Structural and electrical properties of radio frequency magnetron sputtered Cu(In$_{x}$Ga$_{1-x}$)Se$_{2}$ thin films with additional post-heat treatment

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**ABSTRACT**

Cu(In$_{x}$Ga$_{1-x}$)(Se,S)$_{2}$ (CIGSS) thin films were deposited using a single quaternary target of Cu(In$_{0.75}$Ga$_{0.25}$Se$_{2}$) by rf magnetron sputtering, followed by sulfurization. The effects of substrate temperature and post-sulfurization on the properties of CIGSS films were investigated. As the substrate temperature increased, the crystallinity of the films increased significantly and the grain size also increased. Energy dispersive X-ray spectroscopy of CIGS films showed that Cu, Ga and Se contents approached the stoichiometry of CIGS films with increasing substrate temperature. Post-sulfurization of as-deposited CIGS films was carried out to improve their properties. The resultant CIGSS thin films revealed a noticeable increase in (112) peak for films deposited under 200 °C, while the intensities of the (220)/(204) and (312)/(116) peaks increased as well. Grains with a size of approximately 100 nm were grown after sulfurization. The results of EDX of CIGSS thin films after sulfurization indicated that the Cu content increased slightly and the Ga and (Se + S) contents decreased significantly. The band gaps of the films were also noticeably reduced after sulfurization. The carrier concentrations of the films after sulfurization decreased greatly at substrate temperatures below 400 °C, while they showed little change at temperatures above 400 °C. The resistivity of the films after sulfurization increased with increasing substrate temperature and showed little change at temperatures above 400 °C. As a result, CIGS films were transformed to the chalcopyrite phase with well crystallized grains through sulfurization.

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1. Introduction

Cu(In$_{1-x}$Ga$_{x}$)(Se,S)$_{2}$ (CIGSS) thin film solar cells are one of the most promising solar cells for the replacement of Si solar cells. CIGSS thin films which are used as an absorbing medium are a compound semiconductor material with a chalcopyrite structure [1]. These films are a direct band gap material with the capability to achieve high efficiency solar cells with a thickness of approximately 1–2 μm due to the high absorption coefficient of $10^{-5}$ cm which is the highest among currently available semiconductors [2,3].

The deposition of Cu(In$_{1-x}$Ga$_{x}$)(Se,S)$_{2}$ (CIGS) thin films has been known to be very difficult because of multi-component compounds with complicated structures. CIGS thin films have been prepared by a variety of deposition methods including co-evaporation, chemical spray pyrolysis (CSP), electrode position and sputtering [2,4–6]. CIGS thin films deposited by the co-evaporation method have been shown to have the highest efficiency (>20%); however, it is hard to meet the stoichiometry of CIGS thin films from various metal sources and run reliable processes with sources loaded in sequence for multiple-stage processes. It is also difficult to scale up for large-area deposition due to the complexity of the method [7,8]. The CSP method has primarily been used for CuInSe$_2$ and CuInS$_2$ films as a chalcopyrite semiconductor. This is expected to be a promising deposition method because large-area films with good uniformity can be grown at low cost. However, the efficiency of cells fabricated by CSP to date has not been good [9,10]. The electrode position method has emerged with various advantages such as low cost and large scale deposition with a non-vacuum system for CIGS deposition but has the disadvantages of poor uniformity and pinhole formation when thin films are prepared. Additionally, the films must be deposited very thickly and have not shown high efficiency [11–13]. The sputtering method, which is very effective for scale up to a large deposition area, has drawn a great deal of attention due to its ability for use in mass production and good reproducibility. This technique generally involves separate two-stage processes that involve the deposition of metallic precursors from the single, binary and ternary targets with Cu, In and Ga elements, and the selenization process [14–16]. The current popular sputtering method for deposition of CIGS films employs metal deposition from three single targets of Cu, In and Ga, and these deposited metal films are subsequently selenized by Se vapor from H$_2$Se gas or Se pellets [17,18].

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Among these deposition methods for CIGS thin films, the sputtering method has begun to receive a great deal of attention as a stable and reproducible technique for mass production with the capability of large-area deposition [19]. Recently, sputtering using a single quaternary target containing Cu, In, Ga and Se has been reported for preparation of CIGS films without an additional selenization process. This can provide a simple cost-effective deposition process for CIGS films when compared to other deposition methods. However, it is difficult to regulate the stoichiometry of the films and increase the grain size in the films when this sputtering method is used because of the low deposition rate of Se, which influences the efficiency of the absorber layer [19–24].

In this study, post-sulfurization after sputtering deposition was applied to reduce issues such as Se vacancy or grain control associated with the sputtering method using a single quaternary target without selenization. The effects of substrate temperature and post-sulfurization on the structural, optical and electrical characteristics of CIGS thin films were also examined.

