The effect of substrate temperature on Cu(In,Ga)Se₂ layers deposited by dual thermal evaporation

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ABSTRACT
This paper focuses on the preparation of CulnₓGa₁₋ₓSe₂ (CIGS) by a dual thermal evaporation method only without post-salinization treatment. The effect of substrate temperature on the deposition of stoichiometric layers has been explored. Fabricated CulnₓGa₁₋ₓSe₂ layers were described by energy-dispersive X-ray (EDX), diffraction of X-ray, Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), Ultraviolet-Visible-Near IR Spectroscopy and the four-point probing technique. CIGS layers of chalcopyrite structures were fabricated successfully with a bandgap of 1.35 eV. The stoichiometry, the grain size and roughness of layers are affected dramatically by the substrate temperature due to re-evaporation of the selenium content during deposition at high temperature. Electrical measurements explain the relationship between electrical conductivity and the value of metal/Se.

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1. Introduction
One of the high favourable absorber layer for solar cells is CulnₓGa₁₋ₓSe₂ (CIGS) [1]. Several techniques have been used to prepare CIGS layers, for example; flash-evaporation [2], sputtering [3], electrodeposition [4], spray pyrolysis [5], sequential vacuum evaporation [6], molecular beam epitaxy [7], hot-wall epitaxy [8], co-evaporation [9], spin coating [10], chemical ion exchange [11], nanoparticle-ink fabrication [12], and solvothermal synthesis. The highest efficiency recorded for CIGS thin-film solar cells is 23.35% [13]. Co-evaporation technique is the most used technique for the preparation of high efficient CulnₓGa₁₋ₓSe₂ solar cells. It is a complicated deposition method because it requires precise monitoring of the temperature of four sources simultaneously. Typically, the co-thermal evaporation technique consists of four sources, which in turn increase the cost of the technology and the difficulty of use.

To our knowledge, this is the first research that shows how to optimize the preparation of CIGS from elemental powder by only two heated sources. Then, the capability of using a dual thermal evaporation technique to get stoichiometric CIGS layers was investigated by studying the structure, the morphology and the optical characteristics at different temperatures of the substrate.

2. Experimental details
Copper (Cu – 99.99%), Indium (In – 99.99%), Gallium (Ga – 99.99%) and Selenium (Se – 99.999%) powders were weighed in masses of 28, 28, 0.6 mg, and 0.37 g, respectively. Copper, indium and gallium were placed in boat 1 (molybdenum boats, 84–52 TED Pella, INC), while selenium was placed in boat 2. The films were deposited by heating the two boats simultaneously. The substrates were standard soda-lime microscope slide glass. The distance between the substrate and the boats was 14 cm, and the distance between the boats was 2.5 cm. The vacuum of the system at the beginning was approximately 10⁻⁵ mbar. The currents of the first and second boats were 120 and 50 A, respectively. The layers were deposited at different substrate temperatures, 28, 100, 120, 200, and 250°C. The duration of the deposition depends on the complete evaporation of all elements from the boats, which was around 5 min. The thicknesses of the deposited films were measured by the stylus profilometer (Dektak 150).

Shimadzu XRD-6000 diffractometer was used to examine the texture of the deposited thin films with CuKα radiation (λ = 1.5418 Å), generated at 40 kV and 30 mA. Field-emission scanning electron microscope FESEM (FEI Quanta 250) and a desktop scanning electron microscope (JEOL – JCM 6000) were used for images acquisition and energy-dispersive X-ray...
Figure 1. The atomic composition of the layers prepared at various temperatures of the substrate.

Figure 2. The reliance of the thickness of CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ layers on the substrate temperature.

Figure 3. XRD diffraction of CIGS layers deposited at different temperatures.

Figure 4. The reliance of the grain size of CIGS layers on the substrate temperature.

