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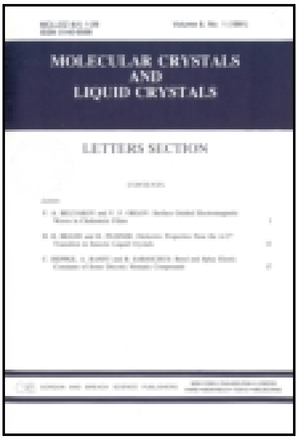

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Comparative study of Cu(In,Ga)Se_2 solar cells fabricated by using Cu-Ga alloy targets with different Ga contents

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Comparative study of $Cu(In,Ga)Se_2$ solar cells fabricated by using Cu-Ga alloy targets with different Ga contents

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In this study, in an effort to increase the surface Ga contents of $Cu(In,Ga)Se_2$ absorber, a high Ga-containing sputter target (Cu-30 at%Ga) was used to produce a precursor and was compared with Cu-22 at%Ga target in terms of photovoltaic performances of completed solar cells. The precursors consisted of multi-stack of CuGa/In and were selenized by using Se vapor at 530°C. The higher efficiency was obtained from the high Ga target with substantial improvement of open-circuit voltage and short-circuit current density. The increased hole concentration with more Ga addition in the absorber was found to be responsible for the higher open-circuit voltage.

Keywords CIGS Solar Cell; Thin film solar cell; precursor; sputter CIGS; selenization

Introduction

Solar cells based on the $Cu(In,Ga)Se_2$ (CIGS) compound semiconductor have recorded the highest conversion efficiency among thin film solar cells technologies. Among many processes to synthesize high quality CIGS absorber, so far, vacuum methods are known to have higher perfection for mass production technology [1, 2]. Especially, the 2-step process consisted of the precursor deposition and subsequent thermal processing under the selenium atmosphere, has been known for its advantage in producing large area modules. One of drawbacks of the two-step process for synthesizing CIGS layer is the phase segregation of In-rich CIGS and Ga-rich CIGS, because Se reaction rate with In is faster than that with Ga [3]. The In-rich CIGS surface phase is responsible for the low open-circuit voltage due to increased interface recombination [4]. Although the surface Ga contents could be recovered by annealing the sample under inert gas ambient [5], nowadays, the sulfurization after selenization is normally performed to increase the surface bandgap of the absorber [6]. However, the additional sulfurization process makes the module fabrication time longer and cost more expensive.

In this study, we tried to increase the surface Ga contents by combining two techniques of using a high Ga-containing sputter target and pre-annealing of a multi-stack precursor.

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Cu-30 at%Ga alloy target and pure In target were used to deposit a multi-stack CuGa/In metallic precursor by using DC magnetron sputtering. Also, the precursors were annealed right after the deposition under vacuum in an effort to incorporate more Ga in the intermediate phase such as $Cu_{16}(In,Ga)_9$.

Experimentals

Metal precursor films used in this study were deposited on 25 × 25 mm molybdenum-coated soda-lime glass substrates. Deposition was carried out via the magnetron co-sputtering system using 3-inch In and a CuGa (Ga = 22% or 30%) metal target. For plasma gas, Ar gas (99.999% impurity) was used, with the working pressure maintained at 5 mtorr (0.65 Pa). Sputtering time was adjusted to achieve a precursor thickness of 500–600 nm. The solid state selenization was carried out in a resistive heated quartz furnace. The Cu-In-Ga metal precursor and the Se-coated plate were closely contacted face to face and were heated at the ramp-up rate of 21°C/min in a two-zone furnace. The Se-coated glass was made by evaporating Se onto a sodalime glass substrate in a thermal evaporator at room temperature. The thickness of the Se layer was varied from 1.2 μm to 2.0 μm. Selenization temperature was 530°C, and the ramp-up speed from room temperature to the target temperature was 21°C/min. Once the temperature reached 530°C, reaction was induced for 20 minutes. The N_2 (99.999% impurity) was used to maintain atmospheric pressure of the reaction chamber. Thickness analysis was performed using a surface profiler (alpha-step-DEKTAK 3, DI instruments). X-ray diffraction (XRD-MPD for bulk, PANalytical) was used to determine the crystallography of the precursor and selenized films, while their morphology was observed using a scanning electron microscope (SEM - S4800, HITACHI).

