Incorporation of copper–indium back-end layers in the solution-based Cu(In, Ga)Se2 films: enhancement of photovoltaic performance of fabricated solar cells

Chang-Ying Ou¹, Sudipta Som¹ and Chung-Hsin Lu¹,²,3

¹ National Taiwan University, Department of Chemical Engineering Taipei, Taiwan, Republic of China
² National Taiwan University of Science and Technology, Department of Chemical Engineering, Taipei, Taiwan, Republic of China
³ Advanced Research Center of Green Materials Science & Technology, Taipei 10617, Taiwan, Republic of China

E-mail: chlu@ntu.edu.tw

Keywords: CIGS, thin-film solar cells, photovoltaic device, non-vacuum process

Abstract

The morphology and photovoltaic properties of the solution-based Cu(In, Ga)Se2 films are effectively improved via the incorporation of copper–indium back-end layers in the precursor films. The effects on the concentrations of bimetal-ions solutions to prepare copper–indium back-end layers are investigated in this study. The incorporation of copper–indium back-end layer in the precursor film enhances the internal diffusion between gallium-ions and indium-ions during selenization reaction. Hence, the porous structure in the back-contact region of prepared CIGS films becomes densified, and the bandgap distribution of films shows a gradient profile. The densified morphology and gradient bandgap reduce the carrier recombination and improve the carrier collection of solar cells. In contrast to the pristine precursor film, the precursor film with a copper–indium back-end layer increase the conversion efficiency of prepared solar cells from 8.34% to 11.13%. The enhancement of conversion efficiency is attributed to the improvement of short-circuit current density and fill factor from 25.70 mA cm⁻² to 31.79 mA cm⁻² and 57.65% to 65.70%, respectively. This study reveals that the photovoltaic properties of solution-based CIGS solar cells can be improved significantly via the incorporation of copper–indium back-end layers into the precursor films.

1. Introduction

Thin film solar cells are promising for solar power generation in recent years and Cu(In, Ga)Se2 (CIGS) one of the potential candidates owing to direct bandgaps, high absorption coefficients, and superior cell performance. CIGS films with broad single-phase composition range and tunable bandgaps have attracted considerable attention as light absorbers for highly efficient photovoltaic devices [1–3]. Various vacuum processes are generally utilized to fabricate CIGS films, including co-evaporation processes and two-step fabrication processes that involve sputtering precursor and post-selenization reaction [4–6]. The efficiency of CIGS solar cells fabricated via co-evaporation method exceeds 20% [7]. Recently, CIGS-based solar cells prepared by the two-step process for the laboratory-scale exhibits high conversion efficiency of 22.9% [8]. However, vacuum processes for the preparation of CIGS films are marred by problems such as complicated manufacturing processes and low material utilization.

To address the problems of vacuum processes, researchers have developed nonvacuum processes for preparing CIGS films, including spray pyrolysis [9], electrodeposition [10, 11], and solution coating [12, 13] processes. These nonvacuum approaches are utilized to prepare the precursor film first and then high-temperature treatment in the selenium-containing atmosphere for the selenization reaction to fabricate CIGS films. The highest conversion efficiencies of CIGS solar cells based on a solution processes were 17.0%, the corresponding CIGS films were prepared by the low-temperature pulsed electron deposition method [10].
Although the nonvacuum processes can be utilized to prepare the CIGS films, but the small particle sizes and high defect densities of solution-based CIGS films result in the poor photovoltaic performance of prepared solar cells. The photovoltaic performance of solar cells is influenced by the morphology and bandgap distribution of CIGS films [14, 15]. The small sizes of CIGS particles induce the non-smooth surface and porous morphology of films. A rough surface of CIGS films leads to the inferior coverage of buffer layers to form additional shunt paths, results in the low open circuit potential and fill factor of solar cells [16, 17]. The porous microstructure of CIGS films increases the possibility of carrier recombination during the carrier transfer, which deteriorated the photovoltaic conversion efficiency of solar cells [18]. On the other hand, the bandgap distribution of CIGS films influences cell performance. According to previous literature [19, 20], gradual increasing the bandgap of CIGS films from surface to back-contact region enhances the collection of photo-generated current and increases the short current density of solar devices. The inverse bandgap distribution of CIGS surface reduces the carrier recombination in the space charge region, and improves the open circuit potential of solar cells [21].

