

Characteristics of CIGS thin films grown by downward co-evaporation using downward effusion cells

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We present Cu(In,Ga)Se₂ (CIGS) thin films grown by downward co-evaporation using a downward effusion cell. CIGS thin films were prepared using the three-stage process. A composition monitoring technique was used to precisely control the relative composition of Cu, In, Ga, and Se. In this study, the vapor pressures were measured and controlled using a vapor fluxmeter. The vapor pressures of Cu, In, Ga, and Se were $\sim 3.1 \times 10^{-5}$ to 4.2×10^{-5} , $\sim 1.3 \times 10^{-4}$ to 2.0×10^{-4} , $\sim 2.0 \times 10^{-5}$ to 3.7×10^{-5} , and 3.8×10^{-4} Pa, respectively. With Cu/(In + Ga) ~ 0.9 and Ga/(In + Ga) ~ 0.3 , the Al/ZnO/CdS/CIGS/Mo/soda lime glass (SLG) solar cell demonstrated a conversion efficiency above 12%. The ZnS/CIGS solar cells were fabricated, and their photovoltaic properties were characterized. The characteristics of the CIGS thin films were investigated using X-ray diffraction (XRD) to determine their photovoltaic properties. The construction of the downward co-evaporation system for CIGS thin-film solar cells was completed and performance tested.

Key words: CIGS, Solar cells, Downward evaporator, Molecular flux.

Introduction

Cu(In,Ga)Se₂ (CIGS) thin films have achieved the highest efficiency for thin-film solar cells, above 20.3%, and have potential applications in a broad range of technologies [1, 2]. 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 Al/ZnO/CdS/CIGS/Mo/soda lime glass (SLG) does not accurately reflect electrical p-n junction devices [3]. Materials and thin-film units of various compositions are manufactured by a variety of methods; physical and chemical methods are used to prepare CIGS solar cells. The 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, magnesium fluoride (MgF₂) electron beam deposition, and aluminum (Al) thermal deposition.

In this study, the CIGS thin films were grown by downward co-evaporation using a downward effusion cell and the performance of the thin films was tested. The CIGS thin films were prepared using the three-stage process, and a composition monitoring technique was used to precisely control the relative composition of Cu, In, Ga, and Se [1]. The vapor pressures were measured and controlled using a vapor fluxmeter. Figure 1 shows schematic diagram of the downward co-evaporation system. The Al/ZnO/ZnS/CIGS/Mo/SLG solar cells were fabricated, and their photovoltaic properties were characterized. The nontoxic zinc sulfide (ZnS) material was employed as a buffer layer for the CIGS solar cell. Molybdenum (Mo) is commonly used in back contacts for CIGS thin-film solar cells, and Mo is deposited by onto an SLG substrate. We deposited CIGS thin films onto Mo/SLG using the three-stage process [1, 2]. The vapor pressures were changed using a vapor fluxmeter for CIGS sources. The ZnS was deposited by an RF sputtering method using a moving gun [4]. The ZnO

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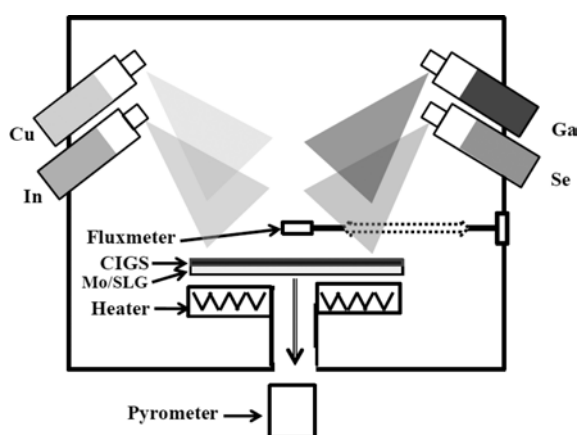


Fig. 1. Schematic diagram of the downward co-evaporation system.

was deposited by the pulsed laser deposition (PLD) method using a substrate mesh [5]. The aluminum grid was deposited through a thermal evaporation method using a tungsten boat.

Experimental Details

A schematic diagram of the CIGS solar cell fabrication process is shown in Figure 2. Generally, Mo films deposited at low pressures exhibited dense microstructures, while those deposited at high pressures exhibited porous microstructures [6]. The Mo electrode (1 μm thickness) was grown on SLG by DC sputtering method.

