu(In,Ga)Se_2$ films prepared via the selenization process. The precursor films were supposed to exhibit a $Cu_3Ga$/CuIn/In structure (Fig. 5(a)). CuIn alloy is produced in a reaction between $Cu_3Ga$ and In during the sputtering process. Selenium species reacts with the metal compounds on the surface of the precursor films to form $Cu(In,Ga)Se_2$. A portion of $Cu_3Ga$ near the substrate would remain owing to the low reaction temperature. Raising the selenization temperatures facilitates selenium species to diffuse into the inner layer and promotes unreacted species to form $Cu_{2-x}Se$ (the hexagonal-shaped particles) and $Cu(In,Ga)Se_2$. $Cu(In,Ga)Se_2$ is successfully obtained after further increasing the selenization temperature to 450 °C.

The band gap of the prepared $Cu(In,Ga)Se_2$ films was calculated from the following equation [16]:

$$\alpha h\nu = k(h\nu - E_g)^{1/2} \tag{1}$$

where $\alpha$ denotes the absorption coefficient, $k$ is a constant, $h\nu$ is the photon energy, and $E_g$ is the energy of band gap. The value of the band gap was obtained from extrapolating the straight line portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha = 0$. The optical band gap of the 550 °C-heated $Cu(In,Ga)Se_2$ films was 1.17 eV as shown in Fig. 5. It reported that the gallium ions are added into $CuInSe_2$ to obtain $Cu(In,Ga)Se_2$ with a wider band gap of approximately 1.1–1.2 eV [17,18] to increase the conversion efficiencies of CIGS solar cells.

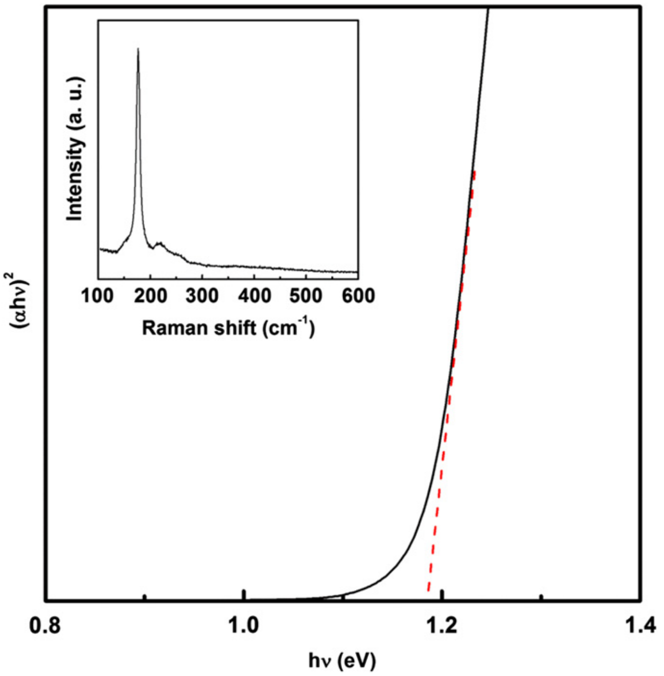

Fig. 5. Absorbance spectra of the sputtering-derived $Cu(In,Ga)Se_2$ films. Inset plot: Raman spectrum of the corresponding film.

The Raman spectrum of the 550 °C-heated $Cu(In,Ga)Se_2$ films is illustrated in the inset in Fig. 5. Two major peaks at 174 cm$^{-1}$ and 214 cm$^{-1}$ were observed. The main peak at 174 cm$^{-1}$ is attributed to the A1 mode of $Cu(In,Ga)Se_2$. The A1 mode phonon is owing to the motion of Se atoms with other cation atoms at rest [19,20]. The other peak appearing at 214 cm$^{-1}$ is attributed to the E mode of $Cu(In,Ga)Se_2$. It is demonstrated that single-phased chalcopyrite $Cu(In,Ga)Se_2$ was successfully synthesized.