In the present study, solution-based CIGS films with large grain size and bandgap gradient were successful synthesized by using precursor films that contained a copper–indium back-end layer. The copper–indium back-end layer was prepared using a solution containing copper and indium ions. The effects of the metal ion concentration of the solution on the phase formation and morphological properties of the CIGS films were investigated. Furthermore, the photovoltaic characteristics of the obtained solar devices were studied in detail by using the prepared CIGS films.

2. Experimental

Precursor films of CIGS absorbers were fabricated through a spin-coating process using metal ion-based solutions. Two different approaches, namely process A and process B, were adopted to prepare the precursor films of the CIGS absorbers. The structures of the precursor films prepared using these two processes are schematically illustrated in Figure 1. In both processes, copper nitrate (Cu(NO3)2·3H2O), indium nitrate (In(NO3)3·3H2O), and gallium nitrate (Ga(NO3)3) were used as reactants. Process A was used to fabricate standard precursor films. In this process, the standard ion-based solution was prepared first. The molar ratio of copper ions (Cu2+) to IIIA group elements (In3+ and Ga3+) and gallium ions (Ga3+) to IIIA group elements in the standard ion-based solution were 0.85 and 0.3, respectively. The total concentration of metal ions in the standard ion-based solution was fixed at 0.60 M. Reactants in the calculated molar ratios were dissolved in ethanol solution. The prepared solution was spin-coated on Mo-coated soda-lime glass and dried at 200 °C for 10 min. The aforementioned steps were repeated ten times to obtain precursor films of the desired thickness for preparing standard CIGS films.

Process B was used to prepare precursor films with a copper–indium back-end layer. For the preparation of the copper–indium back-end layer, an exclusive solution containing copper and indium ions was prepared in ethanol. The molar ratio of copper ions to indium ions was set as 1:1, and the concentration ratios of both metal ions were varied as 0.2, 0.4, and 0.6 M. The mixed solution was then spin-coated on a Mo-coated soda-lime glass substrate and dried to prepare the copper–indium back-end layer. Subsequently, the standard ion-based solution containing copper, indium, and gallium ions in the same molar ratios as those described in process A was spin-coated on the copper–indium back-end layer and dried at 200 °C for 10 min. This spin-coating process was repeated nine times to prepare precursor films of the desired thickness. The as-prepared precursor films of CIGS absorbers obtained using processes A and B were subjected to reduction at 500 °C for 60 min in a 5 vol% hydrogen atmosphere. The reduced films were then selenized with selenium vapor at 550 °C for 40 min in a 5 vol% H2/95 vol% N2 atmosphere for synthesizing CIGS films. Herein, the CIGS films prepared using process

![Figure 1. Schematic of prepared precursors with and without a copper–indium back-end layer by using a solution-based spin-coating technology.](image-url)
A are designated as sample A1, and those prepared through process B by using bimetal-ion solution concentration ratios of 0.2, 0.4, and 0.6 M are designated as samples B1, B2, and B3, respectively.

The crystalline phases of the prepared CIGS films were determined using an x-ray diffraction (XRD) system with Cu Kα radiation (λ = 0.154 nm). Secondary ion mass spectrometry (SIMS, Cameca IMS–4f) was performed to determine the elemental depth profiles of the prepared CIGS films. The morphology of the prepared films was analyzed using a scanning electron microscopy (SEM) system (JEOL JSM-7600F) and an atomic force microscopy (AFM) system (Seiko E-sweep System). The photovoltaic performance of the precursor films prepared through processes A and B after selenization was analyzed by fabricating solar devices. The architecture of the solar cells comprised the following layers: SLG/Mo/prepared CIGS films/cadmium sulfide (CdS)/intrinsic zinc oxide (i-ZnO)/tin-doped indium oxide (ITO)/Ni:Al. Chemical bath deposition was used to prepare the CdS buffer layers. The i-ZnO layers, ITO layers, and top electrodes were deposited using radio frequency magnetron sputtering. The external quantum efficiency of fabricated CIGS solar cells was analyzed for investigating the bandgap values and carrier collection of prepared films. The CIGS solar cells were characterized using current-voltage (I–V) measurements under an AM 1.5 spectrum with 1000 W m⁻² irradiance at 25 °C.

