

## Characteristics of Cu(In,Ga)Se<sub>2</sub> thin films grown by co-evaporation using a fluxmeter

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Cu(In,Ga)Se<sub>2</sub> (CIGS) thin-film solar cells has best efficiency above 19.9% among thin-film solar cells, and have potential applications in a broad range of technologies. The structure of CIGS solar cells consists of five unit layers, including a back contact, a light-absorption layer (absorber), a buffer, a front transparent conducting electrode, and an antireflection layer, formed sequentially. Materials and thin-film units of various compositions are manufactured by a variety of methods; physical and chemical methods are used to prepare thin-film CIGS solar cells. Because it is difficult to control the composition of the CIGS absorber layer, in this study, the vapor pressures were measured and controlled using a vapor fluxmeter. The vapor pressures of Cu, In, Ga, and Se were  $\sim 2.8 \times 10^{-5}$  to  $4.0 \times 10^{-5}$ ,  $\sim 1.1 \times 10^{-4}$  to  $1.3 \times 10^{-4}$ ,  $\sim 1.9 \times 10^{-5}$  to  $3.7 \times 10^{-5}$ , and  $\sim 2.8 \times 10^{-4}$  to  $4.3 \times 10^{-4}$  Pa, respectively. The characteristics of CIGS thin films were investigated using X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), and photoluminescence (PL) spectroscopy using a helium-neon (HeNe) laser. The temperature dependencies of the PL spectra were measured at a wavelength of 1137 nm. XRD patterns showed several intense peaks at (101), (112), (220)/(204), and (312)/(116), indicating the chalcopyrite structure of CIGS.

**Key words:** CIGS, Solar cells, Molecular beam epitaxy, Molecular flux, Photoluminescence.

### Introduction

Solar cells based on the ternary chalcopyrite compound Cu(In,Ga)Se<sub>2</sub> (CIGS) recently achieved the highest conversion efficiency, 19.9%, among thin-film solar-cell devices [1-3]. CIGS is a promising material for a new generation of cost-effective, high-efficiency polycrystalline thin-film solar cells. The traditional and simplistic description of a CIGS solar cell as a layered structure of the form Al/ZnO/CdS/CIGS/Mo/SLG does not accurately reflect electrical p-n junction devices [3,4]. Materials and thin-film units of various compositions are manufactured by a variety of methods; physical and chemical methods are used to prepare thin-film CIGS solar cells. One process consists of molybdenum (Mo) sputtering, a first patterning, CIGS co-evaporation, cadmium sulfide (CdS) chemical bath deposition, a second patterning, zinc oxide (ZnO) sputtering, a third patterning, silicon nitride (SiN) electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD), and aluminum (Al) sputtering. However, many researchers are using a three-stage process developed at the National Renewable Energy Laboratory (NREL, USA) that includes a quartz crystal sensor because it yields high-efficiency CIGS solar cells. In the three-stage process, the composition of the film can be controlled by monitoring the substrate temperature and the flux ratio throughout the

deposition process [5, 6].

In this study, Mo was deposited by direct current (DC) sputtering on a soda lime glass (SLG) substrate, which is commonly used as a back contact for CIGS thin-film solar cells [7]. We deposited CIGS thin films on Mo/SLG using the three-stage process [1, 2]. We monitored the substrate temperature on the back of the substrate using a pyrometer. Vapor pressures were measured and controlled using a vapor fluxmeter for CIGS sources. The characteristics of CIGS thin films were investigated using X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), and photoluminescence (PL) spectroscopy.

### Experimental Details

A schematic diagram of the CIGS solar cell fabrication process is shown in Figure 1. Generally, Mo films deposited at low pressures exhibit dense microstructures while those deposited at high pressures exhibit porous

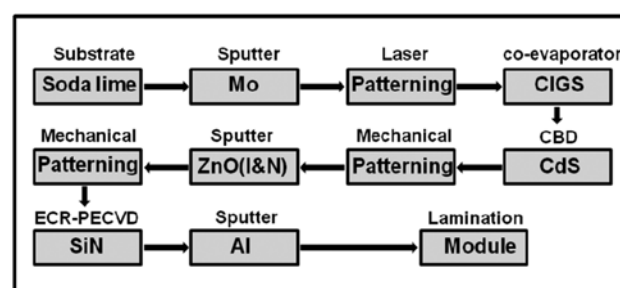


Fig. 1. Fabrication processes of CIGS thin-film solar cells.

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**Table 1.** Vapor pressures of CIGS sources.

