The influence of selenium amount added into the graphite box during the selenization of solution deposited CIGSe thin films.

G M Albalawneh1,*, M M Ramli2,3, M ZM Zain4 and Z Sauli3

1Institute of Nano Electronic Engineering, Universiti Malaysia Perlis, 01000 Kangar, Perlis, Malaysia.
2Geopolymer and Green Technology, Center of Excellence (CEGeoGTech), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
3Faculty of Electronic Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
4Faculty of Mechanical Engineering Technology, Universiti Malaysia Perlis, Perlis, Malaysia.
*Ghadeer.ballawneh@gmail.com

Abstract. Cu(In,Ga)Se2 (CIGSe) semiconductor is an efficient light absorber material for thin-film solar cell technology. The sequential evaporation of precursor solution, followed by the selenization process, is a promising non-vacuum and low-cost approach for CIGSe thin-film fabrication. The main properties of CIGSe thin films are strongly affected by the post-selenization step. Hence, thorough control of selenization parameters is essential for achieving pure crystalline, large grain films needed for high-performance solar cell devices. In this study, the impact of selenium (Se) amount added during the selenization step was evaluated. The structural, morphological, and compositional properties of the selenized thin films were investigated. The CIGSe precursor film was deposited by a spin-coating technique using a thiol/amine-based solution, followed by annealing with different Se amounts (100, 200, and 300 mg) within a partially closed small round graphite container. In all cases, uniform films of 1.2–1.5 µm thickness with a well-defined single chalcopyrite phase were obtained. It was observed that the grain size and Se content increased with increasing Se mass added. Moreover, the sample selenized with 200 mg Se resulted in higher surface coverage, thinner fine-grained layer, and less MoSe2 formation than the excess Se samples.

1. Introduction
Copper indium gallium selenide (CIGSe) chalcopyrite semiconductors have attracted much attention as the solar cell absorber layer with the highest conversion efficiency of over 23% among thin-film solar cells [1–3]. In addition to the high efficiency, the CIGSe thin-film absorbers also have several advantages, such as suitable optical absorption (>105 cm–1), excellent outdoor stability, high defect density, and a tunable bandgap that can be adjusted by varying the Ga content [4,5]. Vacuum deposition techniques such as evaporation or sputtering are commonly used to produce CIGSe solar cells with the highest efficiency. However, conventional vacuum-based techniques result in increased costs and technical obstacles for commercial fabrication [6]. Therefore, solution-based vacuum-free processes are believed to be a scalable, straightforward alternative option that offers an efficient route for a low-cost, large-area, high-throughput, and flexible solar cell production [7,8].

To date, the highest efficiency recorded for a solution-based non-vacuum CIGSe cell has remained around 17.3% prepared by dissolving chalcogenides in hydrazine solution [9]. However, the dangerous nature of hydrazine has restricted this route for large-scale production [10–13]. Thus, alternative free-hydrazine solution routes have been employed for CIGSe absorber layer fabrication [14–19]. Nevertheless, some limitations need to be addressed, such as the preparation process complexity, ink stability, and poor crystallinity of the fabricated film [20–22].
Solution-processed deposition techniques commonly involve two steps. The first stage is the preparation and deposition of homogeneous precursor solution at relatively low temperatures using one of the standard coating methods, such as spin coating, spray coating, or inkjet printing. The second step involves post-selenization at about 450–600 °C to convert the alloy precursor layers into CIGSe absorber layers. Thiol/amine mixtures have recently been used to dissolve several metals and chalcogenide sources effectively to prepare precursor solution and deposit quality CIGSe absorber layers [9,22–24]. Photovoltaic devices based on thiol/amine solutions result in a promising CIGSe absorber properties and device efficiencies up to 13.12% [25–32]. However, some unresolved challenges of this route need to be addressed, such as a) the formation of a bottom layer composed of fine grains, b) a significant elemental reduction in the deposited film, and c) the formation of a thick MoSe2 layer between the Mo and CIGSe layer after selenization, which are all commonly thought to be harmful to solar cell performance [26,29].