Results & Discussion

The X-ray diffraction data measured from the selenized CIGS's from the two different precursors, deposited by using Cu-22 at%Ga and Cu-30 at%Ga targets, are shown in Fig. 1. The low angle (incident angle, $\omega = 0.5^o$) diffraction peaks, which is surface sensitive, of CIGS obtained from Cu-30 at%Ga are obviously shifted to the higher diffraction angles compared to those from Cu-22 at%Ga, which means that it has higher Ga content on the surface than the CIGS from Cu-22 at%Ga precursor. The peak positions of the measured diffraction patterns are equivalent to interplanar spacing of CIGS(220), d(220) = 0.20356 nm for 22 at%Ga and 0.20344 nm for 30 at%Ga. Assuming the Ga fraction is proportional to 1/d, the Ga fraction in $CuIn_{1-x}Ga_xSe_2$ made from 30 at%Ga target is about 0.11, which is 28 % more than 0.09 from 22 at%Ga. The bandgap, E_g of CIGS near surface can be obtained from the following equation [7].;

$$E_{g,x}(CuIn_{1-x}Ga_xSe_2) = 1.65 * x + 1.01 * (1 - x) - 0.151(1 - x)x$$

The calculated bandgaps of CIGS are 1.054 eV for 22%Ga and 1.067 eV for 30%Ga, which can be regarded as practically identical. This result means that the high Ga-containing target doesn't always turn into a higher bandgap absorber especially when the absorber is made by the solid state selenization route, mainly due to the Ga redistribution during selenide formation reaction.

It is also noteworthy to find that the extra shoulder peak indexed as $CuIn_{0.4}Ga_{0.6}Se_2$ appeared only in the high angle ($\omega = 6^\circ$) diffraction patterns. In fact, the d-spacing of the

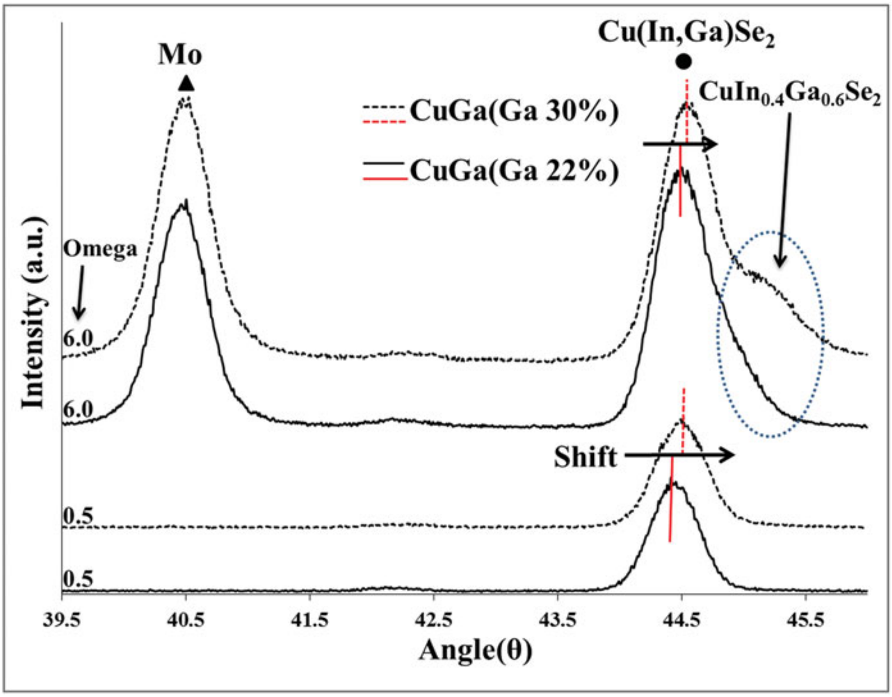

Figure 1. X-ray diffraction spectrums of CIGS layers selenized from the two different precursors. The diffraction spectrums were collected at two different incident angles. The 0.5 degrees of omega represents the surface sensitive diffraction.

