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Properties of $Cu(In,Ga)Se_2$ Thin Film by Co-Evaporation

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$Cu(In,Ga)Se_2$ (CIGS) compound, which has high optical absorption coefficient as direct transition type semiconductor, is very suitable for thin film solar cell due to its high thermal stability and moisture tolerance as well as its low fabrication cost compared to the standard crystalline Si solar cell.

In this research, it was tried to control the absorption capability of CIGS layer by changing $Ga/(In+Ga)$ ratio.

The composition of film was changed by controlling the effusion-cell temperature of Cu, In, Ga at a fixed Se flux. Each sample was analyzed by using SEM (scanning electron microscope), EDS (energy dispersive spectroscopy), XRD (X-ray diffractometer) to confirm the optimum composition ratio of $Cu/(In+Ga) = 0.82\sim0.95$, $Ga/(In+Ga) = 0.26\sim0.31$, $Cu/Se = 0.5$.

Keywords Co-evaporation; $Cu(In,Ga)Se_2$; solar cell; thin film; three-stage process

Introduction

CIGS compound has high optical absorption coefficient ($3 \times 10^5\,cm^{-1}$) with direct transition and its optical band gap could be controlled from 1 eV to 2.7 eV by adding Ga, Al and S elements. Also from the field test where the CIGS module was long-term exposed to solar light with high thermal energy, its efficiency was found to be maintained, which proves its good thermal stability and moisture tolerance [1].

Normally, CIGS thin film solar cell is fabricated by Mo, CIGS, CdS, ZnO, MgF_2, and Al on SLG in sequence. Among the materials, CIGS absorber is a key

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layer in CIGS solar cell and has been successfully fabricated by co-evaporation method using Molecular Beam Epitaxy(MBE) and sputtering method with annealing process [2,3].

A special quality of the CIGS material is its variable band gap, which can be changed by varying the Ga/(In + Ga) ratio. The variation of the Ga/(In + Ga) ratio, x, will affect the band gap according to

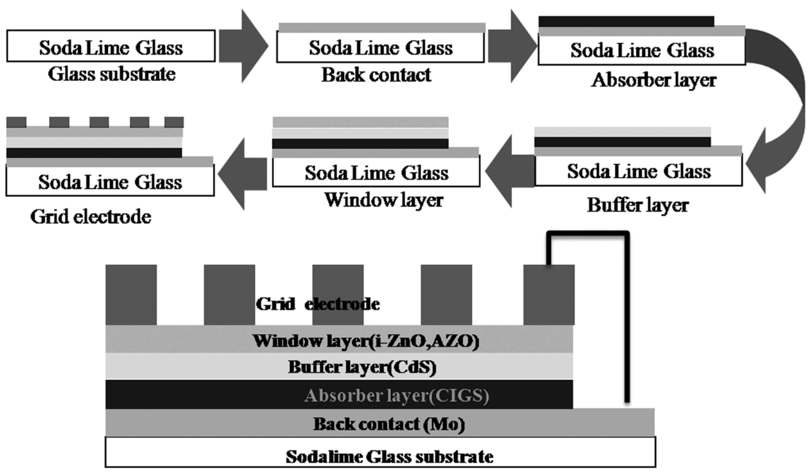
$$E_g\ [eV] = 1.02 + 0.67\ x + bx\ (x - 1) \tag{1}$$

where values between 0.11 and 0.24 have been reported for the optical bowing coefficient, b [4].

In this study, in order to improve the cell efficiency and reproducibility, we examined the optimized composition ratio of CIGS varied by evaporation temperatures of Cu, In and Ga element.

Experimental

General structure and fabrication process for CIGS thin film solar cell are represented in Figure 1. Mo as a back contact electrode was deposited by RF/DC



Material(Thickness)	Process
Ag(20 ㎛)	Screen Printing
Al:ZnO(200 nm)/i-ZnO(75 nm)	RF/DC Sputtering
CdS,(50 nm)	Chemical Bath Deposition
CIGS(1.5~2.5 ㎛)	Co-evaporation
Mo(1 ㎛)	DC Sputtering
Soda Lime Glass(1.8mm)	Cleaning

Figure 1. The fabrication processes and layer stack of CIGS solar cell.

sputtering method with the thickness of 800 nm on soda-lime glass (1.8 mm thickness). And then CIGS thin film of 2,100 nm thickness was deposited on Mo/Glass substrate using the well known three-stage co-evaporation. Evaporation of each element was controlled by varying the temperature of effusion cell. Each elements, copper (Cu), indium (In), gallium (Ga), and selenium (Se) have 99.999% purity(3 mm shot, Cerac Co., Ltd.). Co-evaporation equipment was consisted of PBN container, effusion cell with tantalum heat wire and halogen lamp, which was used to heat up the substrate up to 800°C.

