Improving simultaneous of crystallization and Ga homogenization in Cu(In,Ga)Se₂ film using an evaporated In film

Yi-Cheng Lin, Xu-Jing Yao, Li-Ching Wang, Jyh-Ming Ting

Abstract

We report an improving simultaneous of crystallization and Ga homogenization method of Cu(In,Ga)Se₂ (CIGS) layer by evaporated In film in cell structure of glass/Mo/Cu–In–Ga/CdS/i-ZnO/AZO/Al. Results demonstrate that the evaporated In structure is superior to conventional sputtered In structure for its ability to produce a CIGS film with better crystallization, superior structural characteristics, reduced surface roughness, and more homogeneous distribution of elemental Ga. The device conversion efficiency using the evaporated In structure was found to increase by about 20% from 6.0% to 8.5% beyond what is possible using conventional sputtering In structure.

1. Introduction

CIGS-based solar cells have many advantages over traditional solar cells, including a high conversion efficiency potential, high light absorption coefficient, great stability, no photodegradation during sunlight exposure, no toxic pollutants such as arsenic and cadmium elements, lower materials cost, and thin films [1–4]. Current technologies used in the preparation of the absorber layer in CIGS solar cells include evaporation and sputtering. Although the latter enables the production of cells covering a large area [5], it presents a number of unresolved issues: (1) overly small crystals in the CIGS absorber layer [6], (2) high surface roughness in the CIGS absorber layer [7], and (3) inhomogeneous distribution of elemental Ga, resulting in insufficient band gap at the surface [8–10]. These factors have a crucial influence on the efficiency of CIGS devices [11–13]. To overcome these problems, Yuan [14] found that CIGS grain size and device performance improvement through the intentional introduction of Sn impurity-doping. Liang et al. [15] and Kim et al. [16] found that increased the annealing temperature to 848 K helped the homogeneous distribution of elemental Ga. Cu–Ga–In precursors fabricated by elemental co-evaporation and co-sputtering CIGS films were compared, evaporation precursors could simultaneously improve Ga incorporation and surface smoothness [17]. However, none have studied to resolve the problem of grain growth and inhomogeneous distribution of elemental Ga within the CIGS absorber layer in the same time period based on using the sputtering process. This paper proposes a simple method to resolve these problems in the same time period and studies the mechanism of grain growth of CIGS film.

2. Experimental

Bilayer In/Cu₂₀Ga₃₀ metal precursor films were deposited on samples of Mo-coated soda-lime glass (SLG) (1 cm × 1.5 cm × 1 mm) beginning with elemental In, followed by Cu₂₀Ga₃₀ to yield a Cu–Ga–In film with a total thickness of approximately 600 nm. The In metal precursor film was deposited using evaporation (In(E)) at a temperature of 1273 K and work pressure of 2.2 × 10⁻³ Pa. The Cu–Ga metal precursor film was prepared by sputtering at a power of 80 W and work pressure of 0.399 Pa, as opposed to sputtering (In(S)), which is performed at a power of 30 W and work pressure of 0.399 Pa. We then performed a two-stage annealing process at 623 K for 20 min and 823 K for 30 min using a selenium vapor to form the CIGS chalcopyrite phase. An atomic force microscope (AFM, Veeco Vip-II) was used to inspect the surface roughness of the deposited films, while a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) was used to observe the microstructure of the films.

To investigate the increase in grain size of CIGS produced using the proposed In evaporation process, we intercepted the selenized annealing process at various stages of the procedure (Fig. 1) and used X-ray diffraction (XRD, JEOL TF-SEM JSM7000F, Cu Kα, λ = 1.54052 Å) and a Raman analyzer (Ramboss 500 Micro-Raman System) to investigate the phase transformation of the CIGS absorber layer and identify its influence on the grain growth of CIGS precursor. Raman measurements were taken using a green laser (wavelength of 532 nm) as the light source. Secondary ion mass spectroscopy (SIMS, IMS-6f) was used to investigate the depth profiles of the thin film elements before and after annealing. Extraction voltages were set at 10 and 12.5 kV, respectively. Additionally, the current of the O₂ ion was set to 80 and 120 nA, which impacted the surface of the samples with 5.5 and 8 kV of energy, respectively.

Following CIGS absorber layer, we performed chemical bath deposition of CdS buffer layers. Highly resistive layers of intrinsic ZnO and conductive ZnO:Al were then deposited by sputtering. The structure of the resulting device was SLG/Mo/
3. Results and discussion

3.1. Grain growth

Figs. 2 and 3 present SEM images of the fabricated CIGS devices before and after selenization, with In precursors prepared using evaporation or sputtering, respectively. In Fig. 2, the microstructure presents two distinct patterns prior to selenization. The specimen with the evaporated In precursor (Fig. 2a) yielded a Cu–Ga precursor with a smoother surface, while the specimen with the sputtered In precursor (Fig. 2b) contained island structures, resulting from subsequent Cu–Ga films stacked on the uneven In surface.