3. Results and discussion

3.1. Effects of copper–indium back-end layers on the phase formations and element distribution of prepared Cu(In, Ga)Se₂ films

The precursor films prepared using processes A and B were selenized at 550 °C for 40 min to synthesize CIGS films. Figure 2 illustrates the XRD and grazing incidence diffraction (GIXD) patterns of the CIGS films prepared under various conditions. All diffraction peaks of the prepared CIGS films adequately matched the JCPDS No. 35-1101 standard [22], as presented in figure 2(a). Well-crystallized GIGS films with a chalcopyrite structure were successfully synthesized by incorporating copper–indium back-end layers in the precursor films. Figure 2(b) displays the GIXD patterns of the CIGS absorbers prepared using precursor films with and without the copper–indium back-end layers. The GIXD patterns were compared with the JCPDS cards of CuInSe₂ (No. 89-5649) and CuGaSe₂ (No. 81-0903), as shown in figure 2(b). The diffraction peaks of sample A1 shifted to a high angle when the incident depth of x-ray was increased. Comparing the CuInSe₂ and CuGaSe₂ phases revealed a shift of peak positions, indicating an increase in gallium content from the surface toward the bottom region of the CIGS films. By contrast, the introduction of a copper–indium back-end layer broadened the diffraction peaks of the prepared CIGS films, as displayed in figure 2(b). The widening of the diffraction peaks might have been caused by the non-uniform distribution of indium and gallium elemental phases in the CIGS films. The aforementioned results indicate that the incorporation of a copper–indium back-end layer in the precursor films influenced the distribution of gallium and indium atoms in the prepared CIGS films.

To confirm the influence on the distribution of elements in the prepared CIGS films, SIMS analysis was conducted for all fabricated samples. Figure 3 presents the SIMS depth profiles of different elements in the prepared CIGS films. As indicated in figure 3(a), a high secondary ion intensity of copper atoms was observed in the CIGS absorbers prepared using precursor films with a copper–indium back-end layer. As the bimetal-ion solution concentrations were raised to prepare the copper–indium back-end layer, the secondary ion intensity of copper atoms was increased gradually. This phenomenon was caused by the high concentration of copper atoms present in the bimetal-ion solution. The distribution of selenium atoms is illustrated in figure 3(b); the depth profiles of selenium atoms in all samples were observed to be the same, regardless of whether a copper–indium back-end layer was present in the precursor films, which were the common distribution in the CIGS films [22–24]. As illustrated in figure 3(c), the distribution of gallium atoms exhibited a gradient profile from the back-contact region to the surface region in all samples. Fabrication of CIGS films using precursor films of copper–indium back-end layer decreases the contents of gallium atoms in the surface region. Further increase of concentration of bimetal-ion solution to prepare copper–indium back-end layer decreases the contents of gallium atoms in surface region.

Notably, the distribution of indium atoms showed an inverse gradient profile compared with the depth profiles of gallium atoms, as shown in figure 3(d). When the concentration of the bimetal-ion solution was further increased to prepare copper–indium back-end layers, the gradient distribution of indium atoms was enhanced gradually. The gradient distribution of indium atoms can be attributed to the different reaction kinetics of binary selenides and the corresponding gradual migration of indium atoms to the surface region during the selenization process [25]. Meanwhile, the gallium atoms were gradually accumulated in the back-contact region [26, 27]. Notably, when the bimetal-ion solution concentration was increased for preparing copper–indium back-end layers, the effects of interactive diffusion between indium and gallium atoms in the CIGS films were enhanced. The elemental distribution of indium and gallium atoms influences the bandgap (E_g) of CIGS films strongly. The E_g value of the CIGS films was elevated by increasing the atomic ratios of gallium
atoms to IIIA atoms (GGI value) \(^{[28, 29]}\). When a copper–indium back-end layer incorporated into the precursor films, the gradient distribution of gallium atoms in the prepared CIGS films was enhanced; thus, the GGI ratios of the CIGS films were gradually increased from the surface to the back-contact region, and concurrently, the \(E_g\) values of the prepared films exhibited a gradient distribution.