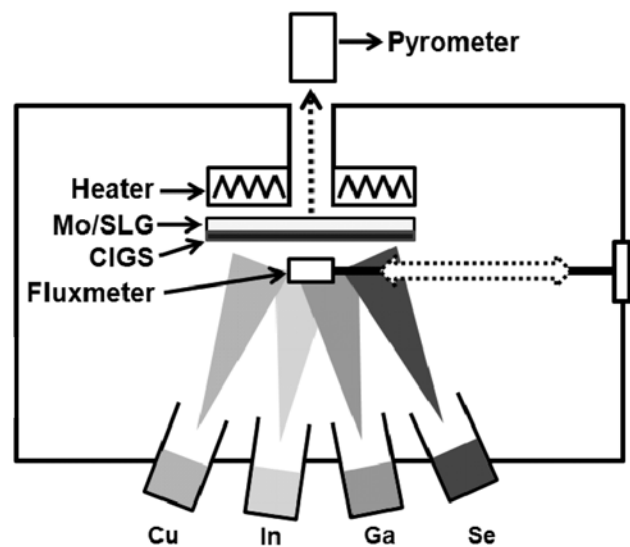
| Sample ID #1 |                                              |          | Sample ID #2                                 |          |
|--------------|----------------------------------------------|----------|----------------------------------------------|----------|
| Element      | Vapor Pressure (Pa)                          | Atomic % | Vapor Pressure (Pa)                          | Atomic % |
| Cu           | $2.8 \times 10^{-5}$                         | 24.32    | $2.8 \times 10^{-5}$                         | 26.16    |
| In           | $1.1 \times 10^{-4}$                         | 14.20    | $1.1 \times 10^{-4}$                         | 14.27    |
| Ga           | $3.7 \times 10^{-5}$                         | 11.28    | $1.9 \times 10^{-5}$                         | 8.68     |
| Se           | $2.8 \times 10^{-4} \sim 4.3 \times 10^{-4}$ | 50.20    | $2.8 \times 10^{-4} \sim 4.3 \times 10^{-4}$ | 50.89    |

| Sample ID #3 |                                              |          | Sample ID #4                                 |          |
|--------------|----------------------------------------------|----------|----------------------------------------------|----------|
| Element      | Vapor Pressure (Pa)                          | Atomic % | Vapor Pressure (Pa)                          | Atomic % |
| Cu           | $4.0 \times 10^{-5}$                         | 30.72    | $2.8 \times 10^{-5}$                         | 24.38    |
| In           | $1.1 \times 10^{-4}$                         | 14.98    | $1.3 \times 10^{-4}$                         | 18.91    |
| Ga           | $1.9 \times 10^{-5}$                         | 9.62     | $1.9 \times 10^{-5}$                         | 8.16     |
| Se           | $2.8 \times 10^{-4} \sim 4.3 \times 10^{-4}$ | 46.98    | $2.8 \times 10^{-4} \sim 4.3 \times 10^{-4}$ | 48.55    |

microstructures [8]. The sputtering system (ALPS SC Series) used in this study consisted of four sputtering guns, a DC power supply, a radio frequency power supply, a gas flow controller, a pre-cleaning module, a pumping module, and a chamber module.

The co-evaporation system (AP-MBE110-CIGS) used in this study consisted of copper (Cu), indium (In), gallium (Ga), and selenium (Se) effusion cell sources; a thickness monitor; a vapor fluxmeter; a pumping module; a load-lock chamber; and a process chamber module. The beam equivalent pressures (BEP) of individual effusion cells were measured by a nude ionization gauge, and the variation in substrate temperature was monitored on the back of the substrate using a pyrometer [6, 9]. The Mo electrode (1  $\mu\text{m}$  thickness) was grown on soda lime glass (SLG), and CIGS thin films were deposited on the Mo/SLG substrate by co-evaporating Cu, In, Ga, and Se. The base pressure of the co-evaporation system was  $2.7 \times 10^{-7}$  Pa. Vapor pressures were measured and controlled using a vapor fluxmeter. The vapor pressures of Cu, In, Ga, and Se were  $\sim 2.8 \times 10^{-5}$  to  $4.0 \times 10^{-5}$ ,  $\sim 1.1 \times 10^{-4}$  to  $1.3 \times 10^{-4}$ ,  $\sim 1.9 \times 10^{-5}$  to  $3.7 \times 10^{-5}$ , and  $\sim 2.8 \times 10^{-4}$  to  $4.3 \times 10^{-4}$  Pa, respectively (Table 1). We used the three-stage process [1, 2]. In the first stage, In, Ga, and Se were co-evaporated to form the  $(\text{In,Ga})_2\text{Se}_3$  phase. In the second stage, Cu and Se were co-evaporated to produce a Cu-rich CIGS thin film. In the third stage, In, Ga, and Se were co-evaporated to produce either Cu-poor or stoichiometric CIGS thin films. The temperature of the substrate was maintained at 400 °C during the first stage, and at 600 °C during the second and third stages. After deposition, the sample was cooled to 400 °C and transferred to the load-lock chamber. Then, it was cooled to room temperature using helium gas. We monitored the temperature variation on the back of the substrate using a pyrometer and measured the vapor pressures of sources using a vapor fluxmeter. A schematic diagram for monitoring temperature and measuring vapor pressure are shown in Figure 2 [9]. The characteristics of CIGS thin films were investigated using XRD, SEM/EDS (Hitachi, S-2400, Kyungsung-CIA), and PL spectroscopy using a helium-neon (HeNe)

