Influence of doping iron ions into Cu(In,Ga)Se2 films in the morphology and photovoltaic properties of thin-film solar cells

Guan-Lin Chiu, T. Subburaj, Sudipta Som, Chang-Ying Ou and Chung-Hsin Lu*
Department of Chemical Engineering, National Taiwan University Taipei, Taiwan, R.O.C.

The iron-ion doped Cu(In, Ga)Se2 thin films were prepared on flexible stainless steel substrates via a non-vacuum spin-coating process. The influence of iron-ion doping in the morphology and properties of Cu(In, Ga)Se2 solar cells was investigated in detail. When the molar ratio of iron ions to the total amount of indium and gallium ions in Cu(In, Ga)Se2 was increased, the grain sizes of the Cu(In, Ga)Se2 thin films were reduced and the grain morphology became angular. Iron-ion doping in Cu(In, Ga)Se2 thin films substantially facilitated the formation of grain boundaries and additional shunt paths, leading to high probability of electron-hole recombination. As a result, the conversion efficiency of the prepared Cu(In, Ga)Se2 solar cells decreased dramatically due to iron-ion doping.

Key words: Flexible substrate, Stainless steel, CIGS solar cell, Selenization, Electron-hole recombination.

Introduction

Nowadays, chalcopyrite Cu(In, Ga)Se2 (CIGS) solar cells have become promising highly efficient photovoltaic devices owing to the moderate absorption coefficients, suitable band gaps, and high stability of the CIGS absorber layers in rigid glass substrates [1-7]. The alternative flexible and conformal substrates for CIGS solar cells draw much research attention recently due to their suitability in various applications for curved surfaces, mobile devices, and space uses [8-10]. Several research groups have reported the flexible CIGS solar cells prepared on polyimide sheet and titanium foils [11-14]. However, since the substrate temperature over 500 °C is still required to deposit high-quality CIGS films, stainless steel has demonstrated modern research significance because of the lightweight and non-breakability of these materials [15-16]. Kim et al. [17] have employed the co-evaporation process to construct flexible CIGS solar cells on stainless steel substrate and a high efficiency was achieved. In addition, several studies have shown that the diffusion of sodium ions into the CIGS absorption layers contributes to the growth of the CIGS grains and thereby enhances the photoelectric conversion efficiency [18-20]. Hashimoto et al. [21] have also demonstrated the high performance of CIGS solar cells prepared on stainless steel with the addition of sodium ions.

When the substrate temperatures go over 500 °C during CIGS deposition, iron ions start to diffuse through the molybdenum (Mo) back contact to the absorber layer. This kind of diffusion may degrade the photovoltaic performance of solar cells [22], therefore an additional barrier layer of Al2O3, SiOx, SiN4 or Cr [23] for inhibiting the diffusion during the growth of CIGS is required [24]. Herrman and Kessler et al. [25] have investigated the obstacle layers for flexible CIGS cells on metal foils. In spite of the advantages of the diffusion barrier layer, the presence of additional layers indicates more complicated process and high material and production costs from the industrial point of view. Therefore, further understanding of the effects of iron ions on the CIGS properties may benefit the efficient substitution of the barrier layer. F. Pianezzi et al. [16] have investigated the electronic properties of Cu(In, Ga)Se2 solar cells prepared on stainless steel foils without diffusion barrier. However, the exact influence of iron ions on CIGS solar cells is still unclear.

Hence, the present research work aimed to fabricate Cu(In, Ga)Se2 thin films on flexible stainless steel substrates via the non-vacuum spin-coating process. The effects of doping various amounts of the iron ions on the crystalline structure, surface morphology, and photovoltaic properties of CIGS were investigated. The influence of selenization temperatures on the iron-ion doped Cu(In, Ga)Se2 thin films and solar cells were also explored in details.

Experimental Procedures

Non-vacuum spin-coating technique was adopted to synthesize the undoped and iron-ion doped Cu(In, Ga)Se2 thin films. Analytical grade of copper nitrate (Cu(NO3)2), iron nitrate (Fe(NO3)3), indium nitrate (In(NO3)3), and gallium nitrate (Ga(NO3)3) were used
as starting materials. The molar ratio of copper ions to group III ions (indium ions and gallium ions) was fixed at 0.8, and the molar ratio of gallium ions to group III ions was 0.3. First, the metal nitrates were dissolved in a solvent composed of ethyl cellulose and ethanol in stoichiometric ratio. Ethyl cellulose was used to serve as a binder as well as to increase the viscosity of the obtained mixtures. The molar ratio of iron ions to indium and gallium ions was varied from 0 to 0.015.

The obtained mixture solution with various molar ratios was deposited on the molybdenum (Mo) coated stainless steel substrates via the spin-coating technique. The as-deposited precursor films were then dried in air on a hot plate at 225°C. The spin coating and the following drying processes were repeated to increase the thickness of the films. For the selenization treatment, the precursor films were placed in a tubular furnace at 550°C for 0.5 hrs in the reduced atmosphere (5% H₂/95% N₂) using extra pure selenium powders as the selenium source.

