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Properties of $Cu(In,Ga)Se_2$ Thin Film Solar Cells on Ga Temperature Variation

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In this paper the effect the Ga/(In+Ga) ratio, which was controlled by Ga cell temperature, on the growth behavior of $Cu(In,Ga)Se_2$ (CIGS) thin film and its photovoltaic performance is presented. It was found that both the grain size and the void density of CIGS layer decreased due to higher incorporation of Ga in CIGS by increasing Ga temperature. It was revealed that the CIGS films satisfying the composition ratio of Ga/(In+Ga) = 0.3~0.4 and Cu/(In+Ga) = 0.84~1.04, which were obtained at the Ga temperature of 1033~1035°C, has the comparable diffraction intensity of (112) and (220) peaks. The (112)/(220) peak ratio of either Cu-rich or heavily Cu-poor CIGS films was found to deviate from unity and the solar cells made at these composition range showed lower photovoltaic performances. The highest efficiency of solar cell obtained by adjusting Ga cell temperature was 8.93% on device area of 0.16 cm^2 (fill factor, open circuit voltage, and short circuit current were 50.34%, 576 mV and 30.79 mA/cm^2, respectively).

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

Introduction

Solar cell is divided into Si solar cell, compound semiconductor solar cell and organic solar cell according to the light absorbing layer substance. Among them, compound semiconductor solar cell of chalcopyrite series in I-III-VI_2 family represented by $CuInGaSe_2$(CIGS) has direct transition energy band gap with the highest

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absorption coefficient of $3 \times 10^5\,cm^{-1}$. Theoretically, 0.5 μm thick CIGS can absorb almost all of incident light [1].

NREL (National Renewable Energy Laboratory, USA) has accomplished maximum efficiency of $20.0 \pm 0.8\%$ in single-junction small-area CIGS solar cell with band gap of 1.2 eV [2]. This is the record high efficiency among thin film solar cells, which is close to the highest value of 20.2% accomplished by multi-crystalline Si solar cell. Conversion efficiency higher than 10% can also be obtained by performing sputtering and selenization of metallic precursor [3,4].

In this study, co-evaporation was used to grow absorber layer on soda-lime glass substrate for high efficiency CIGS solar cell. Although growing temperature of CIGS thin film is commonly set at 550°C, but such a high temperature of 500~600°C may cause a plastic deformation of sodalime glass substrate. Therefore, if growing temperature were lowered below the strain point of the substrate, it is advantageous for commercialization and cell process in terms of cost reduction. In addition, four or more metal elements (Cu, In, Ga and Se) are used as starting substances when making CIGS thin film with co-evaporation.

The properties of CIGS thin film may change greatly by growth temperature and deposition time as well as film composition. Especially, the amount of Ga incorporated in the absorber is known to be the most important parameters that will determine the band gap energy of $Cu(In,Ga)Se_2$. While the large energy band gap of absorption layer, which includes higher Ga content, increases open circuit voltage (V_{oc}), but reduces short circuit current (J_{sc}) due to the narrower absorption spectrum. Therefore, the amount of Ga in CIGS should be precisely controlled.

Experimental

$Cu(In,Ga)Se_2$ thin film was manufactured on Mo/Glass substrate using three-stage co-evaporation. Evaporation flux of each element was controlled by adjusting the temperature of effusion cell. The substrate was rotated at 15 rpm to improve uniformity of thin film thickness during the experiment. Co-evaporation equipment used to make CIGS thin film is composed of PBN container, effusion cell with tantalum heating wire, and substrate heating module. Soda-lime glass with 2 mm thickness was used as a substrate, and Mo of 800 nm thickness was deposited on top of the glass using DC sputtering. The source materials include copper (Cu), indium (In), gallium (Ga) and selenium (Se) with 99.999% purity (Cerac, 3 mm shots). Evaporating temperatures of Cu, In and Se were 1310°C, 980°C and 170°C, respectively. The cell temperature of Ga was varied over the range of 1030~1040°C (specifically, 1030°C, 1033°C, 1035°C, 1037°C and 1040°C) for the experiment.