(EDX) analysis. Spectrophotometer (Shimadzu 3150 UV–VIS–NIR) was used to measure the transmittance, $T(\lambda)$, at a normal incidence and the reflectance, $R(\lambda)$, at a reflectance angle of 5°. The Spectral wavelengths were between 190 and 2700 nm with a resolution of 0.1 nm. Atomic force microscope (AFM; Veeco CP-II) was used to investigate the surface morphology of the films layers in noncontact mode at a scan rate of 1 Hz by Si tips. Raman microscope spectrometer (Bruker Senterra) was used to explore the structure of the films. The excitation laser wavelength was a 532 nm (5 mW). The recorded Raman spectral in the range of 60–1554 cm$^{-1}$ with a resolution of 3.5 cm$^{-1}$. The resistivity of the samples was investigated by a computerized 4-point probe system using a Keithley 2420 instrument.

Table 1. The composition of the layers at different substrate temperatures.

| Substrate temperature (°C) | Cu    | In    | Ga    | Se  | Ga/(Ga + In) | Composition               |
|---------------------------|-------|-------|-------|-----|--------------|---------------------------|
| 28                        | 2.26  | 1.14  | 0.89  | 95.71| 0.44         | Cu$_{0.5}$In$_{0.5}$Ga$_{0.39}$Se$_{2}$ |
| 100                       | 6.06  | 4.94  | 1.87  | 87.12| 0.27         | Cu$_{1}$In$_{0.81}$Ga$_{0.3}$Se$_{14.3}$ |
| 200                       | 24.44 | 17.97 | 9.53  | 48.06| 0.34         | Cu$_{1}$In$_{0.73}$Ga$_{0.38}$Se$_{1.9}$ |
| 250                       | 24.83 | 19.28 | 15.42 | 40.47| 0.44         | Cu$_{1}$In$_{0.77}$Ga$_{0.62}$Se$_{1.6}$ |
3. Results and discussion

Figure 1 and Table 1 show the elements concentration of the layers, which changes dramatically with the temperature. The selenium concentration in the films is significant affected by the temperature. It decreases sharply as the temperature increases from 28°C to 120°C and slightly for temperatures between 120°C and 250°C. It’s obvious that there is re-sublimation of unbound selenium atoms from the layers. As a result of that, the concentration of other elements changed to give stoichiometric layers that can be created at 120°C. It is clear that the sensitivity of the Se to the substrate temperature influences the final composition of thin films. Then, Optimum values of $\text{Ga/(Ga+In)} \approx 0.3$ [14] could be achieved for substrate temperatures between 120 and 200°C.

Figure 2 shows that the thickness of the layers decreased dramatically from 1686 nm to 320 nm as the substrate temperature increased from room temperature to 120°C due to the sharp decrease in selenium content in the films. Then, it decreased slightly at approximately 20 nm as the temperature increased to 250°C.
The XRD patterns of the CIGS thin films are illustrated in Figure 3. The films that were prepared at 28 and 100°C have no patterns because the content of selenium is very high and the films are amorphous. Patterns gradually appear as the substrate temperature increases and are shown clearly at 200°C and 250°C. The strong (112) peak was confirmed by the card No. 00-035-1101 of International Centre for Diffraction Data (ICDD) database. It corresponds to the chalcopyrite structure, and its intensity increases with the temperature, indicating the crystallinity of the thin films improved [15], which was also confirmed by the increasing gain size [16], as shown in Figure 4.

The grain size, $D$, of the structure was deduced by Sherrer’s equation [17]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Here $\theta$ is the diffracted angle, $\lambda$ is the wavelength of the X-ray and $\beta$ is the full width at half-maximum of the peak.
in radians. The grain size increased from 198.5 Å to 484 Å as the substrate temperature increased from 120°C to 250°C.

SEM images of the surfaces of the layers are shown in Figure 5. The surfaces of the thin films prepared at 28 and 100°C are very smooth because the films were constructed with a small grain size. Then, from 120°C, the roughness of the surface increased dramatically due to the crystallinity. The images showed no fractures on the sample surface and satisfactory adherent layers, indicating that the deposition of CuInxGa1−xSe2 layers by the dual evaporation mechanism is suitable for creating typical CIGS thin films. It is obvious that substrate temperature dramatically influences the surface shape, which is also confirmed by the AFM images shown in Figure 6. The roughness was deduced from the AFM images and plotted in Figure 7. The roughness increased rapidly for deposited samples between 100°C and 120°C and then increased slightly.