The In precursor has a low melting point and high surface tension, which makes it susceptible to the formation of island structures.
during sputtering deposition [5]. Thus the island structures in Fig. 2b are likely the result of sputtering. Furthermore, despite passing through a two-stage selenized annealing process, the island structures continued expanding (Fig. 3b). Fig. 3 presents SEM images of the thin film surfaces and cross-sections following two-stage selenized annealing. As can be seen, the specimen fabricated with the evaporated In precursor permitted the infiltration of additional Se into the In/Cu–Ga precursor, with a subsequent reaction resulting in the formation of a CIGS absorber layer. The thickness of the In/Cu–Ga precursor increased from 0.6 \( \mu \text{m} \) (Fig. 2a) to approximately 1.8 \( \mu \text{m} \) (Fig. 3a), with a significant increase in grain size and without the formation of islands. This differs considerably from the grain growth pattern found in the specimen fabricated with a sputtered In precursor (Fig. 4b). Moreover, the surface morphology of the evaporated specimen is smoother, presenting a surface roughness measurement of \( \text{Rms} = 61.2 \text{ nm} \), as shown in Fig. 4a. In contrast, the roughness of the sputtered In structure in Fig. 4b reached 117.9 nm after selenization. This tendency agrees with previous studies [17].

Fig. 5 provides a comparison of the XRD results from the CIGS devices produced using evaporation and sputtering. The XRD patterns clearly exhibit the maximum intensity of a major diffraction peak (112) as well as minor peaks (220)/(204) and (312)/(116) chalcopyrite structures. A comparison of peaks (112) and (220) shows that the structure of the specimens produced via evaporation (Fig. 2a) produced a peak of greater intensity and superior crystalline characteristics. Table 1 presents the chemical composition of the CIGS devices following selenization with either evaporated or sputtered In precursors. The results show that Se content and Cu/III ratios fall within the stoichiometric range of CIGS chalcopyrite structures [18]. Moreover, the specimens produced with evaporated In contain higher Se content and lower ratios of Cu/III and Ga/III. Fig. 6 presents the Raman spectra of the specimens produced using the two In processing methods after selenization. The SLG/Mo/In\(_{1-x}\)/Cu–Ga structure shows the formation of Cu\(_2\)Se [19]; this secondary phase does not appear in the SLG/Mo/In\(_{1-x}\)/Cu–Ga structure.

#### Table 1

<table>
<thead>
<tr>
<th>In precursor processes</th>
<th>Compositions (at.%)</th>
<th>Composition ratio</th>
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<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>In</td>
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<tr>
<td>Evaporation</td>
<td>24.07</td>
<td>21.68</td>
</tr>
<tr>
<td>Sputtering</td>
<td>24.51</td>
<td>20.81</td>
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</table>

![AFM images of annealed CIGS absorber layer with various In precursor processes: (a) evaporation and (b) sputtering.](image1)

![XRD patterns of annealed CIGS absorber layer with various In precursor processes: (a) evaporation and (b) sputtering.](image2)

![Raman spectrum of annealed CIGS absorber layer with various In precursor processes: (a) evaporation and (b) sputtering.](image3)
To reveal the cause of the dramatic increase in the grain size of CIGS, we examined the influence of phase transformation in various stages of the selenization process. The temperature profile is outlined in Fig. 1. Condition (I) indicates selenization at 823 K followed by direct air cooling; Condition (II) indicates an additional increase in temperature after the first stage of selenization, followed by soaking for 10 min prior to air cooling. The other conditions include increasing the soaking time by an additional 10 min. Fig. 7 presents the Raman spectra of evaporated and sputtered In precursor structures during various stages of selenization. We employed this figure in the analysis of phase transformation during the various stages of selenization. Under Condition (I), the structure of the sputtered In precursor presented higher CIGS phase peaks and both types of In precursor structures presented secondary phases of InSe₂ and In₃Se₅; however, Cu₂-Se secondary phases were absent. Among the many secondary phases of In and Se [20,21], InSe₂ is produced over a wide range of temperatures [22] and is commonly encountered at temperatures above 623 K. This phenomenon was apparent under Condition (II) as well. Under Condition (III) a significant drop was observed in the peak value of the InSe₂ in the SLG/Mo/In(S)/Cu–Ga device. Conversely, the intensity of the InSe₂ peak in the SLG/Mo/In(E)/Cu–Ga device decreased only slightly. When

![Raman spectrum of CIGS absorber layer in various time segments during selenized annealing process with different In precursor processes: (a) evaporation and (b) sputtering.](image1.png)

