Research Article

The Effects of Annealing Parameters on the Crystallization and Morphology of Cu(In,Ga)Se_2 Absorber Layers Prepared by Annealing Stacked Metallic Precursors

Chia-Ho Huang¹ and Dong-Cherng Wen²

¹ Department of Mechanical Engineering, Lunghwa University of Science and Technology, Taoyuan 33306, Taiwan

² Department of Mechanical Engineering, China University of Science and Technology, Taipei 11581, Taiwan

Correspondence should be addressed to Chia-Ho Huang; chhuang@mail.lhu.edu.tw

Received 24 February 2014; Revised 7 May 2014; Accepted 7 May 2014; Published 11 June 2014

Academic Editor: Ho Chang

Copyright © 2014 C.-H. Huang and D.-C. Wen. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

CIGS films are prepared by single-stage annealing of the solid Se-coated In/Cu-Ga bilayer precursor. The annealing processes were performed using various Ar pressures, heating rates, and soaking times. A higher Ar pressure is needed to fabricate highly crystalline CIGS films, as no extra Se-vapor source is supplied. As the heating rate increases, the surface morphologies of the CIGS films become looser and some cracks are observed. However, the influence of soaking time is insignificant and the selenization process only requires a short time when the precursors are selenized at a higher temperature with a lower heating rate and a higher Ar pressure. In this study, a dense chalcopyrite CIGS film with a thickness of about 1.5–1.6 μm , with large grains ($\sim 1.2 \mu\text{m}$) and no cracking or peeling is obtained after selenizing at a temperature of 550°C, an Ar pressure of 300 Torr, a heating rate of 60°C/min, and a soaking time of 20 min. By adequate design of the stacked precursor and controlling the annealing parameters, single-stage annealing of the solid Se-coated In/Cu-Ga bilayer precursor is simplified for the fabrication of a fully crystallized chalcopyrite CIGS absorber layers with good crystallization and large grains.

1. Introduction

Chalcopyrite Cu(In,Ga)Se_2 (CIGS) is a good absorber for high-efficiency thin film solar cells because of its favorable band gap and high-absorption coefficient for solar radiation [1]. Of the various ways of preparing CIGS absorber, postselenization of precursor layers is one of the leading methods [2, 3], with an efficiency of around 20% for high temperature annealing of vacuum-sputtered metals under selenium vapor (i.e., selenization) [4, 5]. In spite of such an excellent device performance, a complete understanding of the material produced is required, because the properties of films depend greatly on the process parameters and affect the quality of the resulting CIGS films. In particular, postselenization has an important effect on the structure and morphology of films. In order to reliably obtain the requisite film properties, it is essential to understand the effect of thermal annealing parameters on film properties.

Two selenization techniques, namely, conventional furnace annealing and rapid thermal processing, have been developed. In traditional annealing, Cu-Ga-In metallic precursors are selenized in selenium vapor, obtained from diethylselenide (DESe) or other organometallic precursors [6]. However, the low heating rate during selenization can cause Se to evaporate during the annealing process and can also cause the dewetting of Se. Furthermore, the use of toxic H_2Se gas is limited in most cases. Although these problems can be avoided by rapid thermal annealing of the metallic precursors with Se pellets, instead of H_2Se gas [7, 8], the incomplete reaction of the metallic precursors with Se often leaves an unreacted Cu-Ga metallic layer on the backside of the sample during the annealing, even after long annealing times [9]. A one-step sputtering process, using a single quaternary target, has been developed to simplify the fabrication process of CIGS absorber and to eliminate the waste of excess Se [10, 11]. The influence of working pressure

on the efficiency of CIGS based device was studied and the results show that the average efficiency of 6-7% is obtained at a wide working pressure range of 0.4–2.7 Pa by using KCN treatment and the best cell efficiency can reach 8% at the working pressure of 0.67 Pa [11]. However, it is still difficult to obtain high quality CIGS films by directly sputtering from a single CIGS target. Postselenization is necessarily used to improve device performance [12].