The phase purity and crystalline nature of the obtained films were characterized via an X-ray diffractometer (XRD, Philip X'Pert/MPD) operated at 45 kV and 40 mA using CuKα irradiation. Grazing incident X-ray diffraction (GIXD) was also employed to investigate the crystalline phases of the prepared films at different penetration depths. The surface morphologies of the obtained films were examined via a scanning electron microscope (SEM, Jeol JSM-7600F).

The solar cell devices with the structure of ITO/i-ZnO/CdS/FCIGS/Mo/SS were fabricated. The 80-nm-thick cadmium sulfur (CdS) buffer layers were deposited on the prepared iron-ion doped CIGS films via chemical bath deposition technique. Subsequently, 100-nm thick intrinsic zinc oxide (i-ZnO) layer and 400-nm thick indium tin oxide (ITO) layer were deposited on the surface of CdS layers via radio-frequency (RF) sputtering. The current-voltage characteristics of the obtained solar devices were then determined under the illumination of AM 1.5 spectrum at room temperature in air with four probe measurements.

**Result and Discussion**

The X-ray diffraction patterns of the prepared Cu(In, Ga)Se₂ thin films are shown in Fig. 1. The molar ratio of iron ions to the total amount of indium and gallium ions in Cu(In, Ga)Se₂ is defined as s. The value of s was varied from 0 to 0.015. All the prepared films with different s values displayed the XRD peaks of single phase chalcopyrite and the diffraction peaks were in accordance with ICDD card no. 35-1102 [26]. From Fig. 1, it is found that when the s value was increased, the diffraction peak intensity in the formed films was decreased. Furthermore, the formation of additional shoulders in the peaks of (220) and (312) was also observed with increasing the s value.

![Fig. 1. XRD patterns of Cu(In,Ga)Se₂ thin films with different values of s equal to (a) 0, (b) 0.005, (c) 0.010, and (d) 0.015 prepared on Mo-coated stainless steel substrates. The molar ratio of iron ions to the total amount of indium and gallium ions in Cu(In,Ga)Se₂ is defined as s.](attachment:Fig_1.png)

Grazed incidence XRD was performed on the synthesized films with different s values at different penetration depths in attempt to elucidate the occurrence of additional shoulders and diffraction peak intensity variation. The grazed incidence XRD patterns for the films without doping iron ions (s = 0) at different penetration depths are displayed in Fig. 2. The penetration depth at different incidence angle could be calculated according to the following equation [27, 28].

![Fig. 2. Grazing incident X-ray diffraction patterns of Cu(In,Ga)Se₂ thin films without iron-ion doping (s = 0) at different incident angles equal to (a) 1°, (b) 2°, (c) 3°, and (d) 4°. The molar ratio of iron ions to the total amount of indium and gallium ions in Cu(In,Ga)Se₂ is defined as s.](attachment:Fig_2.png)
\[ D(\omega) = \frac{\sin(\omega)}{\mu} \]  \hspace{1cm} (1)

where \( \omega \) is the incidence angle of the X-ray, and \( \mu \) is the absorption coefficient of the material. As the incidence angle was increased from 1° to 4°, the respective penetration depth of the Cu(In, Ga)Se\(_2\) thin film was increased from 0.26 m to 1.04 mm. Without iron-ion doping (s = 0), the phase of Cu(In, Ga)Se\(_2\) thin film remained unchanged at different penetration depths and showed a single-phased chalcopyrite structure. It is also observed that the relative intensity of the additional shoulders in the diffraction peak was increased with an increase in the incidence angle, indicating the gallium gradient across the thin film as a result of indium ions replaced by gallium ions. As the large indium ions were replaced by the small gallium ions in the lattice, the lattice constant decreased, thereby resulting in shifting of diffraction peaks to high angles. As the incidence angle changed from 1° to 4°, the concentration of gallium ions increased from the surface to bottom and the intensity of additional shoulders also increased. In addition, it is found that the intensity of the diffraction peaks ascribed to Mo and MoSe\(_2\) also increased with the incidence angle due to the usage of Mo-coated stainless steel as the substrate.

The grazed incidence XRD patterns of Cu(In, Ga)Se\(_2\) thin film with s = 0.015 at different depths are shown in Fig. 3. The intensity of the diffraction peaks increased with the incidence angle (\( \omega \)) of the X-ray. At \( \omega = 2° \), the additional shoulders appeared in the thin film with s = 0.015 were not as steep as those in the thin film with s = 0 in terms of gallium concentration gradient. This phenomenon was due to the participation of iron ions in the growth of Cu(In, Ga)Se\(_2\) thin films. In addition, the substantial existence of the additional shoulder diffraction peaks suggests that iron-ion doping would cause the formation of both CuInSe\(_2\) and CuGaSe\(_2\) phases.