2. Experimental details

CIGS thin films were prepared using a single quaternary target with an rf magnetron sputtering system (A-Tech system, Korea) on 15 × 15 × 2 mm² soda lime glasses. The target was a 3 in. diameter material (Kojundo, Japan) composed of the quaternary components Cu, In, Ga and Se at the ratio of 25 at.% Cu, 18.8 at.% In, 6.2 at.% Ga and 50 at.% Se. Prior to deposition, the glass substrates were ultrasonically cleaned in acetone, ethanol, and deionized water in sequence.

The deposition chamber was evacuated to 0.93 × 10⁻⁴ Pa using a turbomolecular pump backed by a mechanical pump. The substrate temperature in the chamber could be raised to 550 °C and Ar at 30 sccm was used as a sputtering gas. The rf power and process pressure used in this study were 80 W and 0.67 Pa, respectively. The distance between the target and the substrate was fixed at 5.5 cm and the substrate temperature was varied from room temperature to 550 °C and Ar at 30 sccm was used as a sputtering gas. The rf power and process pressure used in this study were 80 W and 0.67 Pa, respectively. The distance between the target and the substrate was fixed at 5.5 cm and the substrate was rotated at 10 rpm. All deposited CIGS films were adjusted to a thickness of 500 nm. Prior to film deposition, pre-sputtering was carried out for 15 min to remove the contaminants on the target surface. The deposited thin films were then heat-treated at 525 °C for 1 h under an H₂S flow.

In this study, the influence of the substrate temperature and sulfurization process on the properties of CIGS thin films was investigated. The thickness and deposition rate of CIGS films were measured using a surface profiler (Tencor-P1). X-ray diffraction (XRD) analysis (Philips XPert PRO XRD system, Cu Kα irradiation, λ = 1.5405 Å) using 40 kV voltage and 30 mA current was employed to examine the crystalline structure of the films. Grazing incidence configuration with an incident angle of 1° was used for minimization diffraction peak from the substrate. The microstructure and surface morphology of the films were observed using field emission scanning electron microscopy (FESEM) (Hitachi S-4300) with the operating voltage of 15 kV. Energy dispersive x-ray spectroscopy (EDX) (INCA Energy) was utilized to investigate the contents of each element in the films with the accelerating voltage of 15 kV and collection time of 100 s. The band gaps of CIGS films were evaluated from the optical transmittance through the films using UV–Vis spectroscopy (Cary 300). The carrier concentration and resistivity of CIGS films were measured using the Van der Pauw method through the Hall effect measurement system (HMS-3000, ECOPIA) using a 0.1 μA current in a 0.55 T magnetic field at room temperature. Indium soldering in Hall effect measurement was applied onto the surface as the ohmic contact.

3. Results and discussion

CIGS thin films that were 500 nm thick were deposited using a single quaternary target by rf magnetron sputtering on soda lime glasses. The deposition condition was an rf power of 80 W, chamber pressure of 0.67 Pa and target–substrate distance of 5.5 cm. The substrate temperature was varied from room temperature (RT) to 550 °C and additional post-sulfurization was carried out at 525 °C for 1 h in a tube furnace.

Fig. 1 shows the XRD patterns of CIGS thin films deposited at different substrate temperatures. XRD patterns showed that most CIGS thin films have a strong preferential (112) plane of Cu(In0.7Ga0.3)Se2 (JCPDS 35-1102). Weak (220)/(204) and (312)/(116) planes of Cu(In0.7Ga0.3)Se2 were also observed. CIGS thin films were deposited as polycrystalline and had chalcopyrite structure. The (112) peak increased with increasing substrate temperature, with a noticeable increase occurring from 200 °C and the highest peak intensity was obtained for films deposited at 550 °C. A very weak peak around 25° was observed for films deposited at greater than 300 °C, and these corresponded to Cu-rich selenide phases Cu2Se2 (JCPDS 47-1745) [22].

Fig. 2 shows FESEM micrographs of CIGS films deposited at different substrate temperatures. Observable small grains were seen for films deposited at 200 °C. As the substrate temperature increased from 200 °C to 400 °C, circular grains grew and the grain size increased from 30 nm to 90 nm. Moreover, when the films were deposited at 550 °C, the grains were agglomerated and formed as large grains greater than 100 nm.