The feasibility of fabricating the chalcopyrite CIGS absorber layers by conducting the Se-coated single-layered precursor in a two-step postselenization process has been evaluated [13]. However, the impact of annealing parameters was not studied. In this paper, an alternative selenization process, applying a single-stage annealing of the solid Se-coated In/Cu-Ga bilayer precursors in a vacuum furnace, is proposed to produce single-phase chalcopyrite CIGS absorber. The effect of annealing parameters, such as inert gas pressure, heating rate, and soaking time, on the structure and morphology of the CIGS absorber formed after selenization in an Ar containing atmosphere is determined in this paper.

2. Experimental

CIGS absorber layers were grown on soda-lime glass (SLG) substrates, using a two-step process. The metallic precursor film deposition included DC-magnetron sputtering of the Cu-Ga and In layers at room temperature and thermal evaporation of Se. Preliminary deposition of the Cu-Ga and In layers shows that the thickness of each layer increased linearly with increasing deposition time; thus, the deposition rate of layers can be obtained by measuring the film thickness. The deposition parameters were optimized to obtain an absorber thickness of $\sim 1.5 \mu\text{m}$. The bottom layer of 350 nm thick Cu-Ga alloy film was deposited at a sputtering power of 100 W and Ar pressure of 5.0×10^{-3} Torr, from a Cu-Ga alloy target with 25 wt.% Ga, while In was deposited at a sputtering power of 40 W and Ar pressure of 5.0×10^{-3} Torr from an In target. The thickness of the In layer was adjusted by varying the deposition time to obtain precursor films with atomic compositions of $\text{Cu}/(\text{In} + \text{Ga}) = 0.8\text{--}0.9$ and $\text{Ga}/(\text{In} + \text{Ga}) = 0.1\text{--}0.3$. As no extra Se-vapor source was used during the annealing process, the natural loss of Se during heating was compensated for by deposition of an excess of Se onto the precursor stack. A $2 \mu\text{m}$ overstoichiometric Se layer was deposited at 220°C after preheating to 150°C for 10 min at a rate of 20°C/s . The substrate was rotated at 40 rpm, during deposition, to improve the film's uniformity.

The precursors were then selenized in an Ar atmosphere, using single-stage annealing at a constant temperature of 550°C . In order to determine the effect of annealing parameters, the annealing processes were performed using various Ar pressures and temperature profiles. Ar pressure from 1 Torr to 300 Torr was used, the heating rate was varied between 60°C/min and 240°C/min , and a soaking time at constant temperature from 20 min to 60 min was used. The cooling rate after selenization was about 6°C/min .

The surface morphologies of the films were analyzed using field emission scanning electron microscopy (SEM, JEOL, and JSM-6500F). The phases and crystal structure were

FIGURE 1: The atomic composition ratios of In/Cu-Ga precursors as a function of In deposition time.

FIGURE 2: The surface morphology of the In/Cu-Ga precursor prepared with 120 min of In deposition time.

determined by X-ray diffraction (Rigaku-2000 X-ray diffractometer), using $\text{Cu-K}\alpha$ radiation and an angle of incidence of 1° . The composition of the CIGS films was determined by energy dispersive X-ray fluorescence spectrometry (EDXRF, Solar metrology SMX).

3. Results and Discussion

3.1. Analysis of the Precursors. Firstly, the material properties of the as-deposited precursors are determined. The compositions of the In/Cu-Ga precursors with various In deposition time were analyzed by EDS and their atomic composition ratios are shown in Figure 1. When the In deposition time is 120 min, the precursor has the desired atomic composition of $\text{Cu}/(\text{In} + \text{Ga}) = 0.85$ and $\text{Ga}/(\text{In} + \text{Ga}) = 0.18$, so this time was used for selenization. Figure 2 shows the surface morphologies of this standard precursor. Some large and discontinuous island-like grains are precipitated onto the flat surface. The EDS results show that the island-like grains are detected as In-rich alloys. However, the smoother background is detected to be Cu-rich alloys. The island-like grains are thought to be In hillocks, which form automatically,

FIGURE 3: The XRD patterns of the In/Cu-Ga precursor produced using an In deposition time of 120 min. JCPDS: Cu_2In (00-026-0552), Cu_3Ga (00-044-1117), and In (03-065-9292).

