Research Article

Fabrication of a Cu(InGa)Se$_2$ Thin Film Photovoltaic Absorber by Rapid Thermal Annealing of CuGa/In Precursors Coated with a Se Layer

Chun-Yao Hsu, Peng-Cheng Huang, Yu-Yao Chen, and Dong-Cherng Wen

1 Department of Mechanical Engineering, Lunghwa University of Science and Technology, Taoyuan 33306, Taiwan
2 Department of Industrial Engineering, Shanghai Dianji University, Shanghai 201306, China
3 Department of Mechanical Engineering, China University of Science and Technology, Taipei 11581, Taiwan

Correspondence should be addressed to Dong-Cherng Wen; dcwen@cc.cust.edu.tw

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Cu(InGa)Se$_2$ (CIGS) thin film absorbers are prepared using sputtering and selenization processes. The CuGa/In precursors are selenized during rapid thermal annealing (RTA), by the deposition of a Se layer on them. This work investigates the effect of the Cu content in precursors on the structural and electrical properties of the absorber. Using X-ray diffraction, field emission scanning electron microscopy, Raman spectroscopy, and Hall effect measurement, it is found that the CIGS thin films produced exhibit faceted grains and a single chalcopyrite phase with a preferred orientation along the (1 1 2) plane. A Cu-poor precursor with a Cu/(In+Ga) ratio of 0.75 demonstrates a higher resistance, due to an increase in the grain boundary scattering and a reduced carrier lifetime. A Cu-rich precursor with a Cu/(In+Ga) ratio of 1.15 exhibits an inappropriate second phase (Cu$_{2-x}$Se) in the absorber. However, the precursor with a Cu/(In+Ga) ratio of 0.95 exhibits larger grains and lower resistance, which is suitable for its application to solar cells. The deposition of this precursor on Mo-coated soda lime glass substrate and further RTA causes the formation of a MoSe$_2$ layer at the interface of the Mo and CIGS.

1. Introduction

The use of polycrystalline Cu(InGa)Se$_2$ (CIGS) thin films as the absorber material for thin film solar cells allows easier commercial production because of the suitability of its bandgap and its high absorption coefficient for solar radiation [1]. An important feature of CIGS is that high-efficiency solar cells can be processed with a large range of Cu contents. The Cu content of the final film has a significant influence on the modular and cellular properties. At low Cu contents (Cu/(In+Ga) < 0.7) the conductivity of the CIGS is very low, and therefore shunt paths, either within a single solar cell or at the boundaries between cells in a module, are suppressed. Cu-rich CIGS (Cu/(In+Ga) > 1) is inappropriate for use as an absorber material, since the formation of a highly conductive Cu$_{2-x}$Se phase produces shunt paths.

Although several manufacturing processes have been developed [2–4], the two-stage method is the easiest to perform on an industrial scale [5, 6]. For a two-stage method, the compositional uniformity and surface morphology of metallic precursors affect the quality of the absorber layer. To ensure the compositional uniformity of precursor films, many procedures using stacked metal or alloy layers, such as In/CuGa, CuGa/In, CuGa/In/CuGa, or In/CuGa/In films, have been proposed [7, 8]. In traditional two-stage growth processes, Cu–Ga–In metallic precursors are selenized in an elemental Se vapor or a H$_2$Se/Ar gas mixture to form CIGS. However, Ga accumulation near the Mo side of the substrate/Mo/CIGS structure is often observed during the selenization of Cu–Ga–In precursors, yielding phase-separated CuInSe$_2$ (CIS) and CuGaSe$_2$ (CGS), which subsequently result in lower open-circuit voltages [9]. Dejene [10] reported that the concentration of Ga in the quaternary alloys is altered by variation in the relative thickness of GaSe with respect to InSe and Cu,
during the formation of the precursors. Koo et al. [11] successfully employed the rapid thermal annealing (RTA) of glass/Mo/(In,Ga)$_2$Se$_3$/CuSe stacked precursors that results in improved Ga homogeneity and greater control of MoSe$_2$ formation.

Compared to the other selenization methods, the progressive RTA treatment minimizes the defect density in the CIGS thin film by reducing the thermal budget and reaction time; thus, the conversion efficiency of solar cells is remarkably improved [12]. Therefore, good control of precursor structure, process parameters, and reaction routes can improve the quality of photovoltaic absorber [13,14]. This study investigates the effect of stacked CuGa/In precursors with different Cu contents on the growth of CIGS thin films. The precursors are selenized during RTA, by deposition of a 2 μm thick Se layer on them.

2. Experimental Details

CIGS films were prepared using a two-stage process. The first stage involved the deposition of multilayer precursors on either thin soda lime glass (SLG) or Mo-coated SLG substrates, using DC-magnetron sputtering of CuGa alloy with 25 wt.% Ga and elemental In targets and the thermal evaporation of Se. Based on the preliminary experiments and our previous study [15], the bottom layer of a 300-nm-thick CuGa film was deposited at a power of 100 W and at room temperature. The In layer was prepared at room temperature, using a power of 40 W. Thickness of the In layer was adjusted by adjusting the deposition time, to produce precursors with Cu/(In+Ga) atomic ratios of 0.75, 0.95, and 1.15. The top 2 μm of the Se layer was deposited at 250 °C, after preheating to 150 °C for 10 min at a rate of 15 °C/s. The substrate was rotated at 20 rpm during deposition, to improve the film uniformity.

