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# A simple chemical route for composition graded Cu(In,Ga)S<sub>2</sub> thin film solar cells: multi-stage paste coating<sup>†</sup>

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In order to realize the modulation of band-gap profile in low-cost and printable  $Culn_xGa_{1-x}S_2$  thin-film solar cells, a simple chemical route, namely a multi-stage paste coating method, was developed. In particular, with this method, multiple coatings with two precursor solution pastes with different compositions were applied. Elemental analysis techniques confirmed the formation of three different graded Ga distributions (front, back, and front-and-back gradient) throughout the absorber films depending on the coating sequence with two different pastes. The back gradient cell showed the largest power conversion efficiency of 7.29%, which was almost two times larger than those of the non-graded cells.

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# Introduction

Solution processing for thin film synthesis is a very attractive technique due to its cost-effective and high-throughput prospects. Recently, nanoparticle ink-or precursor solution pastebased coating techniques have attracted significant attention in the photovoltaics (PV) research field for large scale and low-cost device production.<sup>1-3</sup>

Among many types of PV's, chalcopyrite  $Cu(In_xGa_{1-x})$ ( $S_ySe_{1-y}$ )<sub>2</sub> (CIGSSe) thin-film solar cells are one of the most promising solar cells that can be achieved by the solution process. They have many merits for solar electricity generation due to their high efficiency, low fabrication cost, and durability.<sup>4,5</sup> Moreover, absorber films with various bandgaps can be easily fabricated through simple substitution of In with Ga and/or Se with S. For example, the band-gap ( $E_g$ ) of CIGSSe can gradually be increased in the range of 1.04 eV (CuInSe<sub>2</sub>) and 2.43 eV (CuGaS<sub>2</sub>).<sup>6</sup>

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Commercially available CIGSSe modules are fabricated by vacuum-based processes such as co-evaporation or sputtering, often exhibiting a composition gradient along the absorber film thickness (*e.g.* double grading).<sup>7</sup> Such non-uniform composition profile is considered to substantially influence the solar cell performance.<sup>8</sup> The modulation of the  $E_g$  profile can be classified into single (front or back) gradient and double (front and back) gradient.<sup>9</sup> For the conventional vacuum processes, experimental and simulation studies have been intensively carried out to understand and control the composition grading film formation processes, which made a CIGSSe solar cell reach over 20% in power conversion efficiency (PCE).<sup>7-10</sup>

In contrast to vacuum processes, the solution-based chemical processes of chalcopyrite thin films is not yet well established, often showing a wide range of PCE's of the fabricated solar cells.<sup>2,11,12</sup> In this regard, alternative approaches for absorber film synthesis and cell architectures should be attempted. Success in these new trials will help us to simultaneously raise the PCE and lower the cost of the solution-based thin film solar cells. In particular, only a few studies have been carried out for composition gradient throughout the absorber film in the solution-based processes.13,14 Most researches have been focused on improving the entire film quality without considering the composition profile which may be a crucial contributor for enhancing the solar cell performance of the solution-processed CIGSSe thin film solar cells as evidenced by those processed in vacuum. We have also developed a unique solution method for preparing high performance CIGSSe solar cells. Particularly, we have been focusing on high band-gap (>1.5 eV) absorber films such as  $Cu(In_xGa_{1-x})S_2$  to achieve high voltage generating thin film solar cells.<sup>15,16</sup> However, all Cu(In<sub>x</sub>Ga<sub>1-x</sub>)S<sub>2</sub> absorber films used in the studies have non-graded composition characteristics throughout the film thickness.