Great efforts have been made to improve the solution-based CIGSe absorber quality. Selenization is an essential step to transform coated raw films into good uniformity, high-quality, single-phase CIGSe films with improved crystal size suitable for solar cells[9,22–24]. The selenization process also enlarges grain size, which effectively decreases grain boundary concentration, potentially boosts carrier mobility, reduces the occurrence of electron-hole recombination, and subsequently increases current generation [33–38]. The influence of selenization parameters, such as temperature ramping rate, annealing temperature, annealing time, and partial pressure of selenium (Se) on the final film, has been widely studied by many researchers [39–41]. However, the effect of Se mass added during the selenization step on the crystallinity and grain growth of the CIGSe absorber layer has not been broadly investigated. In this work, a thiol/amine-based CIGSe precursor solution was spin-coated to deposit a dense CIGSe layer. Selenization was accomplished using Se pellets in a partially closed graphite box whose design was improved compared to the one used in earlier works and those reported in the literature. The Se mass added during the selenization step was varied, and its influence on the morphological, structural, and compositional properties was reported.

2. Experimental methods

2.1 Materials.
Copper(II) acetylacetonate (Cu(acac)2, 99.9%), gallium(III) acetylacetonate (Ga(acac)3, 99.99%), and Se pellets (Se, 99.99%) were purchased from Sigma-Aldrich. Indium(III) acetate (In(OAc)3, 99.9%), 1,2-ethanedithiol (C6H12S2, 95%), 1,2-ethylenediamine (C2H4N2, 99%), and Se powder (Se, 99.99%) were purchased from Acros (Belgium).

2.2 CIGSe precursor solution preparation
To prepare the CIGSe precursor solution, Cu(acac)2 (481.3 mg, 1.84 mmol), In(OAc)3 (408.7 mg, 1.4 mmol), Ga (220.2 mg, 0.6 mmol), and Se (315.8 mg, 4 mmol) were transferred into a flask. Then, 10 ml of ethylenediamine and 1 ml of ethanedithiol were added. After overnight stirring at 65 °C, a homogeneous dark brown ink was obtained. The resultant ink remained stable for up to three weeks.

2.3 Deposition and selenization of CIGSe films
The CIGSe films were deposited onto 2.5 × 2.5 cm molybdenum (Mo)-coated soda-lime glass (SLG) substrate. The films were produced by spin-coating using the previously prepared ink. The solution was first deposited at a rotation speed of 100 rpm for 5 s, followed by 3,000 rpm for 30 s, with approximately 0.2 ml of the solution was used for each coating step. The samples were annealed using hot plate at 300 °C for 2 min to remove organic additives after each coating cycle. Then, 10 ml of ethylenediamine and 1 ml of ethanedithiol were added. After overnight stirring at 65 °C, a homogeneous dark brown ink was obtained. The resultant ink remained stable for up to three weeks.
investigated by loading different amounts of Se (100, 200, and 300 mg) into the graphite box during the selenization step.

2.4 Characterization.

The structure of the CIGSe absorber was investigated by X-ray diffraction (XRD) recorded on a Bruker D8 Advance X-Ray diffractometer with a Cu Kα anode (λ = 0.1542 nm). The surface morphology and grain size of the CIGSe absorber layer were assessed by a JEOL JSM 6460 scanning electron microscope (SEM) using 20 kV acceleration voltage. For verification of the CIGSe layer thickness, SEM cross-sectional images were taken from mechanically cleaved samples and then the images were analyzed with the software MountainsMap from DigitalSurf®. Energy dispersive X-ray spectroscopy (EDX) was performed for elemental analysis, with an opening size of 30 µm² and 20 kV voltage.

3. Results and discussion

In this work, the influence of selenization conditions on the final CIGSe film properties was investigated. Spin-coated CIGSe precursor films were selenized with varied Se amounts introduced into the graphite box while keeping all other selenization parameters constant. Optimising the Se amount is expected to enable more control on the Se pressure and diffusion into the precursor film, which leads to a more uniform structural and chemical homogeneity [33–38].