The *J–V* curve of the fabricated solar cells with $Cu(In,Ga)Se_2$ films selenized at 500 °C as the absorber layer is shown in Fig. 6. The open-circuit voltage ($V_{oc}$), the short-circuit current density ($J_{sc}$) and the fill factor (FF) were 0.43 V, 32.1 mA/cm$^2$ and 60.15%, respectively. The efficiency of a solar cell is calculated by the following equation [21]:

$$\eta = \frac{V_{oc} J_{sc} \mathrm{FF}}{P_{in}} \tag{2}$$

where $\eta$ is the efficiency, $V_{oc}$ is the open-circuit voltage, $J_{sc}$ is the short-circuit current density, FF is the fill factor, and $P_{in}$ is the incident power. The incident power ($P_{in}$) is equal to the irradiance of AM1.5G spectrum, normalized to 100 W/cm$^2$. The efficiency of the produced $Cu(In,Ga)Se_2$ cell was 8.34%. It is confirmed that the selenization conditions are critical to

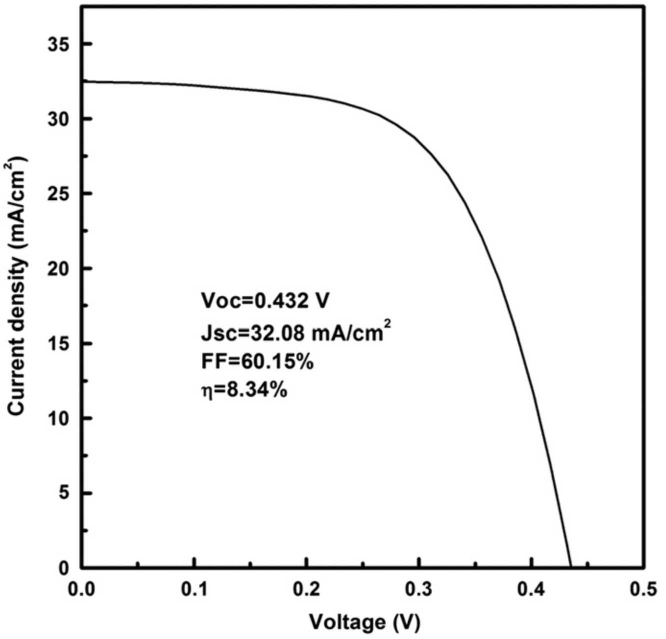

Fig. 6. Current–voltage curve of the fabricated Cu(In,Ga)Se$_2$ solar cell.

obtain Cu(In,Ga)Se$_2$ films with a uniform morphology for probable applications in solar devices.

## 4. Conclusions

Cu(In,Ga)Se$_2$ films were prepared via the sputtering method with a following selenization process. The selenization route employing Se pellets as the selenium source led to the synthesis of pure-phased Cu(In,Ga)Se$_2$ films on selenization at 450 °C for 0.5 h. The enhanced incorporation of gallium ions into Cu(In,Ga)Se$_2$ upon heating at high temperatures was reflected in the shift in diffraction angles of the (112) peaks towards the higher angles, as well as the uniform morphology of the obtained films. The reaction mechanism of Cu(In,Ga)Se$_2$ during the selenization process was deduced. Cu(In,Ga)Se$_2$ and Cu$_{2-x}$Se phases were formed first, followed by the reaction of selenium with other residual species to produce Cu(In,Ga)Se$_2$ phase. The efficiency of the fabricated Cu(In,Ga)Se$_2$ solar cell was 8.34%.

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## References

[1] C.H. Wu, F.S. Chen, S.H. Lin, C.H. Lu, Preparation and characterization of CuInSe$_2$ particles via the hydrothermal route for thin-film solar cells, Journal of Alloys and Compounds 509 (2011) 5783–5788.

[2] S.C. Chien, F.S. Chen, C.H. Lu, Sol–gel assisted preparation and characterization of silver indium diselenide powders, Journal of Alloys and Compounds 509 (2011) 8927–8932.

[3] C.H. Lu, C.H. Lee, Microemulsion-mediated solvothermal synthesis of copper indium diselenide powders, Solar Energy Materials and Solar Cells 94 (2010) 1622–1626.

[4] F.S. Chen, C.H. Wu, C.H. Lu, Low-temperature synthesis of Cu(In,Ga)Se$_2$ thin films using selenium-containing precursors, International Journal of Applied Ceramic Technology 9 (2012) 853–860.