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<sup>†</sup> Electronic supplementary information (ESI) available: XRD patterns of the CIGS films, SEM images of the CIGS film and CIS film prepared by only paste A and B, respectively, EPMA and AES analysis of the CIGS film prepared by only paste A, shunt conductance data of the trilayered CIGS thin film solar cells measured under dark and light conditions, the *J*–*V* characteristics of the CIGS thin film solar cell device with the trilayered non-graded absorber film. See DOI: 10.1039/c5ra20751g

In this study, we successfully fabricated Ga-graded Cu(In<sub>x</sub>-Ga<sub>1-x</sub>)S<sub>2</sub> thin films using a simple chemical route, namely a multi-stage paste coating method. There has been no explicit study of the cells with graded Ga composition intentionally fabricated by a chemical route. The photovoltaic performance of the cells strongly depended on the different types of the Ga gradient in the absorber layer. The quantum efficiency data suggested that the back gradient of the cell raised the carrier collection probability with the help of the spatial modulation of  $E_{\rm g}$ . The solar cells with back gradient exhibited the largest PCE of 7.29%, which was almost two times larger than that of a cell with a uniform composition absorber layer.

## **Experimental**

#### Preparation of the pastes

A precursor mixture solution (paste A) was prepared, by dissolving the proper amounts of  $Cu(NO_3)_2 \cdot xH_2O$  (99.999%, Sigma Aldrich, 1.0 g),  $In(NO_3)_3 \cdot xH_2O$  (99.99%, Sigma Aldrich, 1.12 g), and  $Ga(NO_3)_3 \cdot xH_2O$  (99.999%, Alfa Aesar, 0.41 g) in anhydrous ethanol (80 mL), followed by an addition of ethanol solution (20 mL) with terpineol (Aldrich, 13.7 g) and ethyl cellulose (Sigma Aldrich, 0.75 g). A precursor mixture solution (paste B) was prepared, by dissolving the appropriate amounts of  $Cu(NO_3)_2 \cdot xH_2O$  (99.999%, Sigma Aldrich, 1.0 g), and  $In(NO_3)_3 \cdot xH_2O$  (99.999%, Sigma Aldrich, 1.0 g), and  $In(NO_3)_3 \cdot xH_2O$  (99.999%, Sigma Aldrich, 1.6 g) in anhydrous ethanol (80 mL), followed by the addition of ethanol solution (20 mL) with terpineol (Aldrich, 13.7 g) and ethyl cellulose (Sigma Aldrich, 0.75 g). After the mixture solutions were condensed at 40 °C under reduced pressure, a viscous paste with rheological properties suitable for spin-coating was prepared.

#### Synthesis of the $Cu(In_xGa_{1-x})S_2$ films

The Cu(In<sub>x</sub>Ga<sub>1-x</sub>)S<sub>2</sub> thin films were synthesized by multiple paste coating and subsequent two step heat treatment of oxidation and sulfurization. The paste was spin-casted onto a Mo-coated glass substrate, and the film was then dried at 150 °C for 10 min under ambient conditions using a hot plate. This process was repeated up to the desired film thickness (~2 µm). The dried film was then annealed at 350 °C for 1 h under atmospheric conditions in a furnace, resulting in a mixed oxide film of Cu, In, and Ga. The Cu(In<sub>x</sub>Ga<sub>1-x</sub>)S<sub>2</sub> alloy film was formed by reacting the resulting oxidized film with dilute H<sub>2</sub>S gas (H<sub>2</sub>S(1%)/N<sub>2</sub>) at an elevated temperature (500 °C) for 30 min.

#### Fabrication of the solar cell device

The solar cell devices were fabricated according to the typical configuration (Mo/CIGS/CdS/i-ZnO/n-ZnO/Ni/Al). In our process, a 60 nm thick CdS buffer layer was prepared on CIGS film by chemical bath deposition (CBD), and i-ZnO (50 nm)/Al doped n-ZnO (500 nm) layers were deposited by radio-frequency (RF) magnetron sputtering on the CdS layer. A Ni (50 nm) and Al (500 nm) grid was deposited as a current collector by electron beam evaporation. The active area of the completed cells was 0.44 cm<sup>2</sup>.