FIGURE 4: Cross-sectional SEM image of the solid Se-coated In/Cu-Ga precursor.

because of the high diffusion coefficient and low melting point of In [14]. Figure 3 shows the corresponding XRD pattern of the metallic precursor in Figure 2. As reported by Park et al. [15], a pure In peak and intermetallic Cu_2In and Cu_3Ga , as equilibrium phases at room temperature, are observed. The Cu_2In reflexes are of lower intensity than those for Cu_3Ga , which suggests that the latter phase is prominent. Figure 4 shows the cross-sectional SEM image of the solid Se-coated In/Cu-Ga precursor layer, deposited on the SLG substrates. Clearly, an expected 350 nm thick of Cu-Ga alloy film and 2 μm of Se without peeling or cracking are observed. The Se layer evaporated onto the In/Cu-Ga layer yields a smooth surface and penetrates into and fully surrounds the In islands. The Se-coated In/Cu-Ga precursors were subsequently moved to the furnace, for selenization in an Ar containing atmosphere.

3.2. The Effect of Ar Pressure. As no extra Se-vapor source was supplied, the amount of Se that can react with In/Cu-Ga precursors, during annealing, is determined by the working pressure in the reaction chamber. There are two ways to

FIGURE 5: XRD patterns of the CIGS films, selenized using different Ar pressures.

control the working pressure. The first method uses the autogenous pressure, which is governed by the degree of evaporation of Se, and the second method uses an external control on the amount of internal pressure by pumping the inert gas into the chamber. The second method was used because of its simplicity.

Figure 5 shows the XRD patterns for the selenized CIGS films at different Ar pressures, from 1 to 300 Torr. For these runs, the heating rate during annealing was maintained at 90°C/min and the soaking time was 30 min. All of the CIGS films have the chalcopyrite phases, (112), (220)/(204), and (312)/(116), and diffraction peak (112) is the strongest. This shows that the CIGS films are polycrystalline and oriented along the (112) direction, parallel to the substrate. The XRD patterns do not show other complex peaks, which indicates that the single-stage annealing process may form acceptable chalcopyrite structures in CIGS thin films. This is likely, because the ramping rate for furnace annealing of these cases is far slower than for rapid thermal annealing processes; so, the time required to reach the desired temperature is sufficient for selenide compounds to form, ultimately developing CIGS [16].

Figure 5 also shows that the CIGS peaks increase as the Ar pressure increases, which may be attributed to the crystallization quality and grain growth. At lower Ar pressure, the working pressure is not sufficient to allow the Se to stay on the precursor layer. Se evaporates from the layer stack, instead of diffusing into it, so the layer goes from a weak CIGS peak, due to the Se deficiency, which indicates poor crystallinity or smaller grains in these cases. Increasing the Ar pressure decreases the evaporation of Se and improves the chemical reactivity of Se with the In/Cu-Ga precursors. As a result, the intensity of the CIGS peaks increases through the crystallinity improvement and the grain size increases. The change in the microstructure due to the increase in the Ar pressure is also confirmed by the SEM observations. In Figure 6, SEM images for three of the studied Ar pressures are shown for the lowest (1 Torr) and 100 Torr, and the highest Ar pressure (300 Torr).

FIGURE 6: Cross-sectional and top-view SEM images of the CIGS films selenized at (a), (b) the lowest (1 Torr), (c) and (d) 100 Torr, and (e) and (f) the highest Ar pressure (300 Torr).