3.2. Effects of copper–indium back-end layers on the microstructure and morphology of prepared Cu(In, Ga)Se\(_2\) films

Figure 4 illustrates the top-view and cross-sectional micrographs of the CIGS films prepared using precursor films with and without copper–indium back-end layers. The CIGS film (sample A1) prepared using precursor films without any copper–indium back-end layer exhibited a flat and smooth surface, as displayed in figure 4(a). However, the cross-section image of the sample A1 showed small grain sizes and voids in the bottom region (figure 4(b)). This non-dense microstructure in the bottom region has generally been observed in CIGS films prepared using nonvacuum processes \(^{[30, 31]}\). The flat surface with few agglomerated particles was observed along with the reduction in voids from the bottom region of CIGS film prepared using a precursor film of a copper–indium back-end layer with 0.2 M bimetal-ion solution, as illustrated in figures 4(c) and (d). Increasing the bimetal-ion solution concentration to 0.4 M, the amounts of agglomerated particles on the CIGS surface were increased, and the voids in the bottom region were disappeared, as displayed in figures 4(e) and (f). Further...
increasing the concentration of bimetal-ion solution to 0.6 M, the particle sizes of agglomerated particles on CIGS surface were increased with the densification of cross-section microstructure, as shown in figures 4(g) and (h). The results reveal that the incorporation of copper–indium back-end layer in the precursor films effectively
improve the porous morphology in the bottom region of CIGS films. Meanwhile, the surface morphology of CIGS films was influenced by the bimetal-ion solution concentration.

To investigate the surface morphology of CIGS films, an AFM analysis was employed. Figure 5 depicts AFM micrographs of the CIGS films prepared using precursor films with and without copper–indium back-end layers. According to figure 5(a), Sample A1 exhibited a smooth surface with low root-mean-square (RMS) roughness. The CIGS film (sample B1) prepared using a precursor film with a copper–indium back-end layer, the RMS roughness value increased to 211 nm. When the bimetal-ion solution concentration was increased to 0.4 and 0.6 M for preparing copper–indium back-end layers, the RMS roughness of the resulting films increased to 223 and 252 nm, respectively. The surface roughness of the prepared CIGS films presented an upward trend with the bimetal-ion solution concentration, which is consistent with the rugged morphology observed in the previous SEM results (figure 4). Figure 6 presents a schematic of the effects of copper–indium back-end layers during post-selenization. According to the previous researches [32, 33], the formation of various intermediates such as indium selenide and copper selenide as fluxing agents induced the internal diffusion of atoms to promote grain growth in the CIGS films during selenization reaction. The interaction phenomenon resulted in the diffusion of indium atoms toward the surface of CIGS films gradually, and gallium atoms accumulated in the bottom region of the CIGS films, as shown in figure 6(a). When the precursor film with a copper–indium back-end layer was used, the internal atom diffusion was increased and promotion the grain growth of CIGS particles, resulting in the densification of prepared films, as displayed in figure 6(b).

3.3. Effects of concentration of the bimetal-ion solution used to prepare copper–indium back-end layers on photovoltaic performance of prepared Cu(In, Ga) Se₂ solar cells

Figure 7 shows plots of the I–V curves of CIGS solar cells prepared from precursor films with and without a copper–indium back-end layer. Table 1 summarizes the photovoltaic parameters of the prepared CIGS solar devices. The conversion efficiency of solar devices based on the CIGS film (sample A1) was estimated to be 8.34%. The V_{oc}, J_{sc}, and FF values were 563 mV, 25.70 mA cm\(^{-2}\), and 57.65%, respectively. When the CIGS film (sample B1) was prepared using precursor films with a copper–indium back-end layer, the conversion efficiency of the corresponding solar devices increased to 10.52%. The V_{oc}, J_{sc}, and FF values were 542 mV, 30.29 mA cm\(^{-2}\), and 64.06%, respectively. Furthermore, when a copper–indium back-end layer was prepared using a 0.4 M bimetal-ion solution, the conversion efficiency of the CIGS cells increased to 11.13%. Further increasing the concentration of bimetal-ion solution for preparing a copper–indium back-end layer, the conversion efficiency of corresponding solar cells was decreased to 10.41%.