#### Characterization

Composition analysis was carried out by electron probe micro analyzer (EPMA, JEOL Ltd.) and Auger electron spectroscopy (AES, Ulvac-Phi, PHI-680). Structural characterization of the films was carried out by scanning electron microscopy (SEM, FEI, Nova-Nano 200) with an acceleration voltage of 10 kV and X-ray diffraction (XRD, Shimadzu, XRD-6000) with Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm). Photovoltaic performances were characterized using a solar simulator (ABET Technologies, Inc., Sun 2000) and an incident photon-to-current conversion efficiency (IPCE) measurement unit (McScience, K3100).

### **Results and discussion**

In order to realize a Ga-graded absorber film through a multistage paste coating method two kinds of paste solutions were prepared, and used to fabricate the chalcopyrite absorber layers with different compositions. Paste A had the composition ratio of Cu : In : Ga = 1 : 0.7 : 0.3 and was used for Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>)S<sub>2</sub> (CIGS) film. Paste B consisted of only Cu and In ions (Cu : In : Ga = 1 : 1 : 0) and was used for CuInS<sub>2</sub> (CIS) film. The viscosity of the both A and B paste solutions was adjusted to form 650 nm thick films by a single coating process. The desired CIGS film thickness (~2 µm) could be achieved by coating with the paste solution three times.

Three different types of Ga graded films were prepared by multiple times of thin film coating using the two pastes, as illustrated in Fig. 1. For the front gradient cell (hereafter called an F cell), paste B was spin-casted onto a Mo-coated glass substrate first. The film was then dried at 150 °C under ambient conditions using a hot plate. Then, the identical process using paste B was repeated to double the layer thickness. On top of the dried film, paste A was spin-casted and dried at 150 °C. The trilayered stacked films were annealed at 350 °C for 1 h under atmospheric conditions in a furnace, resulting in a mixed oxide film of Cu, In, and Ga. Because of this heat treatment the amount of residual carbon was measured to be around ~5 at% based on EPMA analysis. This film was then sulfurized at 500 °C in  $H_2S(1\%)/N_2$  gas, and the film with B + B + A configuration was



Fig. 1 Schematics of three types of CIGS and CIS stacked film configurations prepared by the multi-stage paste coating method.

synthesized for the front gradient cell (F cell). The reverse film configuration A + B + B, for the back gradient cell (B cell), was also prepared by the multiple coating method: one-time coating using paste A first and two-times of coating using paste B. A sandwich configuration A + B + A for the double gradient cell (FB cell) was also fabricated.

The XRD patterns of the three different films showed an apparent polycrystalline chalcopyrite crystal structure (Fig. S1<sup>†</sup>). Compared with the CIGS or CIS film synthesized by only paste A or paste B, respectively, the main peaks of (112) plane of F, B and FB films are positioned between the CIGS and CIS film indicating the in-between Ga contents in the films from the multi-stage paste coating. The morphologies of the F, B, and FB films were also investigated by cross-sectional SEM images. In general, the CIGSSe film having more Ga contents shows smaller grains.17,18 Our CIGS film also showed a similar tendency; CIS film has bigger grains than of the CIGS film  $(\sim 80 \text{ nm})$  as shown in Fig. S2.<sup>†</sup> The difference of grain size according to the composition was reflected in F, B, and FB films. The F and FB films, where the surface is composed of paste A, shows a small grain size toward surface; unlike B film which consisted paste B on the surface. The effect of stacked paste type in F, B, and FB film was more clearly confirmed by the top-view SEM image shown in Fig. 2, revealing a distinct grain size difference. However, the stacking effect using different pastes at bottom of the film was ambiguous to distinguish the difference.

In order to obtain the graded Ga distribution throughout the absorber layers of the three types of configurations, the EPMA and AES measurements were carried out as shown in Fig. 3. In F cell, the Ga contents close to the surface of the cell (*i.e.*, near the CdS buffer layer) are higher, and gradually decrease as increasing the depth, as expected (Fig. 3a). In B cell, negligible Ga is detected in the front layer, and most of the Ga elements are found in the bottom layer near the Mo backcontact (Fig. 3b). The profile in the FB cell shows higher Ga concentration at both the top and bottom of the absorber (Fig. 3c). It should be noted that the slightly higher Ga concentration (self-Ga grading) near the surface was found even in the layer synthesized by paste A only (Fig. S3<sup>†</sup>). This well explains why narrower and higher Ga content profiles were formed near the surface than the bottom in F and FB cells. All these results show that the three types of Ga gradient cells were successfully prepared by our multi-stage paste coating method.