The 3-stage process adopted in this study is similar to the method suggested by NREL for fabricating CIGS thin film, which is shown in Figure 2 [5].

In, Ga and Se were co-evaporated in the first stage. Cu and Se for Cu-rich layer were evaporated in the second stage. The third stage includes grain growth of CIGS as well as adjustment of film composition to get α-CIGS stoichiometry by evaporating In, Ga and Se again [6].

Evaporating temperature of Cu and Se were 1,380°C, and 210°C, respectively. The cell temperatures of In and Ga were varied over the range of 1,035°C~1,130°C and 980°C~1,000°C, respectively.

The substrate temperature and deposition time were 400°C and 15 min for the first stage, 550°C, 40 min in second stage, and 550°C, 5 min in third stage, respectively. The substrate stage was rotated with 15 rpm speed to obtain good thickness uniformity.

In order to meet the composition ratio condition of Cu/(In + Ga) = 0.82~0.95, Ga/(In + Ga) = 0.26~0.31, Cu/Se = 0.5, which are known to yield the best conversion efficiency, evaporating temperature of In and Ga were varied with fixed evaporating temperature of Se [4,5].

After 10% KCN etching of the CIGS surface to remove residual Cu-rich phase, a CdS buffer layer (ca. 50 nm thick) was deposited by chemical bath deposition. The solar cell fabrication was finished by deposition of i-ZnO/ZnO:Al by RF sputtering

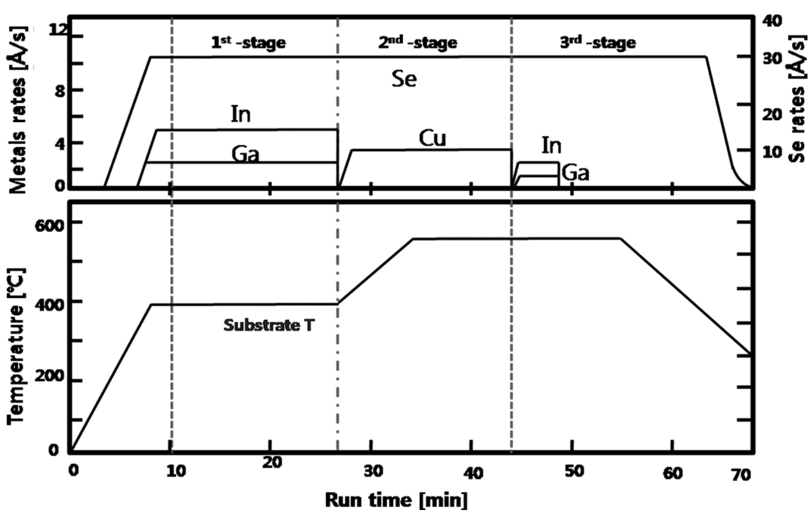


Figure 2. The variation of elemental fluxes and substrate temperature during the 3-stage CIGS deposition process.

Table 1. The effusion cell temperatures of Cu, In, Ga, and Se

Sample No.	Cu temperature [°C]	In temperature [°C]	Ga temperature [°C]	Se temperature [°C]	Film thickness (μm)
Sample 1	1,380	980	1,130	210	3.0
Sample 2	1,380	980	1,080	210	2.1
Sample 3	1,380	1,000	1,050	210	2.2
Sample 4	1,380	1,000	1,030	210	2.1

for front contacts (275 nm thick) and then silk screen printing of Ag contact grid for better current collection. No anti-reflection (AR) coating was applied.

Measurements

The properties of CIGS thin film were examined by XRD, FE-SEM and EDS. Current–voltage (I–V) characteristics of solar cell were measured under simulated AM1.5 condition (100 mW/cm^2) at room temperature. From I–V characterization, the basic parameters of solar cell like V_{OC}, J_{SC}, FF, and efficiency (η) were determined.