Table 1 presents the chemical composition of as-deposited CIGS films at various substrate temperatures using EDX system. CIGS films deposited at room temperature were Cu and Se deficient and had excessive Ga when compared to the stoichiometry of CIGS films. However, films deposited at 200 °C showed a slight increase in Cu/(In + Ga) and Se/(In + Ga), which indicated initiation of the formation of crystalline structures (Figs. 1 and 2). As the substrate temperature increased from 200 °C to 550 °C, the Cu/(In + Ga) and Se/(In + Ga) approached the stoichiometric composition of CIGS films. However, the film deposited at 550 °C showed a slight decrease in Cu/(In + Ga) and Ga/(In + Ga) ratios and a small increase in the Se/(In + Ga) ratio. These results are in good agreement with those shown in Figs. 1 and 2, which demonstrated the well grown grains of CIGS films at high substrate temperature. Since all films had Ga/ (In + Ga) ratios above 0.39, preferential orientation of the (112) plane was obtained, as reported previously [21].

Post-sulfurization of as-deposited CIGS films was conducted to improve their properties by controlling the amounts of Ga and Se and adding S into the films. The post-sulfurization process included heating the as-deposited films at different substrate temperatures in the tube furnace at 525 °C under a H2S flow for 1 h. Fig. 3 shows the XRD patterns of Cu(In1−xGax)(Se,S)2 (CIGSS) films after sulfurization. All

![Fig. 1. XRD patterns of CIGS thin films deposited at different substrate temperatures: (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, and (g) 550 °C.](image-url)
peaks of (112), (220)/(204) and (312)/(116) planes were observed, but the (112) plane was still the predominant orientation. A noticeable increase in (112) peak intensity occurred for films deposited under 200 °C while intensities of the (220)/(204) and (312)/(116) peaks increased as well. Moreover, the peak of the second phase Cu3Se2 that had appeared prior to sulfurization disappeared. In general, the intensities of all peaks increased after high temperature heat treatment. However, the (112) peaks of films deposited at more than 500 °C decreased after sulfurization, while the intensities of (220)/(204) and (312)/(116) peaks increased.

Table 1
EDX result of CIGS thin films deposited at different substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate Temp.(°C)</th>
<th>Cu(%)</th>
<th>In(%)</th>
<th>Ga(%)</th>
<th>Se(%)</th>
<th>Cu/(In + Ga)</th>
<th>Ga/(In + Ga)</th>
<th>Se/(In + Ga)</th>
</tr>
</thead>
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<tr>
<td>RT</td>
<td>19.7</td>
<td>14.6</td>
<td>12.2</td>
<td>46.5</td>
<td>0.74</td>
<td>0.46</td>
<td>1.74</td>
</tr>
<tr>
<td>200</td>
<td>22.2</td>
<td>12.9</td>
<td>12.2</td>
<td>45.0</td>
<td>0.88</td>
<td>0.49</td>
<td>1.79</td>
</tr>
<tr>
<td>400</td>
<td>25.4</td>
<td>13.4</td>
<td>12.8</td>
<td>48.4</td>
<td>0.97</td>
<td>0.49</td>
<td>1.85</td>
</tr>
<tr>
<td>550</td>
<td>21.8</td>
<td>13.9</td>
<td>10.8</td>
<td>46.0</td>
<td>0.88</td>
<td>0.44</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Fig. 3. XRD patterns of CIGSS thin films after post-sulfurization, deposited at different substrate temperatures: (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, and (g) 550 °C.

Fig. 4 shows the FESEM micrographs of CIGSS films after post-sulfurization. The grains of the films were considerably larger than those before sulfurization, especially when the substrate was at RT and 200 °C (Fig. 4(a) and (b)). In addition, the grains of the films deposited at 400 °C and 550 °C improved considerably after post-sulfurization, with the well grown grains of approximately 100 nm being present. The surface morphologies of the films deposited at substrate temperatures of more than 400 °C were very similar, which coincided with the XRD patterns shown in Fig. 3.

The results of EDX of the CIGSS films after post-sulfurization are presented in Table 2. The Cu/(In + Ga) ratios of the CIGSS films after sulfurization increased for the films deposited at substrate temperatures of RT and 200 °C. The Ga/(In + Ga) ratios of CIGSS films after sulfurization decreased significantly when compared to those of the as-deposited CIGS films. This has been due to the diffusion of Ga into the films during the sulfurization process [25]. The decrease of Ga due to diffusion to the films resulted in an increase of (220)/(204) and (312)/(116) planes, which were shown in the XRD patterns of Fig. 3. The (Se + S)/(In + Ga) ratios of the films after sulfurization also greatly decreased, even though S was supplemented to the films under H2S flow at 525 °C for 1 h. This was due to the evaporation of secondary liquid-phase CuSeX at a high temperature of 525 °C and insufficient penetration of S into the films.