The second stage involved the reaction of the Se-coated metallic precursors to the CIGS semiconductor in a RTA system that consisted of a quartz tube reactor with an inner diameter of 62 mm, a quartz sample tray, and an infrared (IR) heater. The quartz sample tray held up to six 2.5 cm × 2.5 cm samples. The IR heater produced a rapid increase in temperature, requiring only 1 min to reach 1000 °C from room temperature. The benefits of high heating rates are that they prevent dewetting of the elemental Se layer at the initial stage of the heating process, and they allow short thermal cycles [14,16]. As no external Se-vapor source was used during the reaction process, the deposition of an excess of Se onto the precursor stack compensates for the natural loss of a portion of Se during heating. To prevent the peel off of film from the substrate during selenization, the reactor was heated at a rate of 1 °C/s. The heating profile for the selenization process is shown in Figure 1, which has three annealing steps. In the first stage, the temperature of the substrate was maintained at 150 °C for 5 min, in order to homogenize the precursors. The temperature was then increased to 350 °C, for 5 min, to form the chalcopyrite phase. Finally, the as-prepared films were selenized at 550 °C for 5 min, to allow recrystallization and grain growth. Schematic of the fabrication process and phase evolution during the rapid thermal annealing of CuGa/In precursors coated with a Se layer is shown in Figure 2.

The surface morphologies of the films were analyzed using field emission scanning electron microscopy (SEM, JEOL, JSM-6500F). Electrical resistivity was measured by the four-point probe method (Mitsubishi Chemical MCP-T600). The carrier concentration and Hall mobility were measured using the van der Pauw method, and Hall effect measurement (Nanometrics/Accent/NAN-HL500PC) was performed at room temperature. The phases and crystal structure were determined by X-ray diffraction (Rigaku 2000 X-ray diffractometer), using Cu-Kα radiation and an angle incidence of 1°. The elemental concentrations and detailed compositional uniformity of CIGS films were determined by X-ray fluorescence (XRF) intensity measurements of the $K_{\alpha 1,2}$ lines. The scanned $K_{\alpha 1,2}$ lines were recorded using a sequential XRF wavelength dispersive spectrometer (SRS3000, Bruker-AXS, Rh-anode, 60 kV). In determining the detailed compositional uniformity the absorbers were repeatedly etched in bromine methanol, followed by XRF $K_{\alpha 1,2}$ line intensity measurements. Chemical etching was conducted at room temperature, and the samples were rinsed in water and blow-dried with nitrogen, before XRF measurements were performed [16]. Raman scattering measurements were performed using a HORIBA's LabRAM HR high-resolution spectrometer with a multichannel detection system, in the backscattering configuration.

3. Results and Discussion

Firstly, the precursors were deposited on a bare SLG substrate, to determine the proper Cu content for the fabrication of solar cells. Table 1 lists the elemental compositions of the as-deposited precursors and the CIGS films. The Cu/(In+Ga) ratios of three precursors were matched to the designed values. However, the selenization process caused this ratio to become slightly increased for samples A and C. Only sample B reached the expected ratio of 0.95 after selenization. In addition, the Ga/(In+Ga) ratio increases as the Cu/(In+Ga) ratio increases.

Figure 3 shows the XRD patterns for the precursors and CIGS films. As reported by Park et. al. [7], a pure In peak and intermetallic Cu$_5$In and Cu$_9$Ga as equilibrium phases at room temperature were observed on the precursor
Table 1: Elemental composition of the as-deposited precursors and CIGS films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor layer Compositions (at%)</th>
<th>Precursor layer Ratios</th>
<th>CIGS layer Compositions (at%)</th>
<th>CIGS layer Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>In</td>
<td>Ga</td>
<td>Cu/(In + Ga)</td>
</tr>
<tr>
<td>A</td>
<td>42.94</td>
<td>44.96</td>
<td>12.10</td>
<td>0.753</td>
</tr>
<tr>
<td>B</td>
<td>48.49</td>
<td>37.04</td>
<td>13.83</td>
<td>0.953</td>
</tr>
<tr>
<td>C</td>
<td>53.52</td>
<td>31.55</td>
<td>14.93</td>
<td>1.151</td>
</tr>
</tbody>
</table>

Figure 2: Schematic of the fabrication process and phase evolution during the rapid thermal annealing of CuGa/In precursors coated with a Se layer.

Despite the chalcopyrite peak being clearly visible in the XRD spectra (Figure 3(b)), the Cu–Se compound peaks overlap with the chalcopyrite peak making a proper identification difficult. To obtain more precise information about the films’ composition, Raman analyses of the films were performed. Figure 6 shows the Raman spectra of the CIGS absorber films with various Cu contents, measured at room temperature. A CIGS peak was observed at 177 cm$^{-1}$ only for samples A and B, with Cu/(In + Ga) < 1, indicating the presence of single-phase chalcopyrite in the film. For sample C, with Cu/(In + Ga) = 1.15, an additional peak appears at 260 cm$^{-1}$, which is attributable to the presence of Cu–Se compounds such as CuSe or Cu$_2$Se and is labeled as Cu$_{2-x}$Se [20]. Kessler et al. [21] noted that the efficiency of solar cells decreases when a second phase (Cu$_{2-x}$Se) is present in the absorber.

