

Research Article

Controlled Orientation and Improved Photovoltaic Characteristics of Cu(In,Ga)Se₂ Solar Cells via Using In₂Se₃ Seeding Layers

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In₂Se₃ films were utilized as seeding layers in the synthesis of Cu(In,Ga)Se₂ films via the spin-coating route. Selenizing the indium-containing precursors at 400°C resulted in the formation of the hexagonal γ -In₂Se₃ with the preferred (006) orientation. Increasing the selenization temperature to 500°C yielded the (300)-oriented γ -In₂Se₃. Using the preferred (006)-oriented In₂Se₃ as seeding layers produced the preferred (112)-oriented Cu(In,Ga)Se₂ film because of the crystalline symmetry. In contrast, the use of the (300)-oriented In₂Se₃ as seeding layers yielded the (220/204)-oriented Cu(In,Ga)Se₂ films. According to results obtained using SEM and the Hall effect, (112)-oriented Cu(In,Ga)Se₂ films had a denser morphology and more favorable electrical properties. Using the (112)-oriented Cu(In,Ga)Se₂ films as the absorber layer in the solar devices resulted in a significant increase in the conversion efficiency.

1. Introduction

Cu(In,Ga)Se₂ is an important absorber material utilized in thin-film solar devices because of a high absorption coefficient and a direct band gap [1, 2]. This material exhibits a chalcopyrite structure and high-quality Cu(In,Ga)Se₂ is generally synthesized via a three-step evaporation process [3, 4]. The process involves firstly depositing (In,Ga)₂Se₃ films, followed by copper and selenium, and finally indium, gallium, and selenium to form Cu(In,Ga)Se₂ films [5]. The deposition of (In,Ga)₂Se₃ with different crystalline structures affects the orientation of the prepared Cu(In,Ga)Se₂ films. The condition of the deposition process influences the crystalline structures of (In,Ga)₂Se₃ [6–8].

In₂Se₃ is used as the precursors to control the orientation of Cu(In,Ga)Se₂ films that are prepared via other vacuum deposition processes [9]. However, the control of the orientation of Cu(In,Ga)Se₂ films that are formed via nonvacuum routes has not been investigated in detail. In this study, In₂Se₃ was prepared via the selenization process and then applied as the seeding layer for controlling the orientation of solution-based Cu(In,Ga)Se₂ films. Metal nitrates were used

as the starting materials in the preparation of the pastes for coating the precursor films. Therefore, the cost of process can be substantially reduced. Indium-containing precursor films can be selenized at various temperatures for controlling the orientation of the obtained seeding layer-In₂Se₃. The preparation of the Cu(In,Ga)Se₂ films via the spin-coating process using the seeding layers was investigated. The relation between the orientation of In₂Se₃ and the orientation of Cu(In,Ga)Se₂ films as well as the electrical properties was discussed. Solar cells with these absorber layers were also fabricated for investigating their device performance.

2. Experimental

For preparing In₂Se₃ seeding layers, indium (III) nitrate was used as the starting materials and dissolved in ethanol. The viscosity of the solutions was increased via adding ethyl cellulose used as a binder. The seeding layers were spin-coated on the glass substrates employing the above solution, followed by heating at 200°C on a hot plate for removing solvent and carbon species. The as-coated seeding layers were

then heated in the range of 200–500°C for 0.5 h in a reducing atmosphere (5 vol% H₂ and 95 vol% N₂) containing Se vapor. Additionally, copper (II) nitrate, indium (III) nitrate, and gallium (III) nitrate were dissolved in ethanol, and then ethyl cellulose was added as a binder. The final molar ratio of copper ions to IIIA ions for Cu(In,Ga)Se₂ was close to that reported in the literature [10]. The as-prepared solutions were spin-coated on the seeding layers to prepare the precursor films, and then the precursor films were heated to 200°C on a hot plate. The precursor films were later selenized at 500°C for 0.5 h for synthesizing Cu(In,Ga)Se₂ films.