The downward effusion cell sources used in this study was used copper (Cu), indium (In), gallium (Ga), and selenium (Se). The beam equivalent pressures (BEP) of individual effusion cells were measured using a nude ionization gauge, and the variation in substrate temperature was monitored on the back of the substrate using a pyrometer [7]. The base pressure of the downward co-evaporation system was 1.6×10^{-6} Pa. Vapor pressures were measured and controlled using a vapor fluxmeter. The vapor pressures of Cu, In, Ga, and Se were $\sim 3.1 \times 10^{-5}$ to 4.2×10^{-5} , $\sim 1.3 \times 10^{-4}$ to 2.0×10^{-4} , $\sim 2.0 \times 10^{-5}$ to 3.7×10^{-5} , and 3.8×10^{-4} Pa,

respectively (Table 1). We used the three-stage process [1, 2] because the composition of the film can be controlled by monitoring the substrate temperature and the flux ratio throughout the deposition process [7, 8]. 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 150°C , and it was then 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. For CdS films suitable for photovoltaic applications, chemical bath deposition (CBD) is the preferred method because it is relatively simple and convenient to implement. The CBD process relies on the slow release of sulfide ions in the presence of a cadmium (Cd) salt and a chelating agent. We were ZnS replace the CdS that are commonly used. ZnS was deposited by an RF sputtering method using a moving gun. The ZnS/CIGS solar cells were fabricated, and their photovoltaic properties were characterized. The ZnS thin film was employed as a buffer layer of the CIGS solar cell, mainly because it did not break vacuum and does not contain toxic cadmium material. The ZnO was deposited by the PLD method using a substrate mesh. The PLD system (AP-PLD230) used in this study consisted of an excimer laser (Compex 205, KrF 248 nm). The characteristics of CIGS thin films were investigated using X-ray diffraction (XRD). 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 downward co-evaporator, varying the vapor pressures of Cu, In, Ga, and Se sources. To replace the CdS buffer layer, a ZnS thin film was deposited.

Figure 3 shows temperature profile of the three-stage growth process. The heater and pyrometer showed that the temperature dropped at about the same moment. A delay in one signal relative to the other was not observed. The temperature drop shown by the pyrometer was much sharper, larger in magnitude, and better defined. The second stage crossing at the point of stoichiometry was only observed in the pyrometer signal. It is possible that as a consequence of non-equilibrium growth conditions, the Cu_{2-x}Se surface segregation still commenced for slightly Cu-poor compositions or was delayed, resulting in

	Thick, Materials	Normal Process	AP Process
Grid	3 μm , Al / 50nm, Ni	E-beam evaporation	Thermal evaporation
AR layer	100nm, MgF_2	E-beam evaporation	None
Window	500nm, n-ZnO / 50nm, i-ZnO (BZO, GZO)	Sputtering (MOCVD)	PLD
Buffer	50nm, CdS (Cd-free $\text{Zn}(\text{O,S,OH})_x\text{In}(\text{OH})\text{S}$)	CBD (Sputtering)	CBD (Sputtering with moving gun)
Absorber	2-3 μm Cu(In,Al,Ga)(Se,S)	Co-evaporation (Sputtering + Selenization, Sulphurization)	Downward Co-evaporation
Back contact	1 μm , Mo	Sputtering	Sputtering
Substrate	2-3mm, SLG (SUS, Ti, Polyimide)	Cleaning	Cleaning

Fig. 2. Fabrication processes for CIGS thin-film solar cells.

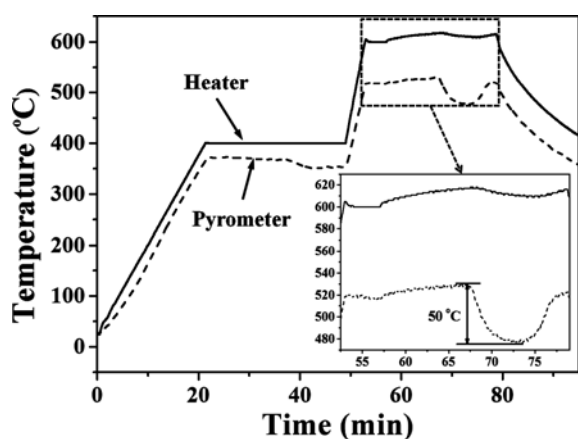


Fig. 3. Temperature profile of the three-stage growth process.

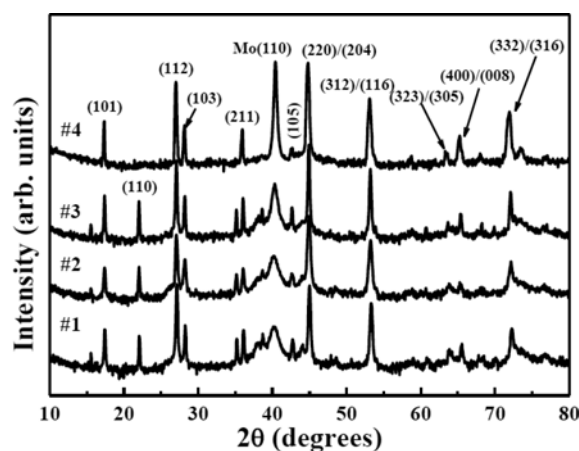


Fig. 4. X-ray diffraction (XRD) patterns of CIGS/Mo/SLG.

slightly Cu-rich overall compositions [7, 9].