On the other hand, it is generally believed that the graphite box provides enhanced control for the selenization step. It was demonstrated that using a round graphite case instead of a rectangle one resulted in a high-quality CIGSe absorber layer with large grains, and it is more efficient to eliminate the fine-grained layer. The circular graphite box has an improved capability to maintain Se vapour during selenization [42,43]. The graphite box used in this work was designed as a simple, round graphite box, similar to the one used previously [42], but with a smaller size and closer distance between the film surface and the Se source. This design is intended to deliver more Se vapour to the film and suppress the internal Se vapour escaping the box. Besides, a closer space between the sample surface and the Se source would result in uniform and higher Se vapour pressure, resulting in good crystallisation of the CIGSe phase [44].

3.1 Morphological analysis

Surface and thickness characterizations were investigated by SEM images, and then the images were colored and analyzed using MountainsMap software. The cross-section view of the selenized film with different Se amounts, as shown in figure 2, indicates acceptable absorber thickness (1.2–1.5 µm) for solar cell fabrication. Furthermore, all films exhibit a bi-layer structure consisting of a fine-grained layer beneath a large-grained layer. The formation of such a structure is one of the primary issues involving the deposition of solution-based CIGSe film. It is commonly thought that films with thick fine-grain layers are detrimental to solar cell performance [13,26,41]. Therefore, increasing the coarse crystalline layer thickness and eliminating the fine-grained layer introduces a reliable indication of solar cell improvement. For the thin film selenized with 200 mg Se, the cross-section film shows that the absorber layer exhibited good film crystallinity with approximately 700 nm thick large-grained top layer. 300 and 100 mg Se Samples showed a thinner coarse layer compared to the fine-grained layer. The SEM cross-section image in the case of adding 300 mg Se shows a feature of grain accumulation, which can be referred to the MoSe₂ formed between the CIGSe layer and the Mo-back contact [30,42].
Figure 2. SEM images of cross-sections of the selenized films with 100, 200, and 300 mg of Se added into the graphite box.

From the perspective of grain growth, the higher the Se mass supplied to CIGSe, the larger the resultant grain size, which was accomplished by increasing the Se vapor diffusion. The diameter of some grains exceeded 3 μm when 300 mg of Se was added. The surface coverage, grain mean area and mean diameter are maximum when 200 mg Se was added to the graphite box compared to 100 and 300 mg. A detailed surface analysis for different Se amounts is shown in figure 3.

Figure 3. Surface morphology and grain size of the selenized films with 100, 200, and 300 mg of Se added during the selenization step.
3.2 Compositional analysis
In CIGSe absorber layer, the \([\text{Cu}] / [\text{In} + \text{Ga}]\) and \([\text{Ga}] / [\text{In} + \text{Ga}]\) ratios have a significant influence on the structural, morphological, optical, and electrical properties. Furthermore, high-efficiency CIGSe absorber layers are obtained with \([\text{Cu}] / [\text{In} + \text{Ga}]\) ratios ranging from 0.8 to 0.9 \([45,46]\). The Cu-poor film can avoid the formation of undesired secondary phases and aids the formation of a p-type CIGSe absorber \([47]\). The \([\text{Ga}] / [\text{In} + \text{Ga}]\) ratio is the most important parameter that will determine the bandgap energy of CIGSe thin-film. Although the higher Ga ratio could increase bandgap values, the gallium-rich absorber layer shows deteriorated photovoltaic. \([\text{Ga}] / [\text{In} + \text{Ga}] = 0.3\) is the optimum ratio for high-efficiency solar cells \([48,49]\). Thus, in this work, the targeted film composition for the films was \(\text{Cu}_{0.92} \text{In}_{0.7} \text{Ga}_{0.3} \text{Se}_2\). The desired ratio for cations was controlled by adding specific ratios in the precursor solutions as described in the experimental section.