CIGS thin film is manufactured by the three-stage process shown in Figure 1. During the stage 1, In, Ga and Se are deposited. In the stage 2, where Cu and Se are supplied, Cu-rich CIGS thin film is formed. The 3rd stage of evaporating In, Ga and Se without Cu flux is performed to complete the p-type CIGS formation, which can be obtained under Cu-poor condition. The excess Cu-containing binary compound such as $Cu_{2-x}Se$, which has metallic nature, should be minimized to get a slightly Cu-poor composition and a device-quality surface chemistry.

The solar cells were finished by deposition of a CdS buffer layer (ca. 80 nm thick) by chemical bath deposition, DC/RF sputtering of i-ZnO/ZnO:Al front contacts (380 nm thick) and silk screen printing of Ag contact grids for better current

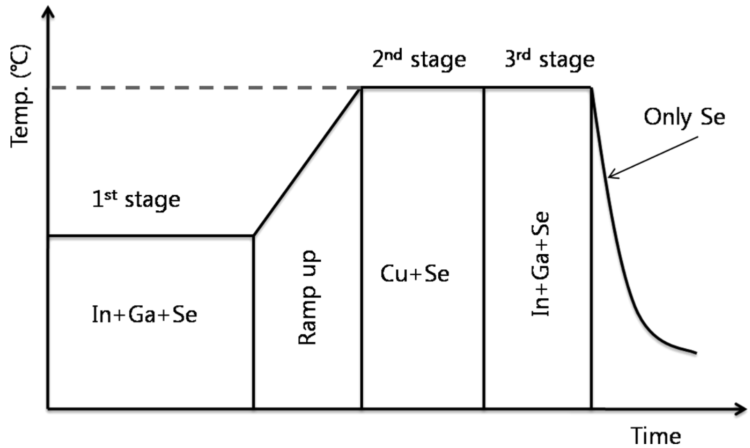


Figure 1. Thermal history curve in three-stage co-evaporation applied in this study.

collection. No anti-reflection (AR) coating was applied. Current density – voltage (J–V) characteristics of solar cells were measured under simulated AM1.5 condition at room temperature.

Measurements

CIGS Thin film properties were examined by: surface profilometry, X-ray diffractometer (XRD) and field emission scanning electron microscopy (FE-SEM) & energy dispersive x-ray spectroscopy (EDS). Current-voltage (J–V) measurements under standard illumination conditions, 100 mW/cm^2 AM1.5 spectrum at 25°C, are the most common tool for solar cell evaluation and characterization. The basic parameters of V_{OC}, J_{SC}, FF, and efficiency (η) were determined from the measured J–V curve. Independent measurements have confirmed 8.93% efficiency under simulated AM1.5 standard test conditions.

Results and Discussion

Table 1 shows EDS results for the CIGS films deposited on soda-lime substrate at various Ga cell temperatures. The ratio of Ga/(In+Ga) increased by elevating the

Table 1. The variation of CIGS film compositions measured by using EDS with respect to the Ga cell temperature

Ga cell temperature (°C)	Cu (at%)	In (at%)	Ga (at%)	Se (at%)	Cu/(In+Ga)	Ga/(In+Ga)	Film thickness (μm)
1030	32.73	15.82	6.49	44.96	1.46	0.29	2.1
1033	26.47	16.32	9.14	48.07	1.04	0.36	2.28
1035	23.11	16.33	10.93	49.63	0.84	0.4	2.3
1037	19.52	18.72	10.54	51.22	0.66	0.36	2.45
1040	16.95	18.9	11.18	52.97	0.56	0.37	2.45

evaporating temperature of Ga. It is well known that the band gap energy of $CuIn_{1-x}Ga_xSe_2$ is determined by the lever rule as follows;

$E_g \quad (x) = (1 - x)E_g(CuInSe_2, \quad 1.07\,eV) \quad + xE_g(CuGaSe_2, \quad 1.7\,eV) - bx(1 - x)b =$ bowing coefficient, $b = 0.15–0.24\,eV$

The optimal ratio of Ga/(In+Ga) is known to be around 0.35, where the band gap energy of CIGS layer corresponds to 1.2 eV, which was experimentally proven to yield a highly efficient ZnO/CdS/CIGS/Mo solar cell by NREL [5]. Considering the EDS results obtained in this study, the suggested Ga/(In+Ga) ratio can be achieved by setting the Ga evaporating temperature at 1033°C. Large surface roughness may