Table 2 shows the sheet resistance, carrier concentration, and Hall mobility of the CIGS films. These selenized films demonstrate p-type conductivity. The resistance is a combined result of both the Hall mobility and the carrier concentration. As the Cu/(In + Ga) ratio increases from 0.75 to 0.95, the grain size increases. A larger grain size reduces the grain boundary scattering and increases the carrier lifetime, which results in an increase in conductivity, due to an increase in Hall mobility and carrier concentration. As a result, the sheet resistance of the CIGS films decreases. When the Cu/(In + Ga) ratio increases to 1.15, the film exhibits the lowest sheet resistance. However, a decrease in the resistance results in the formation of a highly conductive Cu$_{2-x}$Se phase, rather than an increase in grain size, rendering it inappropriate for use as an absorber material.
Based on the above results, the growth conditions for sample B, with a \( \text{Cu/(In + Ga)} \) ratio of 0.95, were used for deposition onto the Mo-coated SLG substrate to produce solar cells. As with a previous study by the authors [15], the Mo back contact was grown using a RF power of 125 W, a working pressure of 3 mTorr, a substrate temperature of 200°C, and a deposition time of 50 min.

Figure 7 shows the depth profile of sample B, prepared on a Mo-coated SLG substrate by RTA of CuGa/In precursors covered with a Se layer. It is clearly evident that this process produces CIS films with a high degree of detailed compositional uniformity, with no evidence of phase segregation. The corresponding XRD pattern of this CIS film is shown in Figure 8. After RTA, the precursor is completely transformed into a chalcopyrite CIS layer, and the Mo layer is partially converted to MoSe\(_2\). The main diffraction peak of the preferred orientation is \((1 1 2)\) at \(2\theta = 26.9^\circ\). No other obvious secondary phases are evident.

Figure 9 shows the cross-sectional SEM and surface morphology for the CIS film from the precursor with a \( \text{Cu/(In + Ga)} \) ratio of 0.95. The columnar Mo back contact with narrow grains extending the full thickness of the film provides an effective pathway for Na diffusion from the SLG substrate to the absorber during selenization [22]. A thin MoSe\(_2\) layer is formed at the interface of the Mo and the CIS. This significantly improves the structural quality of the CIS films and the electrical contact at the Mo/CIS interface [23]. A dense CIS layer with a thickness of about 1.2–1.3 \(\mu\)m, large grains (\(\sim 1.2 \mu\)m), and no cracking or peeling phenomena is observed. The obtained results confirm that a qualified CIS absorber layer was successfully fabricated when a precursor with \( \text{Cu/(In + Ga)} \) ratio of 0.95 was prepared onto the Mo-coated SLG substrate and selenized by RTA. These results allow a better understanding of how precursors influence the structural and electrical properties of the CIS films.
Figure 5: The surface morphology of CIGS absorber films with Cu/(In+Ga) ratios of (a) 0.75, (b) 0.95, and (c) 1.15.

Figure 6: Raman spectra of CIGS absorber films with various Cu/(In+Ga) ratios.

Figure 7: The XRF detailed compositional uniformity of Cu, In, Ga, and Se in the selenized CIGS film from the precursor with a Cu/(In+Ga) ratio of 0.95.

Figure 8: XRD patterns of the CIGS film from the precursor with a Cu/(In+Ga) ratio of 0.95 deposited on a Mo-coated SLG substrate.

4. Conclusions

CIGS thin film absorbers were fabricated by RTA of CuGa/In precursors with various Cu contents. The precursors were prepared by the sequential sputtering of CuGa and In targets and then coated with a Se layer. The results demonstrate that the structural and electrical properties of the absorber are heavily dependent on the Cu/(In+Ga) atomic ratio. Cu-poor precursor with a Cu/(In+Ga) ratio of 0.75 exhibits an initial decrease in CIGS grain size, which results in a higher resistance, due to increased grain boundary scattering and a reduction in carrier lifetime. Cu-rich precursor with a Cu/(In+Ga) ratio of 1.15 exhibits a second phase (Cu$_{2-x}$Se) in the absorber. It is inappropriate for use as an absorber material, even though the film has the largest grain size and the lowest resistance. A CIG precursor with a Cu/(In+Ga)
ratio of 0.95 exhibits a single chalcopyrite structure with larger grains and lower resistance, which is suitable for application to solar cells. The preparation of this precursor on Mo-coated SLG substrate and RTA results in a preferential (1 1 2) orientation of the single chalcopyrite structure CIGS film with a MoSe₂ layer at the interface of the Mo and the CIGS.

Conflict of Interests

The authors certify that there is no conflict of interests with any financial organization regarding the material discussed in the paper.

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References