EDX was used to determine the composition of the selenized thin film using different Se amounts, and the results are listed in table 1. All samples showed slightly poor Cu composition \([\text{Cu} / (\text{Ga} + \text{In})] \sim 0.8\) and \([\text{Ga} / (\text{Ga} + \text{In})] \sim 0.3\), which are the preferred values of high-efficiency CIGSe absorber material \([2]\). In contrast, the Se-to-metals ratio \([\text{Se} / (\text{In} + \text{Ga})]\) noticed an increase from 1.3 to 2.4. It is expected that increased Se partial pressure, corresponding to a higher amount of Se, allows the selenization to occur more deeply and results in a higher Se content.

| Se Amount (mg) | Cu (atm%) | In (atm%) | Ga (atm%) | S (atm%) | Se (atm%) | Cu/(In+Ga) | Ga/(In+Ga) | Se/(In+Ga) |
|---------------|-----------|-----------|-----------|---------|-----------|------------|------------|------------|
| 100 mg        | 24.30     | 20.30     | 9.61      | 4.54    | 41.23     | 0.81       | 0.32       | 1.38       |
| 200 mg        | 20.41     | 16.74     | 8.17      | 4.91    | 49.77     | 0.82       | 0.33       | 2.00       |
| 300 mg        | 17.87     | 16.10     | 6.63      | 4.53    | 54.86     | 0.79       | 0.29       | 2.41       |

3.3 Structural and phase analysis
The XRD spectra of the CIGSe sample deposited on the Mo-SLG substrate and selenized with different Se amounts are displayed in figure 4. All samples have a well-defined chalcopyrite crystal structure and show a preferred orientation of \((112)\) assigned to \(\text{CuIn}_0.7\text{Ga}_{0.3}\text{Se}_2\) chemical formula (JCPDS Card File No, 35-1102), as well as Mo, MoSe\(_2\) secondary phases. It is remarkable that as the Se amount increases, the intensity of MoSe\(_2\) peaks increases. The formation of thick MoSe\(_2\) is referred to the direct contact of Se vapour with the Mo layer through many pores in the CIGSe layer \([50,51]\). Even though the formation of a thin MoSe\(_2\) layer is important to assist the back ohmic contact, thicker MoSe\(_2\) is significantly detrimental to the absorber layer stability for the final solar cell performance \([39-41,52]\). Another aspect of the formation of thick MoSe\(_2\) at the back contact is that it has a significant impact on the adhesion of CIGSe/(MoSe\(_2\))/Mo layers to the substrate \([53]\).

To examine the quality of the CIGSe absorbers selenized with different Se amounts, the full width at half-maximum (FWHM) value of \((112)\) peak was estimated. As listed in the inset data of figure 4, it is clear that the films had the highest peak value of XRD and the narrowest value of FWHM when 300 mg Se was introduced, indicating that the crystallinity of CIGSe absorber improved with the increasing Se amount as the FWHM decreased. However, the Mo/CIGS interface is often of poor quality with a lower Mo(110)/MoSe\(_2\)(110) peak ratios. Hence, a trade-off between the film bulk and the Mo-contact properties has to be made. Therefore, 300 mg Se is considered too much amount and seems to harm device performance. The formation of a thick MoSe\(_2\) layer can also be confirmed by the SEM image shown in figure 2 for 300 mg Se, demonstrating that the CIGSe/Mo interface is presumably considered MoSe\(_2\) because it has a totally different morphology compared to that selenized with a lower Se amount.
Figure 4. Spectra of CIGSe absorbers selenized with 100, 200, and 300 mg of Se and selenized. The table introduces the (FWHM) values of the leading CIGSe peak and Mo/MoSe₂ intensity ratio of the most noticeable peaks.

4. Conclusions
This study focused on optimising the selenization step in a sequential growth process to fabricate a quality CIGSe absorber layer by spin-coating using a thiol/amine-based precursor solution. The selenization step was executed by varying the Se amount. Structural, compositional, and morphological properties of CIGSe thin films were investigated. The findings demonstrated that an increase in the Se amount resulted in enhanced incorporation of Se into the absorber via Se vapour pressure with Se/(In+Ga) ratio ranging from 1.4 to 2.4. In all cases, a well-defined CIGSe phase with a clear bilayer structure was obtained. The sample selenized with 200 mg Se resulted in higher surface coverage and thinner fine-grained layer than the deficient and excess Se samples. The CIGSe films prepared with high Se amounts resulted in larger grains and improved crystallinity. Simultaneously, excess Se induced the formation of a thicker MoSe₂ layer between CIGSe and Mo, which plays a deleterious role in the CIGSe absorber layer performance. The influence of Se content during selenization on solar cell performance is not considered in this study. However, it is believed that there is a reasonable effect on the final photovoltaic device performance.

5. References
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