Figure 4 shows the XRD patterns of the CIGS thin films for the vapor pressures listed in Table 1. The Cu/(In + Ga) ratios were 1.3, 0.8, 1.0, and 0.9 for the various vapor pressures, Sample ID #1, Sample ID #2, Sample ID #3 and Sample ID #4, respectively. On the other hand, the Ga/(In + Ga) ratios were 0.39, 0.30, 0.43, and 0.30 with vapor pressures, Sample ID #1, Sample ID #2, Sample ID #3 and Sample ID #4, respectively. XRD patterns for the 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 national renewable energy laboratory (NREL) group because they exhibited a (220)/(204) preferred orientation. The CIGS absorber layer is a p-type α phase, the so-called (112) α phase, Cu(In, Ga)Se₂ [9]. A Cu-poor Cu-In-Ga-Se material can be either the Cu-poor α phase (chalcopyrite structure), the β phase (ordered-defect chalcopyrite structure), or the γ 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 β phase, extra peaks, such as (110), (211), and (105), were detected in the XRD patterns.

Figure 5 shows the surface morphology of downward

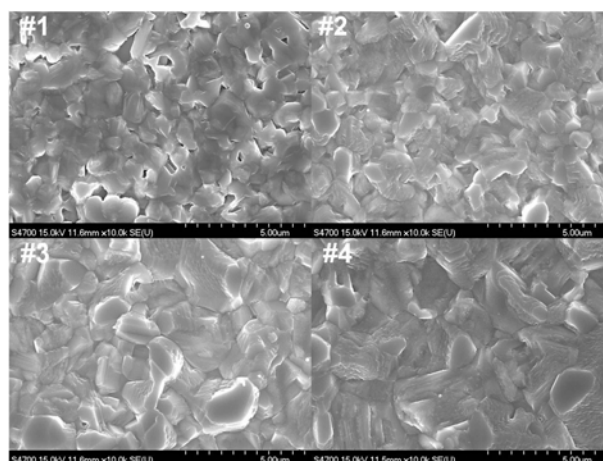


Fig. 5. Surface morphology images of CIGS films.

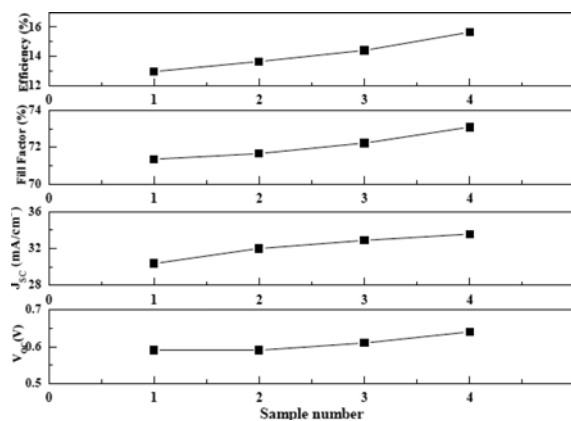


Fig. 6. Photovoltaic properties of CIGS solar cells (Al/ZnO/CdS/CIGS/Mo/SLG).

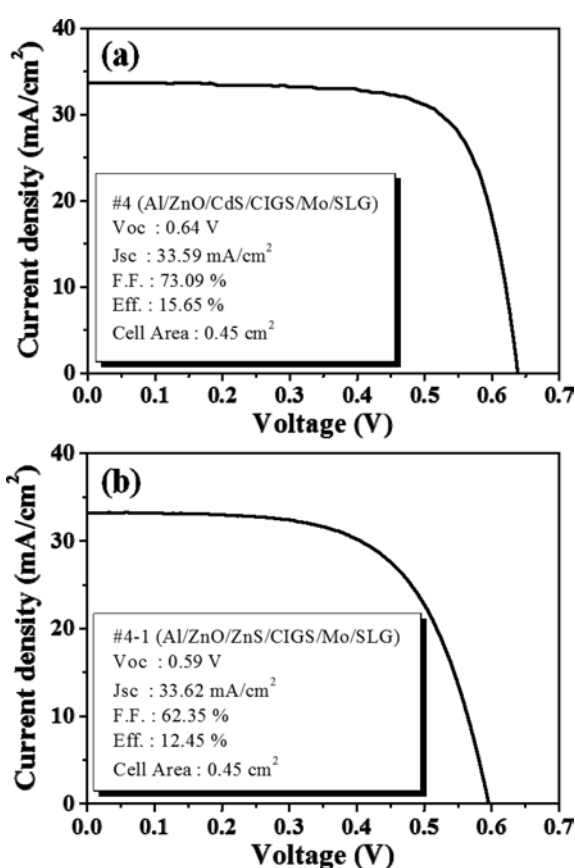
co-evaporated CIGS films. The dependence of surface morphology on the Cu/(In + Ga) ratio differed depending on the type of CIGS thin film. Cu-rich (Sample ID #1) and In-rich (Sample ID #2) CIGS thin films had rough surfaces. On the other hand, the image of Sample ID #4, near-stoichiometric CIGS thin films shows that the film had relatively dense structure and smooth surface with few pores. The grain sizes of the CIGS thin films ranged from 1-1.5 μ m.