Figure 8 shows Raman spectra taken for the prepared films. It is clear that there is no CIGS peak in layers that were prepared at 28, 100 and 120°C. There is no clear CIGS compound peak in the layer that was prepared at 120°C despite it being a stoichiometric film, indicating that the chalcopyrite compound has not been completely formed all over the layer. However, other films prepared at 200 and 250°C have a peak at 174 cm⁻¹, which was assigned to the A1 mode [18] and is the strongest mode generally observed in the Raman spectra of I-III-VI₂ chalcopyrite compounds. The film prepared at 250°C has a higher intensity A1 mode than the film prepared at 200°C because it has a higher Ga content [17].

Figure 7. Roughness of CuInₓGa₁₋ₓSe₂ layers prepared at various temperatures.

Figure 8. Raman spectra of CuInₓGa₁₋ₓSe₂ layers prepared at various temperatures.
To find out the values of the energy band gaps for the films deposited at 120°C, 200°C and 250°C, the photon energy was plotted versus \((\alpha h\nu)^2\), as drawn in Figure 9. The absorption coefficient, \(\alpha\), is deduced by

\[
\alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2}{2T} + \left[ \frac{(1 - R)4}{4T^2} + R^2 \right]^{1/2} \right),
\]

where \(R\) is the reflectance, \(T\) is the transmittance, and \(d\) is the film thickness. The bandgap \(E_g\) is related to the absorption coefficient;

\[
(\alpha h\nu) = A(h\nu - E_g)^{1/2}
\]

where \(h\nu\) is the photon’s energy, \(A\) is a constant. Extrapolation of the curves down to a zero \((\alpha h\nu)^2\) level yields band gap values of 1.47 eV, 1.28 eV and 1.35 eV for layers deposited at 120°C, 200°C and 250°C eV, respectively. The values of the bandgap are affected by the temperature and the content of Ga in the layers. The bandgap of the layer prepared at 200°C is less than that of the layer prepared at 120°C due to the increase in the temperature only because they have a similar Ga content. The energy gap decreased with increasing temperature due to the increase of the grain size and a decrease in the strain in layer [20]. However, the increase in the \(E_g\) of the 250°C film compared to that created at 200°C is due to the Ga content because the 250°C film has more Ga [21, 22]. The resistivity of the layers was deduced by the four-probe method and is listed in Table 2 with the values of \((1-(\text{metal}/\text{Se}))\), which were calculated from Table 1. As shown in Figure 10, there is a correlation between the resistivity of the films and the absolute value of \(1-(\text{metal}/\text{Se})\), specifically at low temperature, i.e. less than 200°C. Hence, the conductivity of the films increases as the value of metal/Se approaches unity.

### 4. Conclusion

Stoichiometric CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) films were prepared from powder elements without salinization by a dual thermal evaporation method. The substrate temperature has a remarkable influence on the composition of layers. Se concentration in the films reduced sharply as the temperature increased from room temperature to approximately 120°C, which dramatically modified the concentration of the elements in the layer. The strong (112) peak in the X-ray diffraction pattern and the peak at 174 cm\(^{-1}\) in the Raman spectra, which are characteristics of the Stoichiometric CIGS, were observed for the layer prepared at 200 and 250°C. The grain size and roughness of the layers increased as the temperature increased due to decreasing selenium content, and the films became more crystalline and stoichiometric. The bandgap is affected by the substrate temperature and the content of Ga. The conductivity of the layers increases as the value of metal/Se becomes close to unity.

### Disclosure statement

No potential conflict of interest was reported by the author(s).