At the lowest Ar pressure, the thickness of the CIGS layer is thinner than that of the other samples and no obvious grains are seen. The low Ar pressure annealing process results in a marked loss of Se, due to vaporization, thereby significantly reducing the thickness of the CIGS layer. For an Ar pressure of 100 Torr, the thickness of the CIGS layer increases and the morphology of CIGS grains becomes more obvious. For the highest Ar pressure, some faceted surface and angled grain boundaries within the film are observed. The CIGS layer has a maximum thickness of about $1.5\text{--}1.6\text{ }\mu\text{m}$ and the grains have a maximum diameter of $\sim 1.2\text{ }\mu\text{m}$, because more Se stays on the surface of the precursor layers and then reacts with the precursors to form CIGS. From these analyses, it is concluded

that the selenization process requires a higher Ar pressure to produce a better morphology and highly crystalline CIGS films, as no extra Se-vapor source is supplied.

3.3. The Effect of Heating Rate. Figure 7 shows the XRD patterns for the selenized CIGS films as a function of heating rate for a soaking time of 30 min and an Ar pressure that is fixed at 300 Torr. The CIGS peaks are smaller when the heating rate is increased. This means that increasing the heating rate for single-stage annealing of the solid Se-coated In/Cu-Ga precursors is detrimental to the crystallinity of the CIGS films. When the annealing temperature is ramped between the melting point of In ($\sim 150^\circ\text{C}$) and Se ($\sim 220^\circ\text{C}$), the Se

TABLE 1: The elemental composition of CIGS films.

Soaking times (min)	Compositions (at %)				Ratios	
	Cu	In	Ga	Se	Cu/(In + Ga)	Ga/(In + Ga)
20	23.9	20.3	5.9	49.9	0.91	0.22
30	23.5	19.8	5.9	50.8	0.91	0.22
40	23.8	20.4	6.0	49.8	0.90	0.22
50	24.1	19.9	6.1	49.9	0.92	0.23
60	23.6	20.1	5.8	50.5	0.91	0.22

FIGURE 7: XRD patterns of the selenized CIGS films as a function of heating rate.

coating is fully incorporated into the surrounding In and diffuses into the Cu-Ga layer. This Se can react with the In and the intermetallic Cu_2In and Cu_3Ga of Cu-Ga precursor layer, subsequently converting itself into the metallic selenides, In_2Se_3 , Cu_2Se , and Cu_3Se_2 [13, 17]. Increasing the annealing temperature to greater than 330°C [18] causes these metallic selenides to react to form the chalcopyrite phase by the following chemical reaction mechanism: $\text{In}_2\text{Se}_3 + \text{Cu}_2\text{Se} \rightarrow 2\text{CuInSe}_2$ [19] and $3\text{In}_2\text{Se}_3 + 2\text{Cu}_3\text{Se}_2 \rightarrow 6\text{CuInSe}_2 + \text{Se(g)}$ [13].

The amount of diffused Se and metallic selenides depends on the time spent in the $150\text{--}220^\circ\text{C}$ temperature range. This time interval is shorter if the heating rate is faster, so the intensity of the CIGS peaks is less and the crystallinity of CIGS films is poor. Figure 8 shows a comparison of cross-sectional and top-view SEM images of selenized CIGS layers produced using heating rates of 60°C/min , 120°C/min , and 240°C/min . The faceted surface and angled grain boundaries of the CIGS structure become more obvious as the heating rate is reduced. The cross-sectional SEM images show that both the grain size and thickness of CIGS films increase with decreasing the heating rate. This observation is consistent with the results of XRD. However, as the heating rate increases, the surface morphologies of the CIGS films become looser and some cracks are observed, because the chalcopyrite structure does not completely form throughout

the entire depth of the precursor. A shorter period of time in the $150\text{--}220^\circ\text{C}$ temperature range causes more Se to evaporate away from the layer stack. The lack of Se results in poor crystallinity of the CIGS layers.