Results and Discussions

The compositions of CIGS thin films deposited at various temperatures of each effusion cells (Table 1), are summarized in Table 2. As indicated in the 6th and 7th column of the table, the sample 1 showed that the quantity of Cu was far too low and Ga was too high, in contrast to the atomic ratio of $Cu/(In+Ga) = 0.82\sim0.95$, $Ga/(In+Ga) = 0.26\sim0.31$, and $Cu/Se = 0.5$, which is known to be optimum for highly efficient CIGS solar cell. By lowering the Ga cell temperature by only 50°C compared to the sample1 condition, the Cu contents increased abruptly with marginal increase of In, which gave Cu-rich with very little variation of the Ga contents (sample 2). In order to match the atomic ratio, the process temperature of Ga was increased by 45°C and In decreased by 20°C and the results matched to the optimum value as described earlier (sample 3). The quantity of Cu seems to be still somewhat high. From a separate composition analysis using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), which can provide the absolute

Table 2. The compositions of CIGS thin film measured by EDS

Sample No.	Cu (at%)	In (at%)	Ga (at%)	Se (at%)	Cu/Se	Cu/ (In+Ga)	Ga/ (In+Ga)
Sample 1	15.37	4.45	27.29	52.39	0.29	0.47	0.86
Sample 2	27.47	5.31	20.28	46.94	0.58	1.07	0.79
Sample 3	26.63	15.82	10.03	47.52	0.56	1.03	0.38
Sample 4	25.02	15.39	11.56	48.03	0.52	0.92	0.42

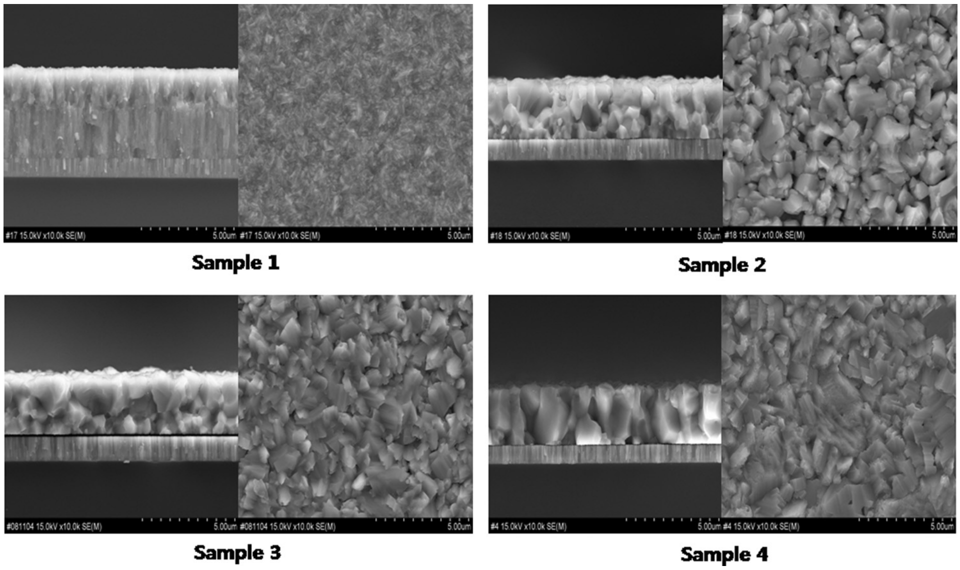


Figure 3. Cross-sectional and plan-view SEM images for the samples.

concentration of each element, it was confirmed that the Cu contents measured by EDS are highly likely overestimated as much as 7%. Therefore, the condition of sample3 is already quite close to the suggested optimum value.

In an effort to increase the doping concentration of CIGS layer, which can be obtained by lowering the Cu/(In + Ga) below 0.95, the process temperature of Ga was increased by 15°C and In and Cu were set at the same temperature as sample 3.

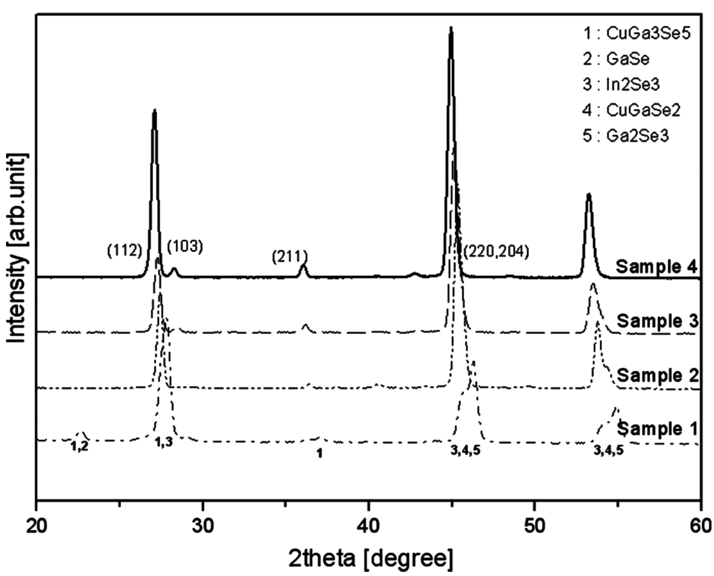


Figure 4. XRD patterns of the samples.