Fig. 5 shows the band gaps evaluated based on the optical transmittance through the films. Using the standard expression for direct transition between two parabolic bands \((a\nu^2) = A(\nu^2 - \nu_0^2)\), the optical band gap \((\nu_0)\) of the CIGS films was calculated by extrapolating the linear \((a\nu^2) vs. \nu^2\) plot to \((a\nu^2) = 0\). The band gaps were measured as a function of substrate temperature for as-deposited CIGS films and post-sulfurized CIGSS films. As shown in Fig. 5, the band gaps of the films showed little change with increasing substrate
temperature before and after sulfurization. However, the band gaps of as-deposited films (2.1 eV) decreased significantly to 1.65 eV after sulfurization. This was caused by the formation of a chalcopyrite structure with well crystallized grains due to the additional sulfurization process.

The carrier concentration of the films is shown in Fig. 6. The concentrations were obtained by measurement of the Hall effect for as-deposited and sulfurized films and compared. The carrier concentrations of the sulfurized films (10¹⁵ to 10¹⁶ cm⁻³) decreased to one order of magnitude lower than those of as-deposited films (10¹⁵ to 10¹⁷ cm⁻³) at temperatures ranging between 100 °C and 400 °C. Conversely, the carrier concentrations of the films before and after sulfurization at above 400 °C showed little change. These findings indicate that secondary phases of Cu and In existed at substrate temperatures below 400 °C and these were transformed to the chalcopyrite phase with well crystallized grains after sulfurization.

Fig. 7 shows the resistivity of the films before and after sulfurization. The resistivity of the films for both cases increased with increasing substrate temperature. As-deposited films showed the resistivity ranging from 10⁻¹ to 10² Ω cm, while the resistivity of the films ranged from 10¹ to 10² Ω cm after sulfurization. The resistivity of the films deposited at substrate temperatures between 100 °C and 400 °C increased by at least one order of magnitude after sulfurization, but that deposited at above 400 °C showed little change. This change in the resistivity with respect to the substrate temperature was very closely related to changes in the carrier concentration.

4. Conclusion

The deposition of CIGS thin films was performed using a single quaternary target of CuIn₀.₇₅Ga₀.₂₅Se₂ by rf magnetron sputtering at an rf power of 80 W and process pressure of 0.67 Pa. The effects of substrate temperature and post-sulfurization on the properties of CIGS films were investigated. As the substrate temperature increased, the crystallinity of the films increased significantly, as did the grain size. Highly crystalline CIGS films with the largest grains were obtained at a substrate temperature of 550 °C. EDX of the CIGS films showed that Cu, Ga and Se contents approached the stoichiometry of CIGS films when the substrate temperature was above 400 °C.

CIGSS thin films after sulfurization showed increases in main peaks of (112), (220)/(204) and (312)/(116) and decreased band

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**Table 2**

EDS result of CIGSS thin films after post-sulfurization.

<table>
<thead>
<tr>
<th>Substrate Temp.(°C)</th>
<th>Cu(%)</th>
<th>In(%)</th>
<th>Ga(%)</th>
<th>Se(%)</th>
<th>S(%)</th>
<th>Cu/(In + Ga)</th>
<th>Ga/(In + Ga)</th>
<th>(Se + S)/(In + Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>26.7</td>
<td>16.5</td>
<td>11.9</td>
<td>4.4</td>
<td>35.8</td>
<td>0.94</td>
<td>0.42</td>
<td>1.42</td>
</tr>
<tr>
<td>200</td>
<td>27.2</td>
<td>15.1</td>
<td>10.2</td>
<td>3.9</td>
<td>38.0</td>
<td>1.08</td>
<td>0.40</td>
<td>1.66</td>
</tr>
<tr>
<td>400</td>
<td>26.4</td>
<td>16.2</td>
<td>11.8</td>
<td>2.1</td>
<td>39.2</td>
<td>0.94</td>
<td>0.42</td>
<td>1.48</td>
</tr>
<tr>
<td>550</td>
<td>27.3</td>
<td>16.0</td>
<td>14.7</td>
<td>2.7</td>
<td>35.4</td>
<td>0.89</td>
<td>0.48</td>
<td>1.24</td>
</tr>
</tbody>
</table>
The grains of the films after sulfurization were considerably larger, with an average size of approximately 100 nm. The EDX results of CIGSS thin films after sulfurization indicated that the Cu content increased slightly and Ga decreased significantly. The carrier concentration of the films after sulfurization decreased greatly at substrate temperatures below 400 °C while it showed little change when the substrate temperature was above 400 °C. These findings implied that secondary phases of Cu and In existed at substrate temperatures below 400 °C and were transformed to the chalcopyrite phase. The resistivity of the films after sulfurization increased with increasing substrate temperature and showed little change at temperatures above 400 °C. Overall, CIGS films were transformed to the chalcopyrite phase with well crystallized grains after sulfurization.

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