shoulder peak is 0.1999 nm, which is smaller than 0.2008 nm of CuIn$_{0.4}$Ga$_{0.6}$Se$_2$ (pdf#35-1101), so that the diffraction came from a phase with a little bit higher Ga than x = 0.6. The absence of the CuIn$_{0.4}$Ga$_{0.6}$Se$_2$ diffraction peak near the film surface, evidenced from the low angle diffraction patterns, suggests that the Ga-rich phase exist in either bulk or bottom of the film and therefore large amount of Ga is still crowded near the Mo back contact.

The morphologies of the two selenized layers are significantly different as shown in Fig. 2. The cross-sectional secondary electron microscopy (SEM) images clarifies that the grain size of CIGS prepared by using the lower Ga target is much larger than that of 30 %Ga. It is well known that the Ga decreases the grain size of CIGS since the selenization of Ga-containing precursor requires a higher reaction temperature [8, 9]. The larger grains in a polycrystalline absorber is favorable for lower density of defects, which otherwise will provide with many recombination centers for the photogenerated free-carriers and reduce the open-circuit voltage (V_{oc}). However, contrary to the expectation, the higher Ga precursor resulted in the higher V_{oc} in spite of its smaller grain size as described below.

The current density-voltage characteristics of the two solar cells are shown in Fig. 3. Both of the absorbers revealed well-overlapped dark and illuminated curves. Therefore, the dark curves can be fitted with a single diode equation and the extracted parameters along with the performances are summarized in Table 1 [10]. The 30 at%Ga precursor showed much better photovoltaic performances, especially the short-circuit current density (J_{sc}) and V_{oc}. The current density available from the standard 100 mWcm^2 solar spectrum (AMG1.5) for a band gap of 1.11 eV is about 43 mAcm^2 [10]. Although the device area

Table 1. The photovoltaic parameters of the CIGS solar cells

	22% Ga	30% Ga
Jsc (mA/cm^2)	34.30	41.88
Voc (V)	0.398	0.451
FF (%)	49.65	50.61
Efficiency (%)	6.77	9.56
Rsh (ohm cm^2)	708	300
Rs (ohm cm^2)	1.01	0.72
Jo (mA/cm^2)	1.1e-1	4.8e-2
Ideality factor	2.86	2.81