Light current density-voltage (J-V) measurements of the trilayered structure solar cells (F, B, and FB) showed distinct features, as Fig. 4a and Table 1 show. F cell shows the lowest PCE (4.70%), mainly due to the small fill factor (FF). B cell shows the highest PCE (6.09%) due to the largest  $J_{sc}$ , in spite of the smallest  $V_{\text{oc}}$ . FB cell has the largest  $V_{\text{oc}}$ , but its PCE (4.93%) is lower than that of B cell. The  $V_{\rm oc}$  of F and FB cells with front surface gradient is larger than that of B cell with back surface gradient. Large  $E_{g}$  near the surface helps to reduce recombination in the space-charge region (SCR), because the recombination probability is inversely proportional to  $E_{g}$ .<sup>19</sup> It is known that the Ga/(In + Ga) ratio mainly affects the conduction band minima, rather than the valence band maxima.<sup>20</sup> Thus, the Ga profiles in Fig. 3a-c suggest that F and FB cells have ascending slopes of the conduction band edge,  $E_{\rm C}$ , near the surface. The back surface gradient creates an electric field, even in the quasineutral region (QNR), as well as the SCR.9 In particular, FB cell will have a notch in  $E_{\rm C}$ , due to the minimal Ga content in the middle of the absorber. The ascending slopes of  $E_{\rm C}$  at the surface of F and FB cells will push photo-carriers away from the surface, deteriorating the carrier collection efficiency.7 As a result, F and FB cells exhibit smaller  $J_{sc}$  than B cell.



Fig. 2 Cross-sectional (a-c) and top view (d-f) scanning electron microscope (SEM) images of the three types of the trilayered films; (a and d) F, (b and e) B, and (c and f) FB.

Fig. 3 Ga composition profiles of the three types of the trilayered films measured by EPMA and AES depth profiling (insets); (a) F, (b) B, and (c) FB.



Fig. 4 (a) Light J-V characteristics under 1 sun illumination and (b) EQE characteristics of the trilayered cells at zero external bias.

 Table 1
 Solar cell performance of the trilayered cells with three different stacked absorber configurations

Name	Ga gradient	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA cm	<sup>-2</sup> ) FF (%)	$\eta^{a}$ (%)	$\langle\eta angle^b$ (%)
F	Front	548	17.5	48.9	4.70	$4.42\pm0.28$
в	Back	526	20.9	55.5	6.09	$5.69\pm0.4$
FB	Front & back	581	15.7	54.2	4.93	$4.75\pm0.18$
<sup><i>a</i></sup> The conver	highest power sion efficiency.	conv	version e	fficiency. <sup>b</sup>	The ave	rage power

The solar cell performance behaviours discussed above could be further understood by means of the external quantum efficiency (EQE) of the trilayered cells (Fig. 4b). As expected from the  $J_{sc}$  data, the EQE characteristics of B cell are better than those of F and FB cells. It is notable that FB cell exhibits the worst EQE at long wavelength range. The  $E_{g}$  values of the single CIS and CIGS layers are 1.44  $\pm$  0.01 eV and 1.6  $\pm$  0.03 eV, respectively, which were measured by ultraviolet-visible (UV-vis) absorption spectroscopy (data not shown). The photon energy of 800 nm wavelength light is 1.5 eV; thus, low energy photons (energy < 1.5 eV and wavelength > 800 nm) would be absorbed by the CIS layer, not the CIGS layer. The FB cell has the smallest amount of CIS layer (roughly 1/3) in the overall film thickness. As a result, the absorption of the FB cell is the smallest, and the lowest EQE is seen at the long wavelengths. When F and B cells are compared, B cell shows improved EQE at long wavelengths.