To investigate the effects of iron-ion doping on peak shift, the magnified view of diffraction peak (112) for Cu(In, Ga)Se\(_2\) thin film is displayed in Fig. 4. The diffraction peak shifted from 26.81° to 27.09° as the s value increased from 0 to 0.015. The indium/gallium ions were substituted by iron ions in the lattice [29, 30], leading to a reduction in the lattice constant...
Influence of doping iron ions into Cu(In,Ga)Se$_2$ films in the morphology and photovoltaic properties of thin-film solar cells

The scanning electron microscopic images of the Cu(In,Ga)Se$_2$ thin film with different s values are shown in Fig. 5. When s = 0, the surface of Cu(In, Ga)Se$_2$ thin film was flat and dense. From Fig. 5 (a), the grain size was found to be approximately 1 mm. As the s value was increased to 0.005, it was observed that the grains became sharp and angular with some small grains scattered among large grains (see Fig. 5(b)). When the s value was further increased to 0.010 or 0.015, the grains appeared irregular with a reduced grain size.

In order to study the influence of iron-ion doping on the photovoltaic characteristics of Cu(In, Ga)Se$_2$ solar cells, the iron-ion doped Cu(In, Ga)Se$_2$ solar cells with different s values were fabricated. The current-voltage curves and photovoltaic characteristics of the prepared Cu(In, Ga)Se$_2$ solar cells with different s value are shown in Fig. 6 and Fig. 7, respectively. In addition, the photovoltaic constraints of the solar cells are tabulated in Table 1.

When s = 0, the conversion efficiency of the Cu(In,Ga)Se$_2$ solar cell was around 7.43%, while the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), and fill factor (FF) were 0.480 V, 26.73 mA/cm$^2$, and 57.97%, respectively (see Fig. 7). When the s value was increased from 0.05 to 0.015, the conversion efficiency reversely decreased from 1.59% to 0.83%, $V_{oc}$ decreased from 0.315 V to 0.233 V, $J_{sc}$ decreased from 10.83 mA/cm$^2$ to 9.46 mA/cm$^2$, and FF decreased from 46.66% to 37.92% (see Fig. 7). It is implied that the more iron ions were doped, the inferior the photovoltaic performance it was. This was due to the increase in the number of grain boundaries caused by iron-ion doping. The electron-hole recombination tended to occur in the grain boundary, which led to reduce collection of photo-current. Thus the value of $J_{sc}$ was decreased. Furthermore, the acceptor-like deep defects caused by iron ions would act as additional

<table>
<thead>
<tr>
<th>s</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.480</td>
<td>26.73</td>
<td>57.97</td>
<td>7.438</td>
</tr>
<tr>
<td>0.005</td>
<td>0.315</td>
<td>10.83</td>
<td>46.66</td>
<td>1.593</td>
</tr>
<tr>
<td>0.010</td>
<td>0.261</td>
<td>10.00</td>
<td>43.08</td>
<td>1.125</td>
</tr>
<tr>
<td>0.015</td>
<td>0.233</td>
<td>9.46</td>
<td>37.92</td>
<td>0.837</td>
</tr>
</tbody>
</table>
recombination centers, and resulted in the reduction of $V_{oc}$ and FF.

The optical properties of the prepared Cu(In, Ga)Se$_2$ thin films were analyzed via UV-Vis-NIR spectroscopy. The band gaps of the prepared films were calculated from the following equation [36] using the UV-Vis-NIR data shown in Fig. 8,

$$\alpha h\nu = \kappa (h\nu-E_g)^{1/2}$$

(2)

where $\alpha$ is the absorption coefficient, $k$ is a constant, $h$ is the Planck's constant, $\nu$ is the frequency of the incident light, and $E_g$ is the band gap. The $\alpha h\nu$ vs $h\nu$ curve of the Cu(In, Ga)Se$_2$ thin films with different $s$ values is shown in Fig. 8. The band gap could be obtained from the extrapolation line. When $s = 0$, the band gap of the Cu(In, Ga)Se$_2$ thin film was 1.08 eV. When the value of $s$ was increased from 0.005 to 0.015, the band gap of the Cu(In, Ga)Se$_2$ thin film was increased from 1.34 eV to 1.37 eV, respectively. The enhancement of band gap energy value directly indicates that reduction of the absorption band width with the increase in $s$ value. Therefore, the obtained devices will utilize less fraction of solar photon from the whole solar spectrum and hence the conversion efficiency has been reduced. It is demonstrated that iron-ion doping poses negative impacts on the photovoltaic performance as well as the microstructures of the Cu(In,Ga)Se$_2$ solar cells.

**Conclusions**

Cu(In, Ga)Se$_2$ thin films doped with different ratios of iron ions to the total amount of gallium and indium ions were successfully prepared on stainless steel substrates via non-vacuum spin-coating process. The conversion efficiency of the iron-ion doped Cu(In, Ga)Se$_2$ solar cell dropped dramatically from 7.43% to 0.83% as the molar ratio of iron ions to the total amount of gallium and indium ions was increased from 0 to 0.015. The grain sizes of the prepared Cu(In, Ga)Se$_2$ films became small, irregular, and angular with iron-ion doping, leading to the increased number of grain boundaries and formation of additional shunt paths. Therefore, the conversion efficiency of the iron-doped Cu(In, Ga)Se$_2$ solar cells was dramatically decreased.

**References**


Influence of doping iron ions into Cu(In,Ga)Se$_2$ films in the morphology and photovoltaic properties of thin-film solar cells