The formed phases in the selenized films were analyzed using an X-ray diffractometer (XRD, Philips X'Pert) operated as 40 kV and 40 mA with Cu K α radiation. The morphology of the obtained films was examined using a scanning electron microscope (SEM, Nova NanoSEM 230). The electrical properties of the prepared films were investigated using a Hall effect measurement (HMS-3000) at room temperature.

Cu(In,Ga)Se₂ solar cells employing the seeding layers were fabricated for investigating solar cell parameters. CdS was deposited on Cu(In,Ga)Se₂ films via a chemical bath deposition method. Subsequently, intrinsic zinc oxide (i-ZnO) and tin-doped indium oxide (ITO) were deposited via the rf-magnetron sputtering. Finally, the Cu(In,Ga)Se₂ solar cells were characterized via the current-voltage (*I*-*V*) measurement under AM1.5G conditions at 25°C.

3. Results and Discussion

In₂Se₃ films with a thickness of 400 nm were coated on glass substrates employing indium-containing pastes and subsequently dried at 200°C. Figure 1 presents the XRD patterns of the indium-containing films that were selenized at various temperatures. Only In₂O₃ was identified when the indium-containing films were prepared without selenization (Figure 1(a)) and those were selenized at 300°C (Figure 1(b)). Following selenization at 400°C, the XRD patterns of the indium-containing layers closely matched the defective wurtzite structure of the hexagonal γ -In₂Se₃ (JCPDS number 70-0250) (Figure 1(c)). γ -In₂Se₃ is known to be yielded as the stable phase at 350°C [11]. Further selenizing at 500°C monotonically increased the XRD intensity of In₂Se₃ films. The ratios of the XRD intensity of the (006) peak to that of the (300) peak for 400°C-selenized In₂Se₃ films and 500°C-selenized In₂Se₃ films were calculated to be 2.92 and 2.37, respectively, revealing that In₂Se₃ films exhibited a preferred (006) orientation upon selenization at 400°C. In contrast, In₂Se₃ films exhibited a slightly preferred (300) orientation after further selenizing at 500°C. Hexagonal In₂Se₃ exhibits many phases such as α -In₂Se₃ and β -In₂Se₃ [12, 13]. Hence, the orientation of In₂Se₃ films can be effected by the phase transition when the selenization process is carried out at high temperatures.

In₂Se₃ films that were selenized at different temperatures were applied as the seeding layers for preparing Cu(In,Ga)Se₂. Figure 2 presents the representative XRD patterns of the 500°C-selenized Cu(In,Ga)Se₂ films that were coated on the seeding layers. The XRD patterns of Cu(In,Ga)Se₂

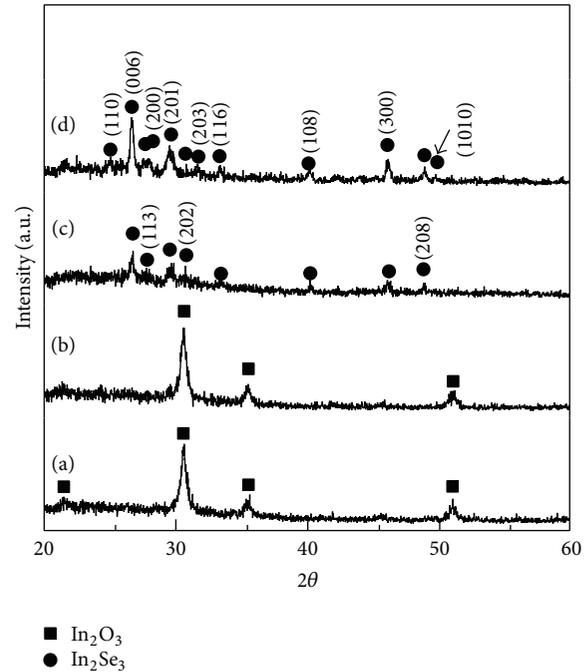


FIGURE 1: X-ray diffraction patterns of the seeding layers (a) without selenization and selenized at (b) 300°C, (c) 400°C, and (d) 500°C.