![XRD patterns of CIGS absorber layer in various time segments during selenized annealing process with different In precursor processes: (a) evaporation and (b) sputtering.](image2.png)
the temperature was increased to 823 K and soaking time was extended to 20 min (Condition (IV)), the intensity of the CIGS phase peak showed an obvious increase. CIGS phase peaks were dominant in the CIGS absorber layers with both types of In precursor structures until the end of Condition (V); In$_x$Se$_{2-x}$ secondary phases did not appear during this process. A comparison of the In precursors under Conditions (III) and (IV) revealed that the sputtered In precursor caused an increase in In$_x$Se$_{2-x}$ secondary phases during the formation of chalcopyrite CIGS. An excessive amount of In$_x$Se$_{2-x}$ secondary phases can inhibit the grain growth of CIGS films [23], which would in turn affect grain growth in the CIGS absorber layers (Fig. 5b). Fig. 8 presents XRD patterns of structures with evaporated and sputtered In precursors during each stage of selenization. Despite the difficulty of identifying In$_x$Se$_{2-x}$ and Cu$_2$Se phases using XRD, we were able to observe the peak intensities. Within the structure of the evaporated In, the intensity of the chalcopyrite diffraction peaks at (112), (220)/(204), and (312)/(116) in each stage exceeded that of the same peaks in the sputtered In structure. These results clearly demonstrate that grain growth conditions are better in absorber layers with evaporated In.

In accordance with the observations in Figs 7 and 8, we derived schematic diagrams of the CIGS grain growth process during selenized annealing using both types of In precursor structures (Fig. 9). Because the sputtered In structure presents a rougher surface and subsequent higher rate of diffusion [24], the In diffuses more easily to produce In$_x$Se$_{2-x}$ phases with Se. A comparison of Conditions (III) and (IV) in Fig. 7 shows that as Cu-In–Ga was converted into CIGS, the sputtered In precursor facilitated the formation of In$_x$Se$_{2}$ phases (InSe$_2$ and In$_2$Se$_3$). Furthermore, the formation of In-rich structures resulted in Cu-poor structures and inhibited the growth of CIGS crystals [23]. This means that the liquid phase of Cu$_2$–Se and the solid phase of In$_x$Se$_{2}$ were both present during the process of CIGS grain growth [22]. Fig. 9a outlines the crystallization process of SLG/Mo/In$_{E}$/Cu–Ga following two-stage selenized annealing. With a smoother surface formed by evaporation, the In is less likely to diffuse and form phases of In$_x$Se. In In-poor (Cu-rich) structures, the growth of CIGS crystals proceeds unhindered.

### 3.2. Ga homogenization

The addition of Ga can increase the energy gap in the ternary chalcopyrite CuInSe$_2$ absorber layer; however, during the process of CIGS crystallization, Ga tends to diffuse towards the Mo back contact, resulting in insufficient Ga content at the surface of the absorber layer. Using SIMS depth profiling analysis, we discovered that the content of Ga in the structure produced with the evaporated
In precursor (Fig. 10a) was far more stable than that produced with the sputtered In precursor (Fig. 10b). This instability results in an insufficient energy gap in the CIGS absorber layer, which in turn decreases the $V_{oc}$ of the CIGS devices.

### 3.3. Cell efficiency

Fig. 11 presents the measurements of cell performance in the CIGS thin film solar cells fabricated from the evaporated In structure and sputtering In structures. The higher $V_{oc}$, $I_{sc}$ and cell efficiency are demonstrated with evaporated In structure than sputtered In structure. The improvement of cell efficiency of 29% in the CIGS cell proposed is found. The CIGS cells with an evaporated In layer structure have a better crystallization and more homogeneous distribution of elemental Ga, which decreases the recombination and increases the surface energy gap of CIGS film and results in a higher $I_{sc}$, $V_{oc}$ and cell efficiency.

### 4. Conclusions

This paper reports an improving simultaneous of crystallization and Ga homogenization method of Cu(In,Ga)Se$_2$(CIGS) layer by evaporated In film in cell structure of glass/Mo/Cu–In–Ga/CdS/i-ZnO/AlOx/Al. Results demonstrate that following a two-stage selenized annealing process, the evaporated In is superior to conventional sputtered In due to its ability to produce a CIGS absorber layer with larger grain size, better structural characteristics, and reduced surface roughness. SIMS shows that the proposed approach also resolves the inhomogeneous distribution of elemental Ga in CIGS cells. Retarding the growth of islands in the evaporated In precursor resulted in a smoother surface, which in turn prevented the diffusion of In in the CIGS absorber layer during selenization. This inhibited the formation of In$_2$Se phases, thereby promoting the formation of Cu$_2$Se phase and facilitating the growth of CIGS crystals. The device conversion efficiency using the evaporated In structure was found to increase by about 29% from 6.0% to 8.5% beyond what is possible using sputtering In structure.

### References