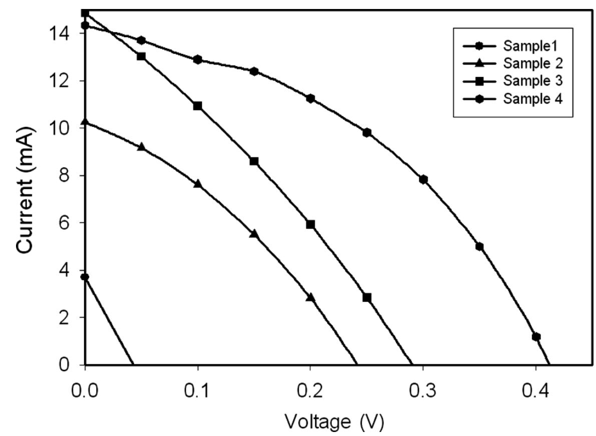


Figure 5. Current–voltage characteristics of CIGS solar cells measured under AM1.5 standard test condition.

As shown in the table, sample 4 revealed that the atomic ratio of Cu/(In + Ga) was 0.92.

From the SEM analysis in Figure 3, the sample 4 was found to have very similar morphology to the result reported by NREL than the other samples [7].

It is well known that the film should have pore-free structure with large grains of over 1 μm so that the shunt paths and the recombination centers generated by the grain boundaries could be minimized.

From the XRD results as shown in Figure 4, the sample 1 have crystal phases of In_2Se_3, GaSe, Ga_2Se_3, In_2Se_3, $CuGa_3Se_5$, and $CuGaSe_3$, not having CIGS crystal phase. The sample 2 includes $CuSe_2$, In_2Se_3 and $CuGa_{0.6}In_{0.4}$ Se_2 As expected from the above EDS results, the sample 3 and the sample 4 were found to have chalcopyrite phases of $CuGa_{0.6}In_{0.4}$ Se_2 and $CuGa_{0.3}In_{0.7}$ Se_2, respectively, without any secondary phase.

Figure 5 shows the current–voltage characteristics of the samples, which were measured at AM1.5 standard test condition. The efficiency of the sample from 1 to 3 was 0%, 2.3% and 3.07%, respectively. In case of sample 4, I-V characteristics revealed a 5.84%-efficiency cell which has $V_{OC} = 410.5$ mV, FF = 41.68%, and $J_{SC} = 34.14$ mA/cm^2 (total area = 0.42 cm^2).

Conclusions

In this study, Cu(In,Ga)Se_2 thin films were deposited on Mo/glass substrate using a three-stage co-evaporation method, where the film composition was adjusted by changing the effusion cell temperature of Cu, In, and Ga with fixed Se. The film fabricated at processing temperatures of Cu 1,380°C, In 1,000°C, Ga 1,030°C, and Se 210°C, was found to have pure chalcopyrite CIGS phase and gave the cell efficiency of 5.84% ($V_{OC} = 410.5$ mV, FF = 41.68%, $J_{SC} = 34.14$ mA/cm^2, total area = 0.42 cm^2). The films deposited at other combination of evaporating temperatures of each elements, were found to have harmful secondary phases and give far lower solar cell performance.

References

[1] Mitchell, K. W., Eberspacher, C., Ermer, J., & Pier, D. (19889). Proc. 20th IEEE Photovoltaic Specialists Conf., 1384–1389.
[2] Romeo, N., *et al*. (1986). Proc. 7th E.C. Photovoltaic Solar Energy Conf., pp. 656–661.
[3] Nishitani, M., *et al*. (1994). Proc. 1st World Conf. on Photovoltaic Energy, pp. 222–225.
[4] Green, M. A. (1992). Solar Cells; Operating Principles, Technology and System Applications, The University of New South Wales, Australia.
[5] Ramanathan, K., Teeter, G., Keane, J. C., & Noufi, R. (2005). *Thin Solid Films*, 480–481.
[6] Ingrid, Repins, Miguel A. Contreras, Brian, Egaas, Clay, Dehart, John, Scharf, Craig, L. Perkins, Bobby, To, & Rommel, Noufi. (2008). *Prog. Photovolt: Res.*, *16*, 235–239.
[7] Rommel, Noufi. (2004). "High Efficiency CdTe and CIGS Thin Film Solar Cells: Highlights of the Technologies Challenges": NREL, USA.