thus obtained were consistent with that reported in JCPDS number 35-1102, confirming that all samples were pure Cu(In,Ga)Se₂ films following selenization at 500°C for 0.5 h. The inset in Figure 2 plots the variation in the XRD intensity ratio of the (112) peak to the (220/204) peak ($I_{(112)}/I_{(220/204)}$) versus the selenization temperature used in the synthesis of the seeding layers. The $I_{(112)}/I_{(220/204)}$ ratio increased with the selenization temperatures of the seeding layers and decreased following selenization at 500°C for the seeding layers. The orientation of In₂Se₃ films that were used as the seeding layers greatly affected the orientation of Cu(In,Ga)Se₂.

Grazing incidence XRD (GIXRD) with a fixed incident angle (ω) of 7° was used to examine the phases formed in the inner layer of the prepared Cu(In,Ga)Se₂ films. Figure 3 displays the GIXRD results of the films that were produced using the seeding layers selenized at various temperatures. The monophasic Cu(In,Ga)Se₂ phase was obtained in all of the films without the detection of impurities. The relation between the ratio of the XRD intensity of the (112) peak to the (220/204) peak and the selenization temperatures of the seeding layers was also estimated and was shown in the inset in Figure 3. The above results imply that $I_{(112)}/I_{(220/204)}$ in the interior of Cu(In,Ga)Se₂ films varied in a manner similar to that of the surface of Cu(In,Ga)Se₂ films as presented in the inset in Figure 2.

The above phenomenon arose from the crystalline symmetry between In₂Se₃ and Cu(In,Ga)Se₂. According to the literature [13], a crystal symmetry exists between the (006)-oriented In₂Se₃ and the (112)-oriented Cu(In,Ga)Se₂. In contrast, a crystal symmetry exists between the (300)-oriented In₂Se₃ and the (220/204)-oriented Cu(In,Ga)Se₂. Hence, the

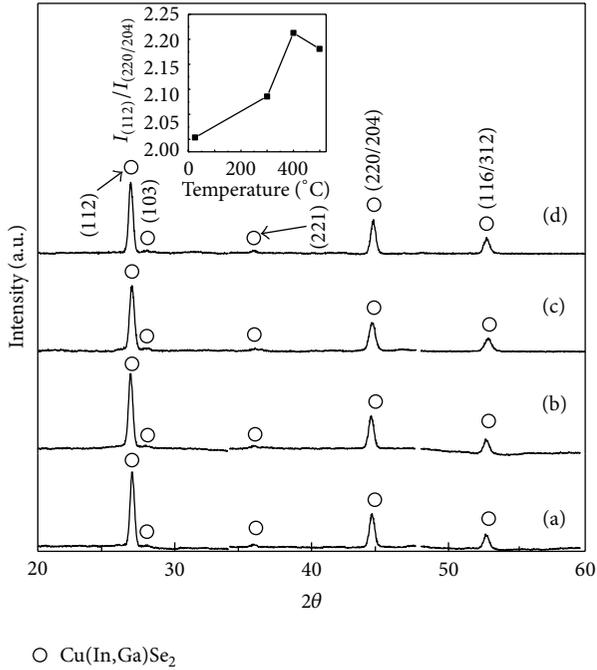


FIGURE 2: X-ray diffraction patterns of Cu(In,Ga)Se_2 films employing the seeding layers (a) without selenization and selenized at (b) 300°C , (c) 400°C , and (d) 500°C . The inset refers to the relation between the intensity ratio of the (112) peak to the (220/204) peak and the seeding layers that were selenized at varied temperatures.