Since the volume fraction of the CIS layer with low  $E_g$  is identical in both F and B cells, the difference in EQE should mainly be attributed to the carrier collection efficiency, rather than the optical absorption. The photo-carriers by long wavelength light can be generated far from the surface, due to the long penetration depth. In order to reach the top-contact, these carriers should overcome the potential gradient due to the aforementioned slope of  $E_C$  of F and FB cells, resulting in poor carrier collection. In contrast, the back gradient generates the electric field in QNR, and raises the carrier collection probability in B cell, improving the EQE.

The EQE data under a reverse bias of B and FB cells are compared, to confirm the electrical gain by the back gradient, as shown in Fig. 5. The reverse bias can enlarge the depletion width in the absorber film, and thereby increase the EQE, in case the electrical recombination loss in the cell is significant.<sup>21</sup> The EQE (-0.2 V)/EQE (0 V) ratio of B cell doesn't change much in the measurement wavelength range, assuring the beneficial role of the composition grading in the carrier collection. In contrast, the EQE of FB cell increases considerably under a reverse bias. The reverse bias will decrease the aforementioned slopes of  $E_{\rm C}$  near the surface, enabling photo-carriers to overcome the potential barrier. The reverse bias EQE data of F cell could not be obtained, since the shunt conductance of F cell increased quite a lot under illumination (Fig. S4<sup>†</sup>).

Based on our investigation of solar cells prepared by the multi-stage coating, the back gradient film revealed the best performance (6.09%). Notably, the efficiency is much higher



Fig. 5 EQE(-0.2 V)/EQE(0 V) of B and FB cells.

than those obtained from the cells with non-graded film (see Fig. S5<sup>†</sup>). To further validate the beneficial role of the Ga grading, we also prepared bilayer structures with the back gradient (B2 cell), as illustrated in the inset of Fig. 6. The thickness of the bilayer absorber film was also carefully adjusted to be almost identical to that of the trilayered film  $(\sim 2 \ \mu m)$  by controlling the spinning speed of coater. Consistently, B2 cell shows very high solar cell performance (highest value of 7.29%), which is even higher than that of the backgradient trilayered film (B). In particular, the  $J_{sc}$  of B2  $(19.9 \text{ mA cm}^{-2})$  is almost similar to the results of the trilayered cell (B), while the  $V_{oc}$  of B2 (622 mV) is substantially increased, compared to that (526 mV) of trilayered cell (B). The main distinction between B2 and B is the volume fraction of the small  $E_{\sigma}$  CIS layer (1/2 in B2 and 2/3 in B). The back gradient can increase Voc by repelling the photo-carriers away from the CIGS/ Mo back contact, where a relatively high recombination velocity is expected.9 The diffusion length in QNR and the recombination velocity near the back contact will determine the contribution of the back gradient of the cell to the measured  $V_{\rm oc}$ value.7

Finally, it should be mentioned that the higher solar cell performance of the Ga-graded cells may not be fully attributed



**Fig. 6** Light J-V characteristics of a bilayer cell (B2) and a schematic of the absorber film (inset).

to the composition gradient effect. The effects from the morphology changes associated with the composition gradient (*e.g.* grain size) could also be responsible for the difference in solar cell performance. Nevertheless, we clearly demonstrated that composition gradient in CIGS thin film solar cells is controllable even in a solution based method through multistage paste coating method, which could be a key technique for enhancing the solar cell performance while still adhering the cost effectiveness of the process.

### Conclusions

CIGS thin films with graded Ga distributions were successfully synthesized by multi-stage paste coating method using two different precursor solutions with different compositions. We found that graded Ga distributions throughout the stacked absorber films persisted even after the heat treatment process (sulfurization). Based on photovoltaic properties of several types of the Ga gradient solar cells, the back gradient film (increasing band-gap towards the back contact) was found to show the largest power conversion efficiency of 7.29%. This result was attributed to high carrier collection probability by the graded band-gap profiles.

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