3.4. The Effect of Soaking Time. Based on the above analyses, it is seen that a higher Ar pressure (300 Torr) and a lower heating rate (60°C/min) are beneficial to the formation of the chalcopyrite phase, so these two parameters are fixed and the influence of soaking time is studied. Figure 9 shows the XRD patterns for the CIGS films selenized at 550°C , for various soaking times. All of the films in this figure have the basic chalcopyrite and the difference in the peaks is insignificant. This means that the selenization process only requires a shorter time at a higher temperature. This is because the chalcopyrite structure completely forms when the precursor is annealed at 550°C for 20 min, which gives a stable structure. After the chalcopyrite structure forms, the growth of chalcopyrite grains in over prolonged soaking times is not apparent, so the difference between the peaks for the films soaked for longer soaking times and those for the 20 min sample is insignificant. Cross-sectional and top-view SEM images of 20 min selenized CIGS film are shown in Figure 10. As is seen, the grain characteristics and surface morphologies of this sample are similar to those for the 30 min sample shown in Figures 8(a) and 8(b), which confirms that a soaking time of 20 min is sufficient to form the chalcopyrite structure, when the precursors are selenized at an Ar pressure of 300 Torr, a heating rate of 60°C/min , and a temperature of 550°C .

The results show that the thickness of the annealed CIGS absorber layers increases with increasing the Ar pressure but decreases with increasing the heating rate. However, the influence of soaking time is insignificant when the Ar pressure and heating rate are fixed.

Table 1 lists the elemental compositions and atomic ratios of the CIGS films annealed at 550°C for different times. Compared with the as-deposited precursor, the $\text{Cu}/(\text{In} + \text{Ga})$ ratios increase from 0.85 to 0.90–0.92 and the $\text{Ga}/(\text{In} + \text{Ga})$ ratios increase from 0.18 to 0.22–0.23, because of the loss of In during selenization at high temperature. However, when the stable structure of the chalcopyrite phase is formed, after annealing at 550°C for 20 min, the difference in composition is insignificant for the samples annealed for a longer soaking time. The composition of all of the CIGS films remains almost constant. The detailed compositional uniformity of CIGS

FIGURE 8: Cross-sectional and top-view SEM images of CIGS films made using (a), (b) the lowest ($60^{\circ}\text{C}/\text{min}$), (c) and (d) $120^{\circ}\text{C}/\text{min}$, and (e) and (f) the highest heating rate ($240^{\circ}\text{C}/\text{min}$).

films was also determined by X-ray fluorescence intensity measurements of the $K_{\alpha 1,2}$ lines [20]. Figure 11 shows the depth profile of CIGS sample annealed at 550°C for 20 min. The high degree of detailed compositional uniformity with no evidence of phase segregation shows that the procedures used in this study are a successful way for the fabrication of single chalcopyrite structure CIGS film.

Finally, a heterojunction solar cell was fabricated and evaluated under simulated AM1.5 ($100\text{ mW}/\text{cm}^2$) conditions at 25°C . In brief, the absorber film was immediately coated with a 50-nm-thick CdS buffer layer. The CdS layer was then covered with a 100 nm highly resistive intrinsic ZnO layer and then a highly doped n-type ZnO film with a typical thickness

of approximately 600 nm. The $2.5\text{ }\mu\text{m}$ Ni/Al front contact was deposited onto the ZnO using DC magnetron sputtering and there was no intentional heating of the substrate. A solar cell with 6.96% efficiency (open circuit voltage (V_{oc}), 537 mV, a short circuit current (J_{sc}) of $29.20\text{ mA}/\text{cm}^2$, and a fill factor (FF) of 47.55%) was produced. This efficiency approximates to the quality of the newly published results [11].

4. Conclusions

A fully crystallized chalcopyrite CIGS absorber is fabricated by single-stage annealing of the solid Se-coated In/Cu-Ga

FIGURE 9: XRD patterns of the CIGS films selenized at 550°C for various soaking times.