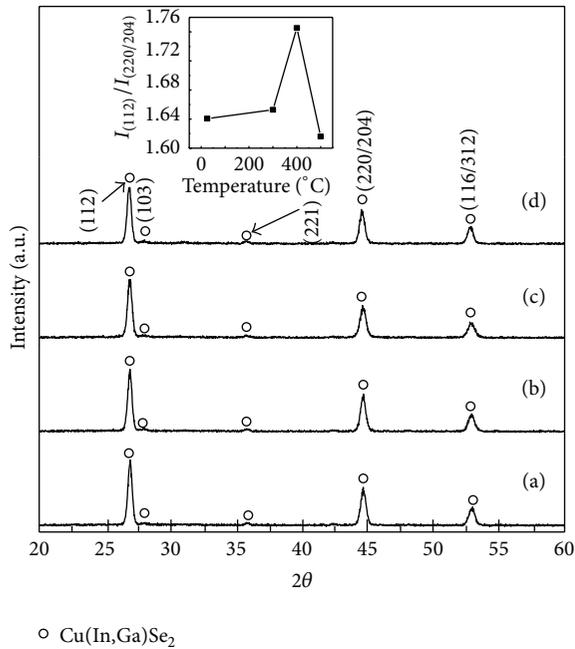


FIGURE 3: Grazing incident X-ray diffraction patterns of Cu(In,Ga)Se_2 films employing the seeding layers (a) without selenization and selenized at (b) 300°C , (c) 400°C , and (d) 500°C as the incident angles were set to 7° . The inset refers to the relation between the intensity ratio of the (112) peak to the (220/204) peak and the seeding layers that were selenized at varied temperatures.

use of the preferred (006)-oriented In_2Se_3 as the seeding layer can produce the preferred (112)-orientated Cu(In,Ga)Se_2 . The preferred (220/204)-orientated Cu(In,Ga)Se_2 is obtained using the preferred (330)-oriented In_2Se_3 as the seeding layer.

Figure 4 shows the SEM images of the microstructures of the selenized Cu(In,Ga)Se_2 films. The inset in Figure 4 displays the cross-sectional micrographs of these films. As shown in Figure 4(a), the microstructure of the films that were prepared using the seeding layer without selenization was porous. Figure 1(a) indicates that these films contained In_2O_3 . During the selenization process, the oxygen species are evaporated, forming pores in the films. The morphology of Cu(In,Ga)Se_2 films thus became increasingly densified as the selenization temperatures of the seeding layers increased (Figures 4(b) and 4(c)). However, as shown in the inset in Figure 4(d), the use of the seeding layer that was selenized at 500°C caused the morphology of Cu(In,Ga)Se_2 film to become irregular. The variation of the morphology of the prepared films was caused by the different orientations of the films.

Reportedly, the (112) planes in Cu(In,Ga)Se_2 have a lower surface energy than the (220/204) planes [14, 15]. The difference between these surface energies is responsible for the difference between sintering effects of the second phase (Cu_{2-x}Se) that is formed during selenization [16]. The fluxing agent of Cu_{2-x}Se phase can easily promote the densification of the (112)-oriented Cu(In,Ga)Se_2 films at elevated temperatures. However, the (220/204)-oriented Cu(In,Ga)Se_2 with the relatively high surface energy would result in the irregular morphology of the films.

Figure 5 presents the carrier concentration and the resistivity of the prepared Cu(In,Ga)Se_2 films. All Cu(In,Ga)Se_2 films exhibited p-type conductivity. Their resistivity was decreased and their carrier concentration increased with increasing the selenization temperatures of the seeding layers. The use of the 500°C -selenized In_2Se_3 as the seeding layer caused the carrier concentration to decrease and the resistivity to be increased. The resistivity of Cu(In,Ga)Se_2 films with the preferred (112) orientation was lower than that of Cu(In,Ga)Se_2 films with the preferred (220/204) orientation [17]. The following equation provides the relationship between the resistivity and the carrier concentration [18]:

$$\frac{1}{\rho} = e(\mu_n \times n + \mu_p \times p), \quad (1)$$

where ρ is the resistivity and μ_n , μ_p , n , and p are the electron and hole motilities, and the electron and hole concentrations, respectively. For p-type Cu(In,Ga)Se_2 films, the product of $\mu_p \times p$ is significant. According to (1), a decrease in the resistivity of Cu(In,Ga)Se_2 increases the carrier concentration of the films. In contrast, an increase in the resistivity of the (220/204)-oriented Cu(In,Ga)Se_2 reduces the carrier concentration.