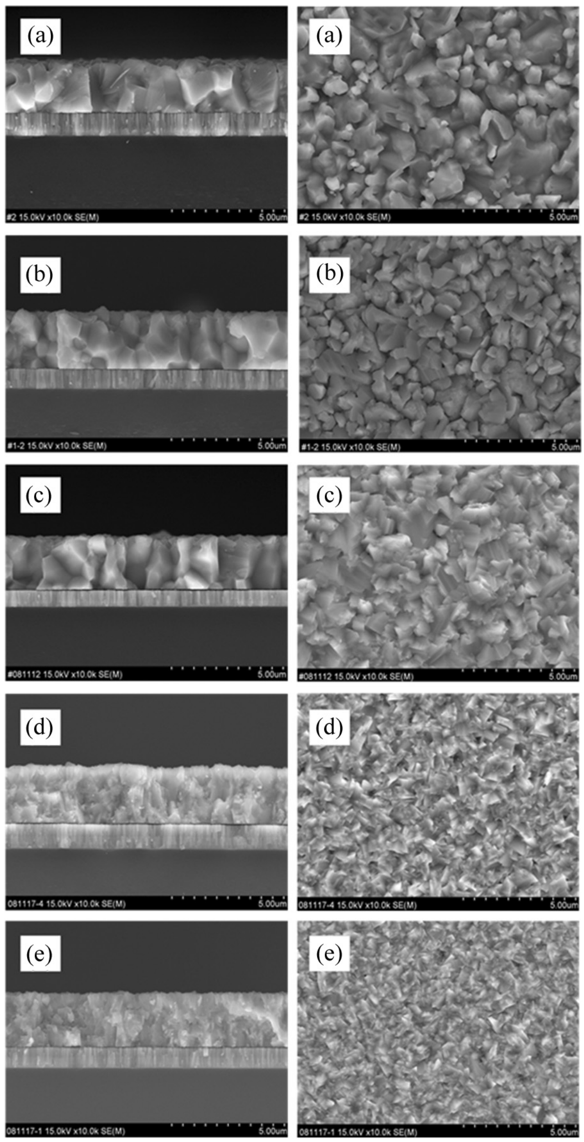
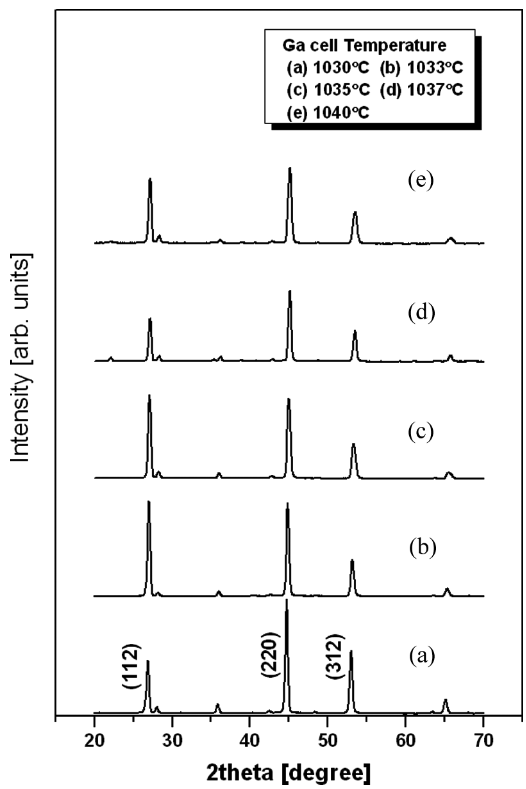


Figure 2. SEM micrographs of CIGS films with different Ga deposition temperature of (a) 1030°C, (b) 1033°C, (c) 1035°C, (d) 1037°C, and (e) 1040°C.

result in an incomplete coverage by CdS buffer layer and hence it can provide a shunt path between p-CIGS and n-ZnO. Thus it is important to make the CIGS surface smooth. In our experiments, we have found that the compositional ratio of Cu/(In+Ga) varied by T_{Ga} have large influence on the surface roughness. As shown in Figure 2, the surface roughness of CIGS films decreases rapidly with increasing T_{Ga} accompanied by lowered compositional ratio Cu/(In+Ga) from 1.46 to 0.56.