### References

[1] Baji Z, Lábadi Z, Molnár G, et al. Post-selenization of stacked precursor layers for CIGS. Vacuum. 2013;92: 44–51.
[2] Akl A, Ashour A, Ramadan A, et al. Structural study of flash evaporated CuInSe\(_2\) thin films. Vacuum. 2001;61(1): 75–84.
[3] Piekoszewski J, Loferers J, Beaulieu R, et al. RF-sputtered CuInSe\(_2\) thin films. Sol Energy Mater. 1980;2(3): 363–372.
[4] Kang S, Kim Y, Choi D, et al. Characterization of electrodeposited CuInSe\(_2\) (CIS) film. Electrochim Acta. 2006;51(21): 433–443.
[5] Nguyen D, Takehara K, Ryo T, et al. Back contact materials for superstrate CuInS₂ solar cells. Energy Proc. 2011;10:49–54.

[6] Deepa K, Jayakrishnan R, Vijayakumar P, et al. Sub-micrometer thick CuInSe₂ films for solar cells using sequential elemental evaporation. Sol Energy. 2009;83(7):964–968.

[7] White F, Clark H. Growth of CuInSe₂ films using molecular beam epitaxy. J Vac Sci Technol. 1979;16(2):287–289.

[8] Agilan S, Mangalaraj D, Narayandass K, et al. Structure and temperature dependence of conduction mechanisms in hot wall deposited CuInSe₂ thin films and effect of back contact layer in CuInSe₂ based solar cells. Vacuum. 2010;84(10):1220–1225.

[9] Jung S, Ahn S, Ho Yun J, et al. Effects of Ga contents on properties of CIGS thin films and solar cells fabricated by co-evaporation technique. Curr Appl Phys 2010;10(4):990–996.

[10] Liu Y, Kong D, Li J, et al. Preparation of Cu(In,Ga)Se₂ thin film by solvothermal and spin-coating process. J Energy Proc. 2012;16(16):217–222.

[11] Joshi A, Taur S, Ghule V, et al. Stoichiometry controlled conversion efficiency in nanostructured heterojunction solar cell of CdS/CuInxSe2-x grown by chemical ion exchange method at room temperature. Sol Energy. 2011;85(7):1316–1321.

[12] Liu P, Chuang L. Fabrication of CIGS nanoparticle-ink using ball milling technology for applied in CIGS thin films solar cell. Powder Technol. 2012;229:78–83.

[13] Green M, Dunlop E. Solar cell efficiency tables (version 56). Prog Photovolt. 2020;28:628–639.

[14] Bernadette P, Jesse C. Characterization of Cu(In,Ga)Se₂ (CIGS) films with varying gallium ratios. J Alloys Compd. 2016;657:873–877.

[15] Guangxing L, Ping F. Properties of CuInGaSe₂ thin-film prepared from multiple layers via ion beam sputtering method. Solid State Lett. 2014;3(3):23–26.

[16] Yılmaz K, Karaagac H. Annealing effects on structural, optical and electrical properties of e-beam evaporated CuIn₀.₅Ga₀.₅Se₂ thin films. Appl Surf Sci. 2010;256:6454–6458.

[17] Maissel L, Giang R. Hand book of thin film technology. New York: McGraw-Hill; 1980.

[18] Witte W, Kniese R, Powalla M. Raman investigations of Cu(In,Ga)Se₂ thin films with various copper contents. Thin Solid Films. 2008;517(2):867–869.

[19] Al-Ani S, Al-Ramadin Y, et al. The optical properties of polymethylmethacrylate polymer dispersed liquid crystals. Polym Test. 1999;18(8):611–619.

[20] Prabahar S, Balasubramanian V, Suryanarayanan N, et al. Optical properties of copper indium diselenide thin films. Chalcogen Lett. 2010;7(1):49–58.

[21] Aissat A, Fathi M, Vilcot P. Development and simulation of a structure based on CuIn₁₋ₓGaₓSe₂ semiconductors alloys for a new generation of photovoltaic cells. Energy Proc. 2012;18:197–204.

[22] Zhao-Hui L, Eou C, Jik K. Properties of the Cu(In,Ga)Se₂ absorbers deposited by electron-beam evaporation method for solar cells. Curr Appl Phys. 2011;11(1):28–33.