FIGURE 10: (a) Cross-sectional and (b) top-view SEM images of CIGS film selenized at 550°C for 20 min.

bilayer precursor, without an extra Se supply. The effect of the annealing parameters, including Ar pressure, heating rate, and soaking time, on the structure and morphology of the CIGS absorber is studied. The results show that the atomic composition of the precursors can be controlled by varying the thickness of the stacked layer. The selenization process requires a higher Ar pressure to produce a better morphology and highly crystalline CIGS films, as no extra Se-vapor source is supplied. The thickness of the CIGS films, after annealing, increases as the Ar pressure is increased. Increasing the heating rate is detrimental to the crystallinity of the CIGS films, because the amount of Se that can react with the metallic precursors depends on the time spent within the melting point range of In and Se. This time interval is shorter if the heating rate is faster. When a higher Ar pressure and a lower heating rate are used, the selenization process requires a shorter soaking time at a higher temperature. A dense CIGS film with a thickness of about 1.5–1.6 μm with large grains ($\sim 1.2 \mu\text{m}$) and no cracking or peeling phenomena is obtained at a selenizing temperature of 550°C, Ar pressure of 300 Torr, heating rate of 60°C/min, and soaking time of

20 min. This study demonstrates that by adequate design of the stacked precursor and by controlling the annealing parameters, single-stage annealing of the solid Se-coated In/Cu-Ga bilayer precursor is a simple way to fabricate fully crystallized chalcopyrite CIGS absorber layers with good crystallization and large grains.

Highlights

- (1) The atomic composition of the precursors can be controlled by varying the thickness of the stacked layer.
- (2) Higher Ar pressure and a lower heating rate are used, and the annealing process requires a shorter soaking time at a higher temperature.
- (3) This study demonstrates that single-stage annealing of the solid Se-coated In/Cu-Ga bilayer precursor is a simple way to fabricate a fully crystallized chalcopyrite CIGS absorber layer with good crystallization and large grains.