![Figure 5.](image-url)
Figure 6. Schematic of the variation in microstructure of fabricated films with and without copper–indium back-end layers.

Figure 7. I–V characteristics of prepared solar cells based on (a) sample A1, (b) sample B1, (c) sample B2, and (d) sample B3.

Table 1. Photovoltaic properties of solar cells based on CIGS films synthesized using different precursor films.

| Samples | V_{oc} (mV) | J_{sc} (mA cm^{-2}) | FF (%) | η (%) |
|---------|-------------|---------------------|--------|-------|
| A1      | 563 ± 2     | 25.70 ± 0.49        | 57.65 ± 1.13 | 8.34 ± 0.33 |
| B1      | 542 ± 7     | 30.29 ± 0.44        | 64.06 ± 1.41 | 10.52 ± 0.43 |
| B2      | 533 ± 4     | 31.79 ± 0.18        | 65.70 ± 0.81 | 11.13 ± 0.20 |
| B3      | 515 ± 4     | 31.40 ± 0.28        | 64.42 ± 0.97 | 10.41 ± 0.32 |
The relationship between the concentrations of the bimetal-ion solution used to prepare copper–indium back-end layers and the photovoltaic parameters of the CIGS solar cells is illustrated in figure 8. The Voc values of the prepared solar cells decreased gradually when the concentrations of the bimetal-ion solution used to prepare copper–indium back-end layers increased. The decrease in Voc values was caused by the rough surface morphology of the CIGS films, which was induced by the incorporation of the copper–indium back-end layer. The rough surface of the CIGS films was considered to result in a non-uniform coverage of the buffer layer, thereby forming shunt paths in the p–n junction region. Another reason for the decrease in Voc values was decreased gallium content on the surface of the prepared CIGS films. As the gallium content in the surface region decreased, the bandgap values of the CIGS films in the surface region were reduced and the Voc values were declined. The Jsc and FF values of prepared solar cells increased significantly when CIGS films fabricated by the precursor film of copper–indium back-end layer. The improvement of Jsc and FF values was attributed to the bandgap gradient and reduce amount of voids in the bottom region of prepared CIGS films which was observed in figures 4(b) and (f). According the previous research [34], the dense structure of the CIGS films restrained the carrier recombination, and the gradient distribution of bandgap enhanced the collection of photo-generated carriers. Hence, the Jsc and FF values were elevated.

For investigating the diode parameters of prepared CIGS cells, the current density (J) is expressed using the diode equation [35]:

\[
J = J_0 e^{\frac{q}{AkT}(V - J_0)} - J_0 - J_{sc} + GV
\]  

(1)

where J0 and q denote the saturated current density and electron charge respectively, A denotes the diode factor which identified the mechanism of carriers recombination in prepared solar cells, k and T denote the Boltzmann constant and temperature (K) respectively, R_s denotes the series resistance, J_{sc} denotes the short-circuit current density, and G denotes the shunt conductance. The G values were extracted from the slope in the reverse bias region of the J-V curves and were used to calculate J' = J - GV. While R_sG ≪ 1, equation (1) can be simplified as below:

\[
V = R_sJ' + \frac{AkT}{q} \ln (J' + J_{sc}) - \frac{AkT}{q} \ln J_0
\]  

(2)

Differentiating equation (2) with respect to J' yields the below equation

\[
\frac{dV}{dJ'} = R_s + \frac{AkT}{q} (J' + J_{sc})^{-1}
\]  

(3)

The value of series resistance (R_s) can be calculated from the intercept of the plots dV/dJ’ versus (J’ + J_{sc})^{-1} and shown in figure 9(a). Furthermore, equation (2) can be rewritten as equation (4):

Figure 8. Correlation between the concentration of bimetal solution for preparing copper–indium back-end layers and performance of fabricated CIGS solar cells.
The value of diode factor ($A$) and saturated current density ($J_0$) can be respectively calculated from the slope and intercept of the equation (4) (as shown in figure 9(b)).