Figure 6 plots the J - V curves for Cu(In,Ga)Se_2 solar cells using the seeding layers that were selenized at different temperatures. Table 1 presents the photovoltaic parameters. The conversion efficiency (η) increased with the selenization temperature of the seeding layers. The efficiency reached 7.0%

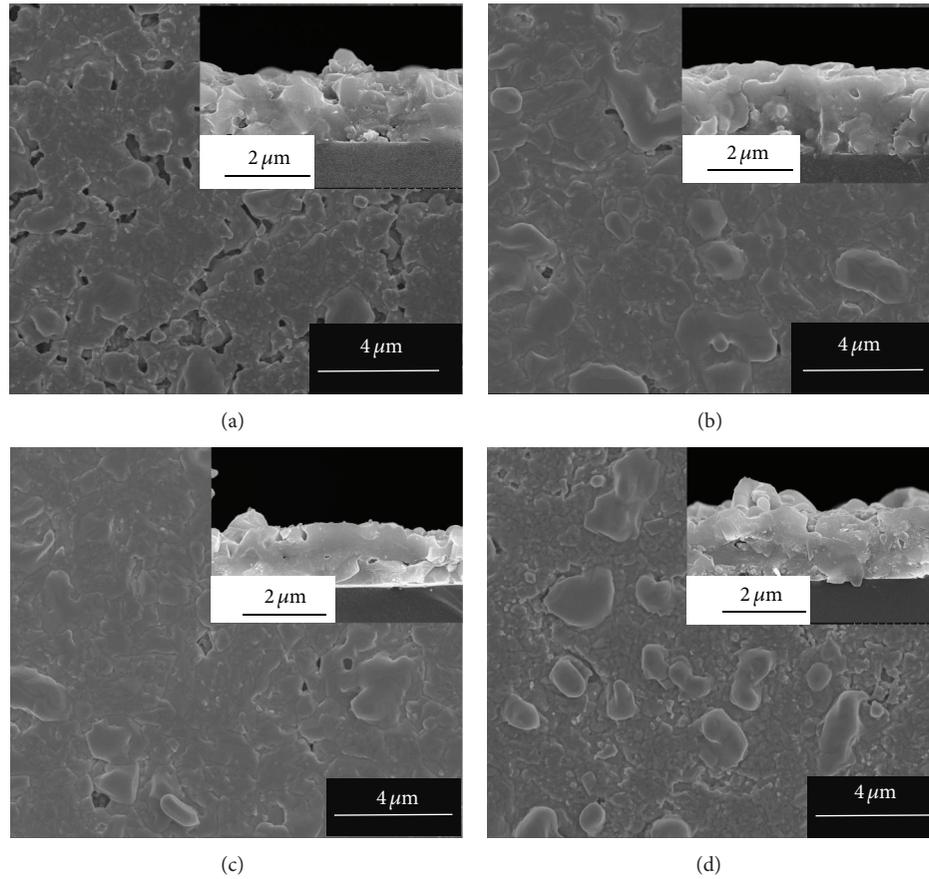


FIGURE 4: Scanning electron micrographs of Cu(In,Ga)Se_2 films employing the seeding layers (a) without selenization and selenized at (b) 300°C , (c) 400°C , and (d) 500°C . Insets refer to the cross-section micrographs of the corresponding films.