Figure 3 displays XRD patterns of CIGS films according to Ga content. CIS film is known to have the preferred orientation of (112) when Ga is not added, and higher Ga/(In+Ga) ratio may change the preferred orientation from (112) to (220) [6]. In this study, however, the preferred orientation was found to change from (220) peak to (112) peak with increasing Ga temperature below 1033°C, which seems to be in contrast to the expectation. This trend is not clearly explained at the moment and will be further investigated later. The preferred orientation is recovered from (112) peak to (220) peak again above 1033°C. With increasing evaporating temperature of Ga, 2θ value of (220) peak was observed to gradually move towards higher diffraction angle, which results from the difference in atomic radii of Ga and In atoms [7]. Upon this, the FWHM (full width at half maximum) of (220) peak increases from 0.094 to 0.156. This refers to reduced size of CIGS crystallite and accords with the SEM image shown above in Figure 2. Incorporation of excessive



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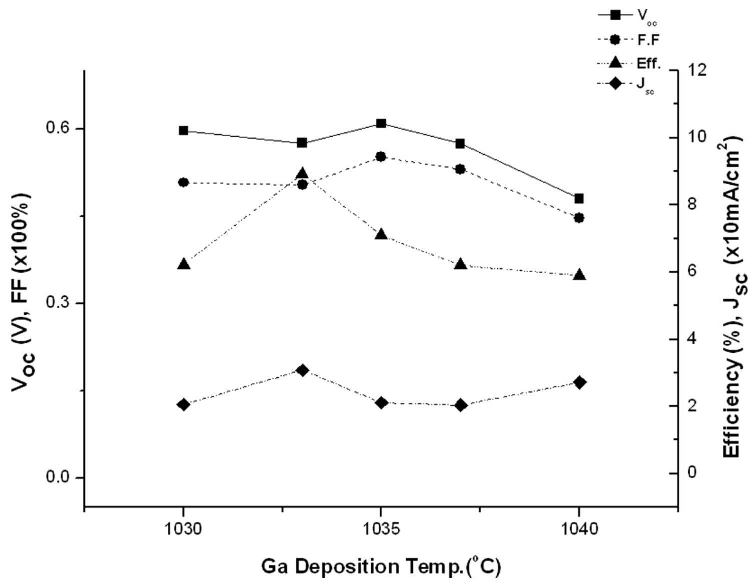

Figure 4. Device performance characteristics of a CIGS solar cell on a sodalime-glass under AM1.5 standard test conditions.

Ga in CIGS lattice causes shrinkage in the grain size of CIGS and possibly denser films. However, such reduction of grain size is linked to reduced transmittance due to increased light scattering and might reduce the cell efficiency [8,9]. Therefore, it is absolutely necessary to supply just enough Ga flux through optimal temperature control of Ga source. Furthermore, the device performance was found to be very sensitive to Ga cell temperature and the highest efficiency was achieved at T_{Ga} 1033°C. Figure 4 shows the performance variation of the devices with respect to the Ga cell temperature. The highest efficiency of 8.93% was obtained from the absorber deposited at $T_{Ga} = 1033$°C. Above 1035°C, the efficiency drops quickly together with decreasing both of fill factor (FF) and V_{oc}. Considering the fact that the Ga/(In+Ga) ratios are not significantly different at this temperature range, as shown in Table 1, the reduction of the performance parameters may stem from the Cu-deficiency rather than Ga contents. A heavily Cu-poor absorber might include $Cu(In,Ga)_3Se_5$ phase of n-type conductivity [10], which will decrease V_{oc} and FF due to the reduction of the effective hole concentration in the absorber and the serial resistance of the complete device as well.

Conclusions

In this study, $Cu(In,Ga)Se_2$ thin film was deposited on Mo/glass substrate using a three-stage co-evaporation method, where the film composition was adjusted by controlling the evaporating temperature of Cu, In, Ga and Se. It was confirmed that the composition ratio of Ga/(In+Ga) between 0.29~0.40 can be successfully controlled by simply varying the Ga cell temperature. The ratio was found to be nearest to the most ideal value (~0.35) at Ga evaporating temperature of 1033°C. While the grain size of CIGS films gradually decreased with increasing Ga temperature, the preferred orientation changed in the sequence of (220)→(112)→(220). A well-behaved solar cell device having 8.93% efficiency ($V_{OC} = 576\,mV$, $FF = 50.34\%$, $J_{SC} = 30.79\,mA/cm^2$, total area $= 0.16\,cm^2$) was successfully demonstrated by applying the Ga temperature adjustment.

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