**Fig. 2.** Schematic diagram of the co-evaporation system.

laser. XRD patterns of the CIGS thin films were acquired using the synchrotron radiation 3C2 beamline at the Pohang Light Source (PLS).

## Results and Discussion

The CIGS thin films were deposited on Mo/SLG substrates using a co-evaporator and varying the vapor pressures of Cu, In, Ga, and Se sources.

Figure 3 shows the XRD patterns of CIGS thin films for the vapor pressures listed in Table 1. The Cu/(In+Ga) ratios were 0.95, 1.13, 1.25, and 0.90 at the various vapor pressures, respectively. The Ga/(In+Ga) ratios were 0.44, 0.38, 0.39, and 0.30, respectively. XRD patterns of CIGS thin films showed intense peaks at (112), (220)/(204), and (312)/(116), indicating the chalcopyrite structure of CIGS. The CIGS thin films were similar to those of the NREL group because they exhibited a (220)/(204) preferred orientation; those of the Korea Institute Energy Research (KIER) group had a (112) preferred orientation. The CIGS absorber layer is a p-type  $\alpha$  phase, the so-called (112)  $\alpha$  phase,  $\text{Cu}(\text{In,Ga})\text{Se}_2$ . A Cu-poor Cu-In-Ga-Se material can be

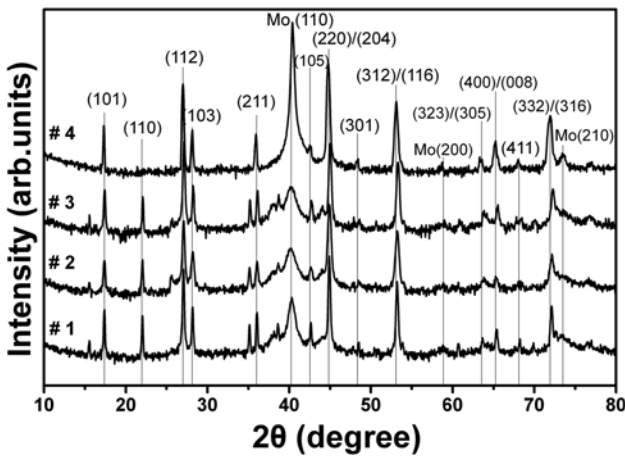


Fig. 3. X-ray diffraction (XRD) patterns of CIGS/Mo/SLG.

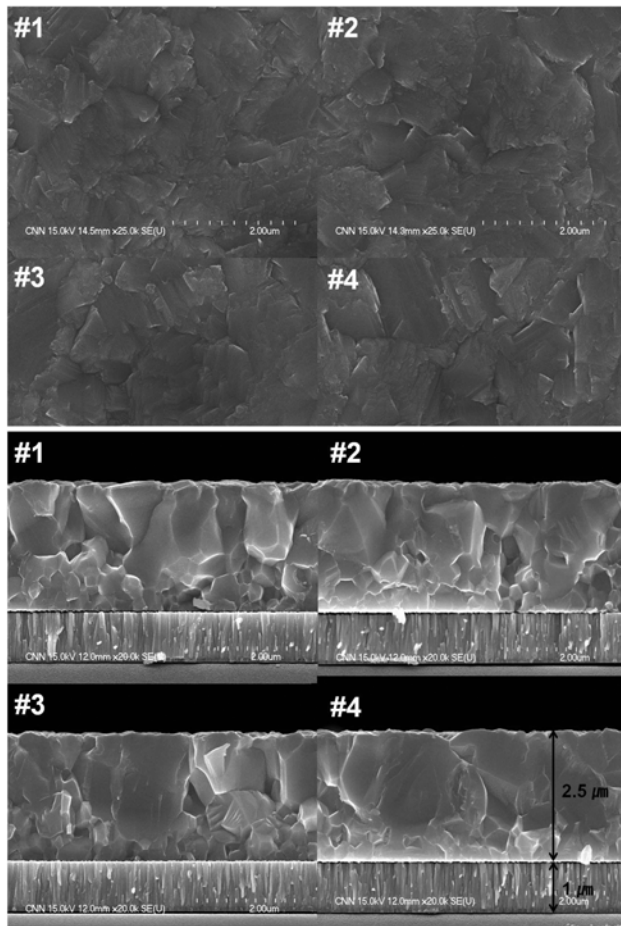


Fig. 4. Scanning electron microscopy (SEM) images of CIGS films: (a) surface morphology, (b) cross sections.