Table 2 summarizes the obtained diode parameters of prepared CIGS solar cells. According to the results in table 2, the diode parameters of fabricated CIGS solar cells were decreased when CIGS films prepared from precursor films with copper–indium back-end layer. As the concentration of bimetal-ion solution was increased...
to 0.4 M for preparing a copper–indium back-end layer, the $R_s$ value of prepared solar cells was decreased to 0.54 $\Omega$–cm. Meanwhile, the $G$ values of CIGS solar cells, which were related to shunt resistance decreased to 1.86 mS cm$^{-2}$. The decrease in the $R_s$ values and $G$ values were attributed to a decrease in the voids of the obtained CIGS films associated with growth in grain size. On the other hand, the $A$ values and $J_0$ values of obtained solar cells were decreased to 1.98 and 7.68 $\times$ 10$^{-4}$ mA cm$^{-2}$ when the concentration of bimetal-ion solution was 0.4 M. The decrease in $A$ values and $J_0$ values displayed that the carrier recombination and leakage current of prepared CIGS films was reduced via the incorporation of copper–indium back-end layer in the precursor films. Further increasing the concentration of bimetal-i ons solution to 0.6 M, all diode parameters of prepared solar cells were slightly increased. The increase in diode parameters was attributed to the decrease of bandgap in CIGS surface and the addition of surface roughness. The low bandgap value in the p-n junction region enhanced the possibility of carrier recombination, and the rough surface of CIGS films induced the formation of additional shunt paths. Therefore, the diode parameters of CIGS solar cells were deterioration. According to the aforementioned results, the preparation of CIGS films by using precursor films with appropriate concentrations of a copper–indium back-end layer can effectively enhance the photovoltaic characteristics of CIGS solar cells through a reduced leakage current and suppressed carrier recombination.

4. Conclusions

The incorporation of copper–indium back-end layers in the precursor films was an effective approach to improve the morphology and photovoltaic characteristics of solution-based CIGS films. The particle sizes and bandgap gradient of prepared CIGS films were increased gradually when the concentration of bimetal-ion solution was raised. The increase in the CIGS particle sizes reduced the formation of grain boundaries and suppressed the carrier recombination. The bandgap gradient of CIGS films enhanced the carrier collection; thereby, the photo-generated current of solar cells was increased. As the copper-indium back-end layer was prepared from the 0.4 M of bimetal-ion solution, the shunt conductivity and saturated current density of prepared solar cells was effectively reduced to 1.86 mS cm$^{-2}$ and 7.68 $\times$ 10$^{-4}$ mA cm$^{-2}$ respectively. Hence, the conversion efficiency of CIGS solar cells was significantly improved to 11.13%. Further increasing the concentration of bimetal-ion solution to 0.6 M, the rough surface with low bandgap of prepared CIGS films resulted in the decrease of open circuit potential and deterioration of the photovoltaic conversion efficiency of solar cells. The present study revealed that the incorporation of a copper-indium back-end layer into the precursor film for preparing CIGS films is an effective method for improving the photovoltaic performance of CIGS solar cells.

Acknowledgments

The authors thank the Ministry of Science and Technology, Taiwan (MOST 108–2218–E–002–042–MY3) for providing financial support and the ‘Advanced Research Center for Green Materials Science and Technology’ from The Featured Area Research Center Program within the framework of the Higher Education Sprout Project, Ministry of Education (107L9006) for providing support in conducting this research work. The authors also thank Ms. Su-Jen Ji, Ministry of Science and Technology (National Taiwan University), for her assistance in SEM experiments.