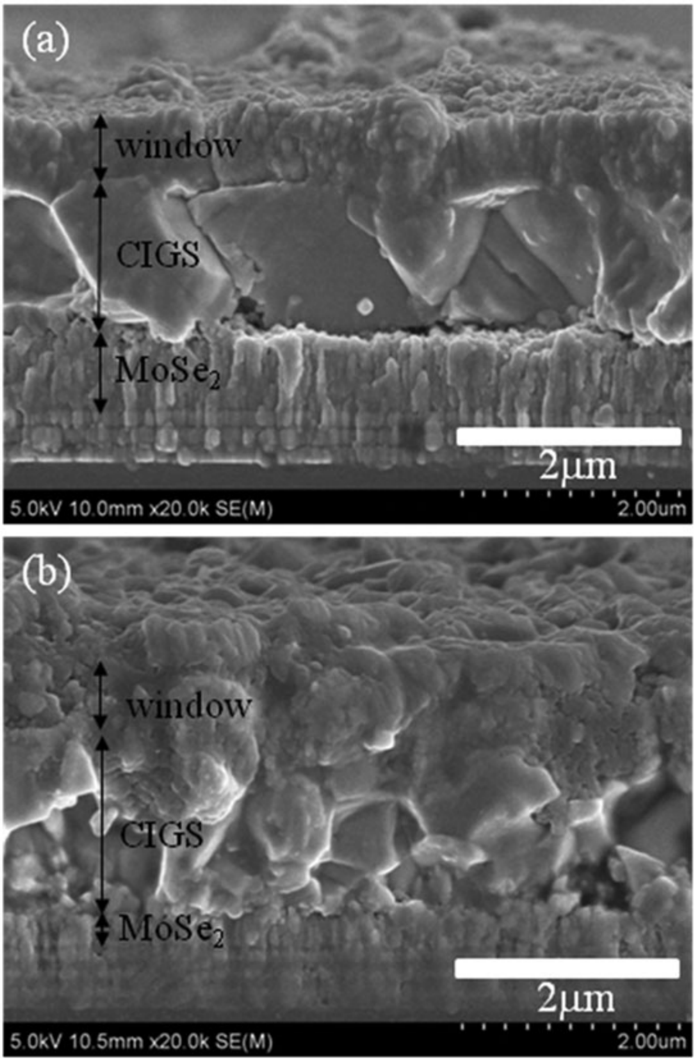

Figure 2. The cross-sectional SEM images of CIGS films obtained from two different precursor deposited using (a) CuGa(22%) and (b) CuGa(30%) target.

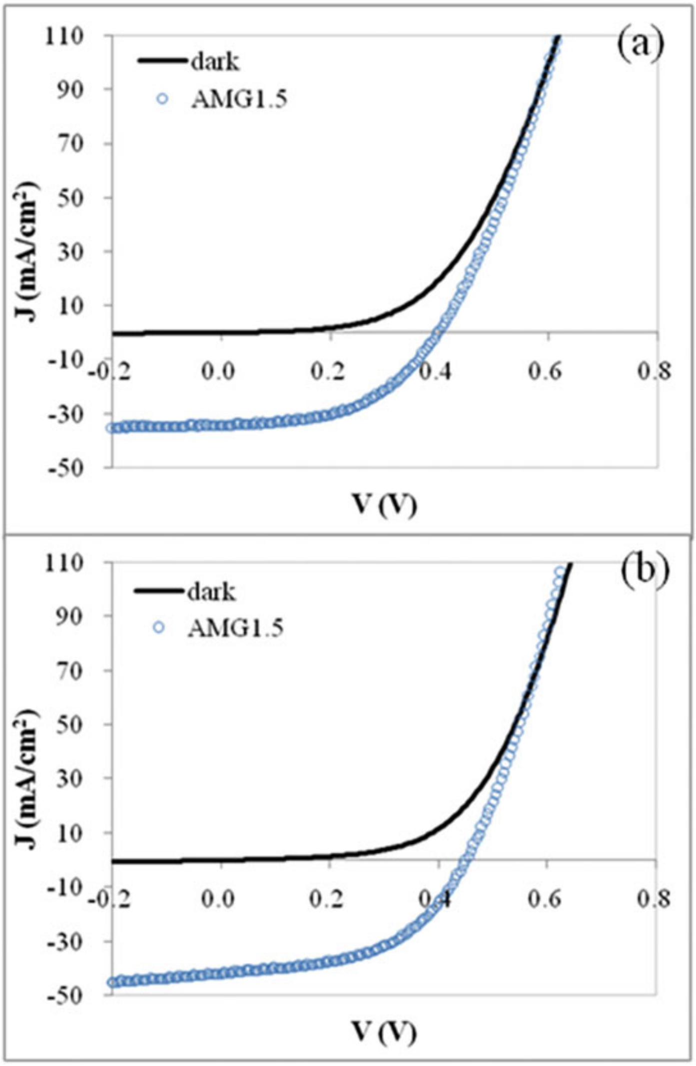

Figure 3. I-V characteristics of solar cells fabricated from CIGS absorbers obtained from (a) CuGa(22%) and (b) CuGa(30%) target.

was carefully measured by using an image analyzer, the J_{sc} value obtained from the 30 at%Ga case seems to be not realistic. The slightly different thicknesses of the two CIGS films, as evidenced in Fig. 2, might also affect the photo-generated current. Therefore, the comparison of the device performances will be focused on the V_{oc}, which is dominated by free carrier density, bandgap energy of the absorber, and recombination mechanism of the photo-generated carriers as far as the absorber thickness is well over 1.0 μm [11]. According to the spectral response data (not shown here), the two absorbers were found to have similar minimum bandgap energy barely larger than 1.0 eV, which suggests that the V_{oc} difference was not originated from the absorber bandgap energy difference.