either the Cu-poor  $\alpha$  phase (chalcopyrite structure), the  $\beta$  phase (ordered-defect chalcopyrite structure), or the  $\gamma$  phase (zinc blende structure) [10]. Sample ID #4 had a simple contracted structure compared with other samples (ID #1, #2, and #3). In the ordered-defect chalcopyrite  $\beta$  phase, extra peaks, such as (110), (222), and (002), were expected in the XRD patterns.

Figure 4 shows the surface morphology and cross

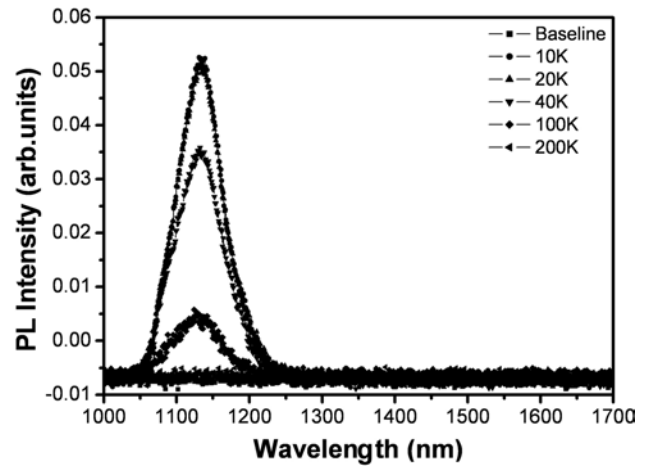


Fig. 5. Photoluminescence (PL) spectra of a CIGS film as a function of temperature.

sections of co-evaporated CIGS thin films. The thickness of the CIGS thin-film cross sections was 2.5  $\mu\text{m}$  and that of Mo was 1.0  $\mu\text{m}$ . The dependence of surface morphology on the Cu/(In+Ga) ratio differed depending on the type of CIGS thin film. Cu-rich and In-rich CIGS thin films had rough surfaces, but near-stoichiometric CIGS thin films had smooth surfaces. The image of sample ID #4 shows that the film had a dense structure and a smooth surface with few pores. The grain sizes of the CIGS thin films ranged from 0.5–0.8  $\mu\text{m}$ .

Figure 5 shows PL spectra of a CIGS thin film grown under  $2.8 \times 10^{-5}$  Pa Cu,  $1.3 \times 10^{-4}$  Pa In,  $1.9 \times 10^{-5}$  Pa Ga, and  $\sim 2.8 \times 10^{-4}$  to  $4.3 \times 10^{-4}$  Pa Se. A HeNe laser (632.8 nm) was used to characterize the CIGS thin films. The PL peak at 1137 nm is a typical band for the chalcopyrite CIGS structure [11]. According to Zott *et al.*, this band is most likely attributable to a free-to-bound exciton transition [12]. Other groups have attributed this band to donor-acceptor recombination [13]. Rega *et al.* studied epitaxial and polycrystalline CIGS thin films with various Ga/(In+Ga) ratios grown by metal-organic vapor phase epitaxy (MOVPE) [14].

## Conclusions

In this study, we prepared CIGS absorber layers by co-evaporation of Cu, In, Ga, and Se using a vapor fluxmeter, and tried to replicate the three-stage process of the NREL to form CIGS thin films. The vapor pressures of Cu, In, Ga, and Se were  $\sim 2.8 \times 10^{-5}$  to  $4.0 \times 10^{-5}$ ,  $\sim 1.1 \times 10^{-4}$  to  $1.3 \times 10^{-4}$ ,  $\sim 1.9 \times 10^{-5}$  to  $3.7 \times 10^{-5}$ , and  $\sim 2.8 \times 10^{-4}$  to  $4.3 \times 10^{-4}$  Pa, respectively. The XRD pattern of sample ID #4 showed (101), (112), (220)/(204), and (312)/(116) peaks, indicating that the film had a chalcopyrite structure. Sample ID #4 had Cu/(In+Ga) and Ga/(In+Ga) ratios of 0.90 and 0.30, respectively. The PL spectra of CIGS thin films were measured at 1137 nm. We obtained near-stoichiometric CIGS thin films with a smooth surface morphology and

few pores. Construction and a performance test of the co-evaporator system for CIGS thin-film solar cells have been completed.

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