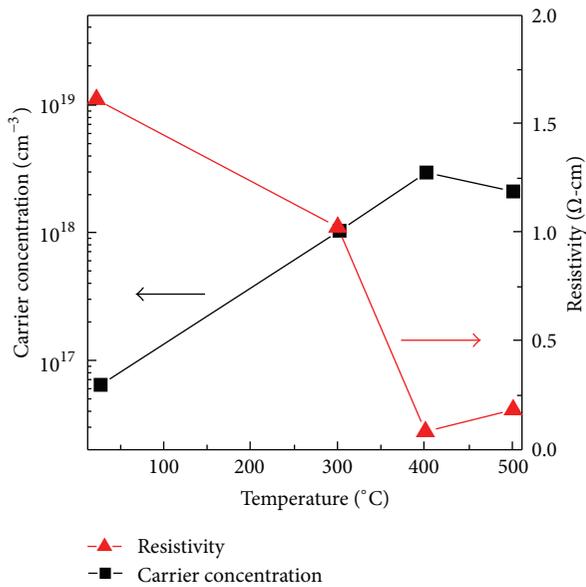


FIGURE 5: Plot of carrier concentration (N_p) and resistivity (ρ) of Cu(In,Ga)Se_2 films employing the seeding layers that were selenized at varied temperatures.

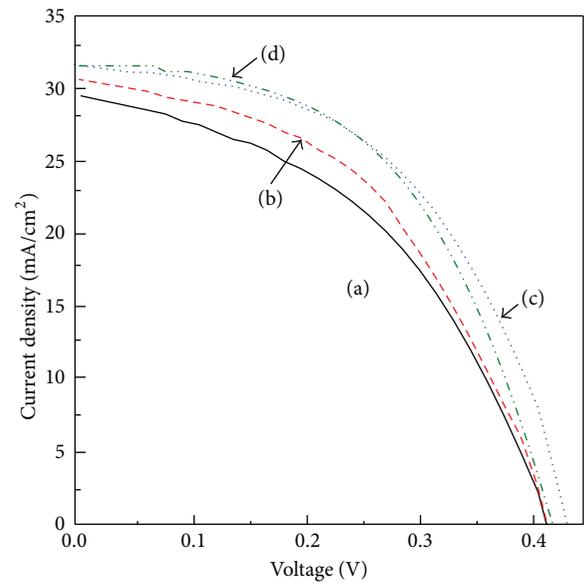


FIGURE 6: Current-voltage characteristics of the fabricated Cu(In,Ga)Se_2 solar cells employing the seeding layers (a) without selenization and selenized at (b) 300°C , (c) 400°C , and (d) 500°C .

TABLE 1: Solar cell parameters of Cu(In,Ga)Se₂ films employing the seeding layers (a) without selenization and selenized at (b) 300°C, (c) 400°C, and (d) 500°C.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
(a)	0.41	29.6	44.9	5.6
(b)	0.42	30.0	47.5	6.1
(c)	0.44	31.6	50.8	7.0
(d)	0.42	31.6	50.3	6.8

for Cu(In,Ga)Se₂ solar cells using the seeding layers that were selenized at 400°C. From Table 1, all samples had the similar short-circuit density (J_{sc}). However, the fill factor (FF) increased with the selenization temperatures of the seeding layers because reducing the resistivity of Cu(In,Ga)Se₂ film could effectively reduce the series resistance of the solar device, improving the fill factor of the cell. Additionally, the use of the 400°C-selenized In₂Se₃ seeding layer increased the open-circuit voltage (V_{oc}). The equation that relates the variation of V_{oc} to the carrier concentration (N_p) in the absorber layer can be described as the follows [19]:

$$\Delta V_{oc} = \left(\frac{2kT}{q} \right) \ln \left(\sqrt{\frac{N_{P2}}{N_{P1}}} \right), \quad (2)$$

where ΔV_{oc} is the variation of V_{oc} , k is the Boltzmann constant, T represents the temperature in Kelvin, q is the charge of an electron, and N_p is the carrier concentration. Equation (2) is based on the assumption that tunneling mechanism and surface recombination are ignored. According to (2), an increase in N_{P2}/N_{P1} in the absorber layer leads to an increase in ΔV_{oc} , resulting in an increase in V_{oc} . Moreover, Cu(In,Ga)Se₂ films with the (112) preferential orientation can reportedly be lattice matched with the buffer layers in the fabrication of solar cells [20, 21], yielding a favorable contact between the p-type Cu(In,Ga)Se₂ and the n-type buffer layers. Hence, V_{oc} can be significantly increased using Cu(In,Ga)Se₂ films with the preferred (112) orientation.