Figure 6 shows the photovoltaic properties of the CIGS solar cells listed in Table 1. In the Cu(In,Ga)Se₂ (CIGS) thin films grown by downward co-evaporation using a downward effusion cell, conversion efficiency of solar cells are 12.98% (Sample ID #1; J_{sc} : 30.37 mA/cm², V_{oc} : 0.59 V, and F.F.: 71.35 %), 13.66% (Sample ID #2; J_{sc} : 32.02 mA/cm², V_{oc} : 0.59 V, and F.F.: 71.66%), 14.42 % (Sample ID #3; J_{sc} : 32.88 mA/cm², V_{oc} : 0.61 V, and F.F.: 72.23%) and 15.65% (Sample ID #4; J_{sc} : 33.59 mA/cm², V_{oc} : 0.64 V, and F.F.: 73.09%), respectively. The higher conversion efficiency of Sample ID #4 is estimated from near-stoichiometric and dense morphology.

As shown in Fig. 7, the CdS/CIGS and ZnS/CIGS solar cells were fabricated, and their photovoltaic

Table 1. Vapor pressures of CIGS sources.

Sample ID #1			Sample ID #2		
Element	Vapor Pressure(Pa)	Atomic %	Element	Vapor Pressure (pa)	Atomic %
Cu	4.2×10^{-5}	31.52	Cu	3.1×10^{-5}	24.45
In	1.3×10^{-4}	14.65	In	2.0×10^{-4}	21.16
Ga	2.0×10^{-5}	9.51	Ga	2.0×10^{-5}	9.12
Se	3.8×10^{-4}	44.32	Se	3.8×10^{-4}	45.27
Sample ID #3			Sample ID #4		
Element	Vapor Pressure(Pa)	Atomic %	Element	Vapor Pressure (pa)	Atomic %
Cu	3.1×10^{-5}	25.01	Cu	3.1×10^{-5}	24.53
In	1.3×10^{-4}	14.05	In	1.3×10^{-4}	19.03
Ga	3.7×10^{-5}	10.79	Ga	2.0×10^{-5}	8.19
Se	3.8×10^{-4}	50.15	Se	3.8×10^{-4}	48.25

**Fig. 7.** Illuminate JV curves for sample (a) Al/ZnO/CdS/CIGS/Mo/SLG (#4) and (b) Al/ZnO/ZnS/CIGS/Mo/SLG (#4-1) solar cells.

properties characterized. The CdS and ZnS thin film was employed as a buffer layer of CIGS solar cell for Sample ID #4 and ID #4-1, respectively. The Al/ZnO/ZnS/CIGS/Mo/SLG solar cell that does not contain toxic material showed a conversion efficiency of 12.45% (J_{SC} : 33.62 mA/cm², V_{OC} : 0.59 V, and F.F.: 62.35%). The nontoxic Al/ZnO/ZnS/CIGS/Mo/SLG solar cell grown by downward co-evaporation using a downward effusion cell represents a promising candidate for developing renewable devices.

Conclusions

In this study, we prepared CIGS absorber layers by downward co-evaporation of Cu, In, Ga, and Se using a vapor fluxmeter and three-stage process of NREL to form CIGS thin films. The vapor pressures of Cu, In, Ga, and Se were $\sim 3.1 \times 10^{-5}$ to 4.2×10^{-5} , $\sim 1.3 \times 10^{-4}$ to 2.0×10^{-4} , $\sim 2.0 \times 10^{-5}$ to 3.7×10^{-5} , and 3.8×10^{-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 ZnS thin film was employed as a buffer layer of the CIGS solar cell for the Sample ID #4-1. The Al/ZnO/ZnS/CIGS/Mo/SLG solar cell showed a conversion efficiency of 12.45% with J_{SC} : 33.62 mA/cm², V_{OC} : 0.59 V, and F.F.: 62.35%. We obtained near-stoichiometric and dense CIGS thin films. The construction and performance testing of the downward co-evaporator system for CIGS thin-film solar cells was thereby completed.

Acknowledgments

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