[5] P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Manner, W. Wischmann, M. Powalla, New world record efficiency for Cu(In,Ga)Se$_2$ thin-film solar cells beyond 20%, Progress in Photovoltaics: Research and Applications 19 (2011) 894–897.

[6] S. Schleussner, U. Zimmermann, T. Wätjen, K. Leifer, M. Edoff, Effect of gallium grading in Cu(In,Ga)Se$_2$ solar-cell absorbers produced by multi-stage coevaporation, Solar Energy Materials and Solar Cells 95 (2011) 721–726.

[7] C. Platzer-Bjorkman, P. Zabierowski, J. Pettersson, T. Torndahl, M. Edoff, Improved fill factor and open circuit voltage by crystalline selenium at the Cu(In,Ga)Se$_2$/buffer layer interface in thin film solar cells, Progress in Photovoltaics: Research and Applications 18 (2010) 249–256.

[8] J.H. Shi, Z.Q. Li, D.W. Zhang, Q.Q. Liu, Z. Sun, S.M. Huang, Fabrication of Cu(In,Ga)Se$_2$ thin films by sputtering from a single quaternary chalcogenide target, Progress in Photovoltaics: Research and Applications 19 (2011) 160–164.

[9] S. Merdes, R. Mainz, J. Klaer, A. Meeder, H. Rodriguez-Alvarez, H.W. Schock, M.Ch. Lux-Steiner, R. Klenk, 12.6% efficient CdS/Cu(In,Ga)S$_2$-based solar cell with an open circuit voltage of 879 mV prepared by a rapid thermal process, Solar Energy Materials and Solar Cells 95 (2011) 864–869.

[10] D. Dwyer, I. Repins, H. Efstathiadis, P. Haldar, Selenization of co-sputtered CuInAl precursor films, Solar Energy Materials and Solar Cells 94 (2010) 598–605.

[11] M. Kemell, M. Ritala, M. Leskela, Thin film deposition methods for CuInSe$_2$ solar cells, Critical Reviews in Solid State 30 (2005) 1–31.

[12] H.K. Song, J.K. Jeong, H.J. Kimm, S.K. Kim, K.H. Yoon, Fabrication of CuIn$_{1-x}$Ga$_x$Se$_2$ thin film solar cells by sputtering and selenization process, Thin Solid Films 435 (2003) 186–192.

[13] R.D. Shannon, Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallographica A 32 (1976) 751–767.

[14] L.L. Kazmerski, M.S. Ayyagari, F.R. White, G.A. Sanbon, Growth and properties of vacuum-deposited CuInSe$_2$ thin-films, Journal of Vacuum Science and Technology 13 (1976) 139–144.

[15] W.J. Tsai, C.H. Chang, J.M. Ting, R.R. Wang, Addition of Na into CuInS$_2$ thin film via co-evaporation, Thin Solid Films 519 (2010) 1712–1716.

[16] L. Oliveira, T. Todorov, E. Chassaing, D. Lincot, J. Carda, P. Escribano, CIGSS films prepared by sol–gel route, Thin Solid Films 517 (2009) 2272–2276.

[17] M. Contreras, L. Mansfield, B. Egaas, J. Li, M. RomeroR. Noufi,Improved energy conversion efficiency in wide-bandgap Cu(In,Ga)Se$_2$ solar cells, Presented at the 37th IEEE Photovoltaic Specialists Conference, 2011, NREL/CP-5200-50669.

[18] M. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D.L. Young, B. Egaas, R. Noufi, Diode characteristics in state-of-the-art ZnO/CdS/ Cu(In$_{1-x}$Ga$_x$)Se$_2$ solar cells, Progress in Photovoltaics: Research and Applications 13 (2005) 209–216.

[19] C. Rincon, F.J. Ramirez, Lattice-vibrations of CuInSe$_2$ and CuGaSe$_2$ by Raman microspectrometry, Journal of Applied Physics 72 (1992) 4321–4324.

[20] F.S. Chen, J.S. Ma, C.H. Lu, Preparation of Cu(In,Ga)Se$_2$ films via direct heating the selenium-containing precursors without selenization, Ceramics International 38 (2012) 5319–5323.

[21] S. Ashok, K.P. Pande, Photovoltaic measurements, Solar Cells 14 (1985) 61–81.