FIGURE 11: The XRF detailed compositional uniformity of Cu, In, Ga, and Se in the CIGS sample annealed at 550°C for 20 min.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] H. Neumann, "Optical properties and electronic band structure of CuInSe₂," *Solar Cells*, vol. 16, pp. 317–333, 1986.
- [2] R. W. Birkmire and E. Eser, "Polycrystalline thin film solar cells: present status and future potential," *Annual Review of Materials Science*, vol. 27, no. 1, pp. 625–653, 1997.
- [3] R. Caballero, C. Guillén, M. T. Gutiérrez, and C. A. Kaufmann, "CuIn_{1-x}Ga_xSe₂-based thin-film solar cells by the selenization of sequentially evaporated metallic layers," *Progress in Photovoltaics: Research and Applications*, vol. 14, no. 2, pp. 145–153, 2006.
- [4] P. Jackson, D. Hariskos, E. Lotter et al., "New world record efficiency for Cu(In,Ga)Se₂ thin-film solar cells beyond 20%," *Progress in Photovoltaics: Research and Applications*, vol. 19, no. 7, pp. 894–897, 2011.
- [5] Y. Goushi, H. Hakuma, K. Tabuchi, S. Kijima, and K. Kushiya, "Fabrication of pentanary Cu(InGa)(SeS)₂ absorbers by selenization and sulfurization," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1318–1320, 2009.
- [6] N. G. Dhere, S. S. Kulkarni, A. H. Jahagirdar, and A. A. Kadam, "Composition and morphology of partially selenized CuIn_{1-x}Ga_xSe₂ thin films prepared using diethylselenide (DESe) as selenium source," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 11, pp. 1876–1879, 2005.
- [7] X. Wang, S. S. Li, W. K. Kim et al., "Investigation of rapid thermal annealing on Cu(In,Ga)Se₂ films and solar cells," *Solar Energy Materials and Solar Cells*, vol. 90, no. 17, pp. 2855–2866, 2006.
- [8] S. Merdes, R. Mainz, H. Rodriguez-Alvarez et al., "Influence of precursor stacking on the absorber growth in Cu(In,Ga)S₂ based solar cells prepared by a rapid thermal process," *Thin Solid Films*, vol. 519, no. 21, pp. 7189–7192, 2011.
- [9] R. Mainz, R. Klenk, and M. C. Lux-Steiner, "Sulphurisation of gallium-containing thin-film precursors analysed in-situ," *Thin Solid Films*, vol. 515, no. 15, pp. 5934–5937, 2007.
- [10] Y. C. Lin, J. H. Ke, W. T. Yen, S. C. Liang, C. H. Wu, and C. T. Chiang, "Preparation and characterization of Cu(In,Ga)(Se,S)₂ films without selenization by co-sputtering from Cu(In,Ga)Se₂ quaternary and In₂S₃ targets," *Applied Surface Science*, vol. 257, no. 9, pp. 4278–4284, 2011.
- [11] C.-H. Chen, T.-Y. Lin, C.-H. Hsu, S.-Y. Wei, and C.-H. Lai, "Comprehensive characterization of Cu-rich Cu(In,Ga)Se₂ absorbers prepared by one-step sputtering process," *Thin Solid Films*, vol. 535, no. 1, pp. 122–126, 2013.
- [12] J. H. Shi, Z. Q. Li, D. W. Zhang, Q. Q. Liu, Z. Z. Sun, and S. M. Huang, "Fabrication of Cu(In, Ga)Se₂ thin films by sputtering from a single quaternary chalcogenide target," *Progress in Photovoltaics: Research and Applications*, vol. 19, no. 2, pp. 160–164, 2011.
- [13] G. S. Chen, J. C. Yang, Y. C. Chan, L. C. Yang, and W. Huang, "Another route to fabricate single-phase chalcogenides by post-selenization of Cu-In-Ga precursors sputter deposited from a single ternary target," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1351–1355, 2009.
- [14] Z.-H. Li, E.-S. Cho, S. J. Kwon, and M. Dagenais, "Formation of CuInSe₂ absorber by rapid thermal processing of electron-beam evaporated stacked elemental layers," *Journal of Materials Science: Materials in Electronics*, vol. 23, no. 4, pp. 964–971, 2012.
- [15] H. Park, S. C. Kim, S.-H. Lee et al., "Effect of precursor structure on Cu(InGa)Se₂ formation by reactive annealing," *Thin Solid Films*, vol. 519, no. 21, pp. 7245–7249, 2011.
- [16] H. K. Song, J. K. Jeong, H. J. Kim, S. K. Kim, and K. H. Yoon, "Fabrication of CuIn_{1-x}Ga_xSe₂ thin film solar cells by sputtering and selenization process," *Thin Solid Films*, vol. 435, no. 1-2, pp. 186–192, 2003.
- [17] D. Bhattacharyya, I. Forbes, F. O. Adurodiya, and M. J. Carter, "Formation of CuInSe₂ by the selenization of sputtered Cu/In layers," *Journal of Materials Science*, vol. 32, no. 7, pp. 1889–1894, 1997.
- [18] J. Koo, S. C. Kim, H. Park, and W. K. Kim, "Cu(InGa)Se₂ thin film photovoltaic absorber formation by rapid thermal annealing of binary stacked precursors," *Thin Solid Films*, vol. 520, no. 5, pp. 1484–1488, 2011.
- [19] J. S. Park, Z. Dong, S. Kim, and J. H. Perepezko, "CuInSe₂ phase formation during Cu₂Se/In₂Se₃ interdiffusion reaction," *Journal of Applied Physics*, vol. 87, no. 8, pp. 3683–3690, 2000.
- [20] C.-Y. Hsu, P.-C. Huang, Y.-Y. Chen, and D.-C. Wen, "Fabrication of a Cu(InGa)Se₂ thin film photovoltaic absorber by rapid thermal annealing of CuGa/In precursors coated with a Se layer," *International Journal of Photoenergy*, vol. 2013, Article ID 132105, 7 pages, 2013.