The free-carrier density of Ga-containing films is found to be one order of magnitude larger when compared to thin films without Ga [12]. Indeed, the high Ga absorber was found

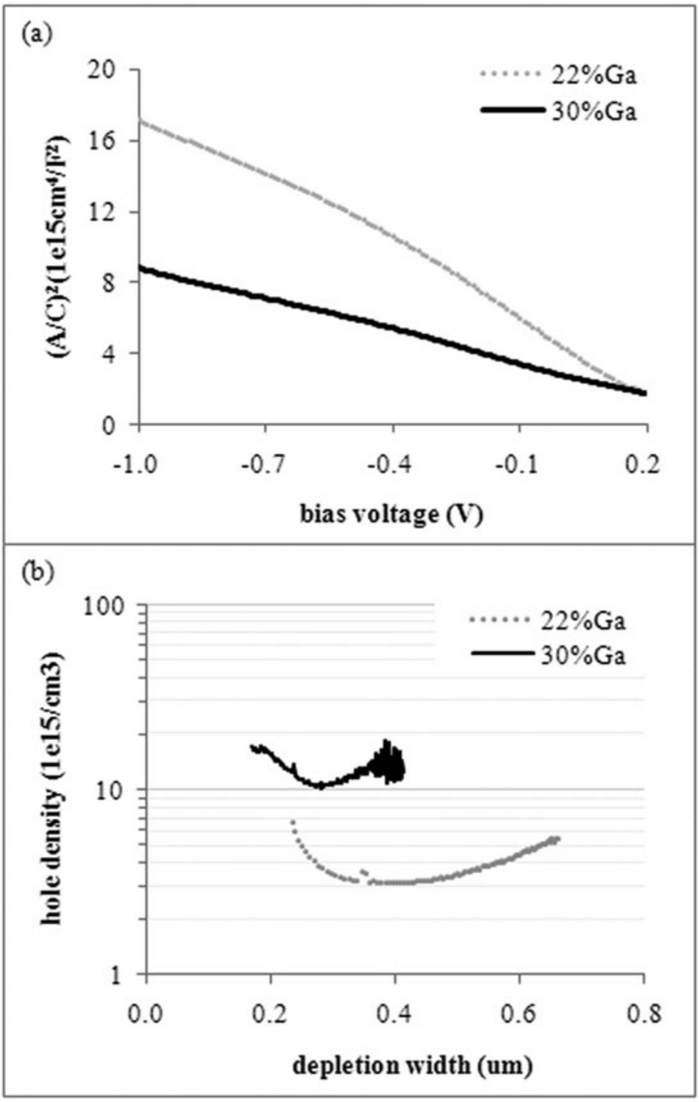

Figure 4. (a) Capacitance-voltage characteristics and (b) hole concentration profile of the absorbers made from the two targets.

to have much higher hole concentration based on the capacitance-voltage measurement as shown in Fig. 4. These features of Ga addition can be explained in terms of the different defect physics, where the formation energy of the deep donor Ga_{Cu} is higher when compared to its counterpart In_{Cu}. Both defects are thought to be the important compensating donor in the respective Ga- or In-rich materials. The higher hole concentration in the absorber, the greater the barrier height due to shift of Fermi level position towards the valence band edge, and hence the V_{oc} increases. Therefore, it can be concluded that the increased hole concentration by adding more Ga in the metal precursor is responsible for the increased V_{oc}.

Conclusion

The solar cells were fabricated and evaluated using the selenized Cu(In,Ga)Se_2 absorbers from the two different metallic precursors sputtered from CuGa (22 at%) and CuGa (30 at%) alloy targets. The higher Ga absorber was featured by the higher open-circuit voltage mainly due to the increased hole concentration. It is believed that most of the additional Ga still is crowded near Mo back contact so that it doesn't increase the surface bandgap energy of the absorber.

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