Nevertheless, the (220/204)-oriented films were associated with poorer solar performance because an increase in the resistivity of the films increased the series resistance, causing the reduction of FF. According to the SEM photographs (Figure 4), the rough microstructure and irregular grains of the films could cause the insufficient coverage of CdS buffer layer. The discontinuous covered Cu(In,Ga)Se₂ surface is possibly damaged by the ion bombardment during the deposition of i-ZnO window layers in the sputtering process, and the defects will be formed [22]. These defects will form the shunt paths and capture the photogenerated electrons, thereby facilitating the surface recombination of the CIGS/CdS interfaces and resulting in the degradation of the cell performance.

To further investigate the seeding effects from In₂Se₃, the PL spectra of the fabricated Cu(In,Ga)Se₂ films without seeding layers and with the seeding layer selenized at 400°C

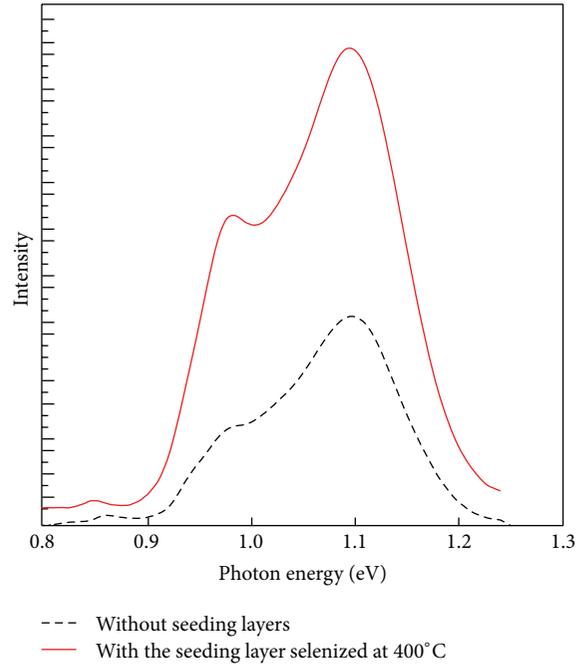


FIGURE 7: PL spectra of the fabricated Cu(In,Ga)Se₂ films without seeding layers and with the seeding layer selenized at 400°C.

are illustrated in Figure 7. It was found that Cu(In,Ga)Se₂ films having the seeding layers exhibited much stronger PL intensity than that without seeding layers. It was reported that the defects on Cu(In,Ga)Se₂ surface caused surface electron-hole recombination and reduced the PL intensity [23]. These results indicated that the seeding effects from In₂Se₃ could effectively reduce the surface recombination of CIGS films, thereby increasing the PL intensity. These results revealed that the electrical properties of Cu(In,Ga)Se₂ films can be improved by using oriented In₂Se₃ as seeding layers.

4. Conclusions

In this study, In₂Se₃ seeding layers were utilized to control the orientation of Cu(In,Ga)Se₂ films. The hexagonal γ -In₂Se₃ with the preferred (006) orientation was obtained when the indium-containing precursors were selenized at 400°C. The preferred (300)-oriented γ -In₂Se₃ was obtained upon selenization at 500°C. The use of the (006)-oriented In₂Se₃ seeding layers resulted in the formation of the (112)-oriented Cu(In,Ga)Se₂ films. These films exhibited densified morphologies and improved electrical properties. The (204/220)-oriented Cu(In,Ga)Se₂ films were formed when the (300)-oriented In₂Se₃ seeding layers were used. The use of the preferred (112)-oriented Cu(In,Ga)Se₂ absorber layers increased the conversion efficiency of the solar device to 7.0%.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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