ORCID iDs

Chung-Hsin Lu @ https://orcid.org/0000-0003-0522-7020

References

[1] Huang F, Yan A H, Zhao H, Li Z, Cai X P, Wang Y H, Wu Y C, Yin S B and Qiang Y H 2014 CIS and CIGS nanomaterials prepared by solvothermal method and their spectral properties Cryst. Res. Technol. 49 953–8
[2] Chien S C, Chen F S and Lu C H 2011 Sol-gel assisted preparation and characterization of silver indium diselenide powders J. Alloys Compd. 509 8927–32
[3] Badgujar A C, Dusane R O and Dhage S R 2018 Sonochemical synthesis of Culn$_{0.7}$Ga$_{0.3}$Se$_2$ nanoparticles for thin film photo absorber application Mater. Sci. Semicond. Process. 81 17–21
[4] Seyrlinga S et al 2011 Culn$_{0.7}$Ga$_{0.3}$Se$_2$ growth process modifications: influences on microstructure, Na distribution, and device properties Sol. Energy Mater. Sol. Cells 95 1477–81
[5] Jseng Y Y, Chao C J, Sung H H and Chen T C 2018 CIGS thin film and device performance produced through a variation Ga concentration during three-stage growth process Mater. Sci. Semicond. Process. 87 162–6
[6] Sheu H H, Hsu Y T, Jian S Y and Liang S C 2016 The effect of Cu concentration in the photovoltaic efficiency of CIGS solar cells prepared by co-evaporation techniqe Vacuum 131 278–84
[7] Chirila A et al 2013 Potassium-induced surface modification of Cu(In, Ga)Se₂ thin films for high-efficiency solar cells Nat. Mater. 12 1107–11
[8] Niki S, Contreras M, Repins I, Povalia M, Kushiyama K, Ishizuka S and Matsubara K 2010 CIGS absorbers and processes Prog. Photovolt. Res. Appl. 18 453–66
[9] Uliczka S, Arrou P, Abbas A, Togay M, Welch L M, Bliss M, Malkov A V, Walls J M and Bowers J W 2019 Deposition and application of a Mo–N back contact diffusion barrier yielding a 12.0% efficiency solution-processed CIGS solar cell using an amine–thiol solvent system J. Mater. Chem. A 7 7042–52
[10] Calixto M E, Dobson K D, McCandless B E and Birkmire R W 2006 Controlling growth chemistry and morphology of single-bath electrodeposited Cu(In, Ga)Se₂ thin films for photovoltaic applications J. Electrochem. Soc. 153 G252–18
[11] Harati M, Iia J, Giffard K, Pellarin K, Hewson C, Love D A, Lau W M and Ding Z 2010 One-pot electrodeposition, characterization and photoactivity of stoichiometric copper indium gallium diselenide (CIGS) thin films for solar cells Phys. Chem. Chem. Phys. 12 15282–90
[12] Badgujar A C, Dusane R O and Dhage S R 2018 Cu(In, Ga)Se₂ thin film absorber layer by flash light post-treatment Vacuum 153 191–4
[13] McLoud S, Alrughbeh E and Agrawal R 2019 Liquid assisted grain growth in solution processed Cu(In, Ga)(S, Se)₂ Sol. Energy Mater. Sol. Cells 195 12–23
[14] Chen J, Shen H, Zhai Z and Li Y 2018 Effect of e-beam evaporated elemental metal stack precursors on the property of Cu(InGa)Se₂ thin films through two-step process J. Mater. Sci.: Mater. Electron. 29 19812–8
[15] Lu C H, Chiu G L, Som S and Ou C Y 2018 Influence of selenization temperatures on the microstructures and photoelectric properties of iron-ion doped Cu(In, Ga)Se₂ thin-film solar cells Vacuum 156 212–8
[16] Garcia J L et al 2015 Synthesis of Cu(In,S)₂Se₄ quaternary alloys by screen printing and selenization-sulfurization sequential steps: development of composition graded absorbers for low cost photovoltaic devices Mater. Chem. Phys. 160 237–43
[17] Park S J, Cho Y, Moon S H, Kim J E, Lee D K, Gwak J, Kim J, Kim D W and Min B K 2014 A comparative study of solution-processed low- and high-bandgap chalcopyrite thin-film solar cells J. Phys. D: Appl. Phys. 47 15505
[18] Septina W, Kurniara M, Ikeda S, Nakajima Y, Hirano T, Kawasaki Y, Harada T and Matsumura M 2015 Cu(In, Ga)(S, Se)₂ thin film solar cell with 10.7% conversion efficiency obtained by selenization of the Na-doped spray- pyrolyzed sulfide precursor film ACS Appl. Mater. Inter. 7 6472–9
[19] Xiao P, Ming Z, Daming Z, Rujun S, Leng Z, Yaowei W, Xunyan W, Xianyu W and Guan O 2018 10.3%-efficient submicron-thick Cu(In, Ga)Se₂ solar cells with absorber fabricated by sputtering In₄Se₃, CuGaSe₂, and Cu₂Se targets Appl. Surf. Sci. 442 308–12
[20] Balestrieri M, Achard V, Hildebrandt T, Lombiez L, Jubault M, Posada J, Lincoat D and Donsanti F 2019 Structural characterization of coevaporated Cu(In, Ga)Se₂ absorbers deposited at low temperature J. Alloys Compd. 794 654–61
[21] Schleussner S, Zimmermann U, Watjen T, Leifer K and Edoff M 2011 Effect of multi-stage grading in Cu(In, Ga)Se₂ solar-cell absorbers produced by multi-stage coevaporation Sol. Energy Mater. Sol. Cells 95 721–6
[22] Rodriguez-Alvarez H, Barreau N, Kaufmann C A, Weber A, Klaus M, Painchaud C, Schock H W and Mainz R 2013 Recrystallization of Cu(In, Ga)Se₂ thin films studied by x-ray diffraction Acta Mater. 61 4347–53
[23] Wu C H, Wu P W, Hsiao R C and Hsu C Y 2018 Growth and characterization of high quality CIGS films using novel precursor stacked and surface sulfurization process J. Mater. Sci.: Mater. Electron. 29 11429–38
[24] Lee S K, Sim J K, N Kissinger J S, Song I S, Kim J S, Back B J and Lee C R 2015 Se interlayer in CIGS absorption layer for solar cell devices J. Alloys Compd. 633 31–6
[25] Li W, Yan X, Xu W L, Long J, Aberle A G and Venkataraj S 2017 Efficiency improvement of CIGS solar cells by a modified rear contact Sol. Energy Mater. 157 486–95
[26] Kamada R, Shafarman W N and Birkmire R W 2010 Cu(In, Ga)Se₂ film formation from selenization of mixed metal/metal–selenide precursors Sol. Energy Mater. Sol. Cells 94 451–6
[27] Wang J, Zhang Y F, Dong F and Zhu J 2001 Control of two-step growth processes of chalcopyrite thin films by x-ray fluorescence spectroscopy Appl. Surf. Sci. 173 62–8
[28] Dullweber T, Hanna G, Kolahi W S, Schwartzlander A, Contreras M A, Noufi R and Schock H W 2000 Study of the effect of gallium grading in Cu(In, Ga)Se₂ Thin Films 361 478–81
[29] Liao K H, Su C Y and Ding Y T 2013 Effects of Ga accumulation on the microstructure of Cu(In, Ga)Se₂ thin films during selenization J. Alloys Compd. 581 230–6
[30] Maria B, Marie B, Armin E Z, Nick L, Christophe V, Samira K, Ief V, Marc M and Joke H 2015 Effect of the burn-out step on the microstructure of the solution-processed Cu(In, Ga)Se₂ solar cells Thin Solid Films 583 142–50
[31] Guo Q, Ford G M, Agrawal R and Hillhouse H W 2013 Ink formulation and low-temperature incorporation of sodium to yield 12% efficient Cu(In, Ga)(S, Se)₂ solar cells from sulfide nanocrystal inks Prog. Photovolt. Res. Appl. 21 64–71
[32] Hiroi H, Iwata Y, Adachi S, Sugimoto H and Yamada A 2012 Characteristics of Cu(In, Ga)Se₂ films prepared by atmospheric pressure selenization of Cu-In-Ga precursors using ditert-butylselenide as Se source J. Electrochem. Soc. 159 H378–83
[33] Scholdstrom J, Kessler J and Edoff M 2005 Two-stage growth of smooth Cu(In, Ga)Se₂ films using end-point detection Thin Solid Films 480 61–6
[34] Dullweber T, Lundberg O, Malmstrom J, Bodegard M, Stolt L, Rau U, Schock H W and Werner J H 2001 Back surface band gap gradings in Cu(In, Ga)Se₂ solar cells Thin Solid Films 387 11–3
[35] Cho Y, Lee E, Kim D W, Ahn S, Jeong G Y, Gwak J, Yun J H and Kim H 2013 Influence of shunt conduction on determining the dominant recombination processes in CIGS thin-film solar cells Curr. Appl. Phys. 13 37–40