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Supplementary Information

Regulating the Starting Location of Front-Gradient Enabled Highly Efficient $Cu(In,Ga)Se_2$ Solar Cells Via a Facile Thiol–Amine Solution Approach

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Experimental

Materials

Copper (Ⅰ) sulfide (Cu_2S, 99.5%), indium (Ⅲ) selenide (In_2Se_3, 99.99 %), 1, 2- ethanedithiol ($HSCH_2CH_2SH$, > 98%), and 1, 2- ethylenediamine ($H_2NCH_2CH_2NH_2$, 99%) were purchased from Alfa Aesar chemical company. Gllium pellets (Ga 99.9999%), selenium (Se, 99.9%), cadmium sulfate ($CdSO_4$ $8/3H_2O$, 99%), and thiourea (NH_2CSNH_2, 99%) were purchased from Aladdin company. Hdrobromic acid (HBr, 40%, Aladdin) were purchased from Sinopharm Chemical Reagent Co,. Ltd. Ammonium hydroxide (NH_4OH, 25%) was obtained from Xilong Scientific Company.

Preparation of four precursor solutions with different Ga ratios

We prepared four different Ga ratios precursor solutions [Ga/(In+Ga) = 10%, 30%, 35%, and 50%] to investigate the influence of different Ga gradients on the performance of solar cells. First, 0.5 mmol of Cu_2S, 2.20 mmol of Se, x mmol of Ga, and (1.09 − x)/2 mmol of In_2Se_3 were added to four 25ml round-bottom flasks. (The detailed amounts of Ga and In_2Se_3 are listed in Table S4.) Then, 3.7 mL of 1, 2 - ethylenediamine and 0.37 mL of 1, 2 - ethanedithiol were mixed into each of the four round-bottom flasks. Then, the four solutions were magnetically stirred at 70 ℃ for 24 h until all of the solids were dissolved. The ratio of the starting materials follows the target of Cu-poor stoichiometry [Cu/(In+Ga) = 0.92 and Ga/(In+Ga) = 0.10, 0.30, 0.35, and 0.50]. Digital photographs of the four CIGSe precursor solutions are shown in Fig. S1. All of the solution preparation processes were performed in an argon-filled glovebox (H_2O and O_2 levels maintained below 1 ppm).

Deposition and selenization of the CIGSe films with different Ga gradients

First, ~ 650 nm thick molybdenum (Mo) back contacts were deposited on a 20 × 20 × 1.0 mm^3 soda lime glass *via* DC sputtering (square resistance: 0.3- 0.6 Ω/□). Then, the prepared CIGSe precursor solutions that had different Ga ratios (Table S4) were spin coated onto Mo-coated soda lime glasses (SLG) at 3000 rpm for 30 s, followed by sintering on a 350 ℃ hot plate for 2 min. The spin-coating/sintering operations described above were repeated according to the schematic description in Fig. 1 and until the precursor film had a targeted thickness (~ 1.74 μm). For each spin-coating/sintering cycle the homogeneous absorber layer was prepared using the same precursor solutions, and the Ga-graded CIGSe absorber layer was prepared using different precursor solution. For example, a typical CIGSe absorber layer for sample C can be deposited by repeating 2 cycles of $Cu(In_{0.50}Ga_{0.50})Se_2$ (~ 294 nm) solution deposition, 4 cycles of $Cu(In_{0.65}Ga_{0.35})Se_2$ (~580 nm), 4 cycles of $Cu(In_{0.90}Ga_{0.10})Se_2$ (~ 483 nm), and finally 2 cycles of $Cu(In_{0.65}Ga_{0.35})Se_2$ (~390 nm). The above preparation procedures were performed in an argon-filled glovebox. Finally, the as-prepared CIGSe thin films that had different Ga gradients were selenized in a round graphite box containing 400 mg of selenium (Se, 99.9%) at 550 ℃ for 15 min in a rapid thermal processing (RTP) furnace (MTI, OTF-1200X-4-RTP, ramp to 550 ℃ at 8.7 ℃ s^{-1}) with a nitrogen flow of 80 mL min^{-1}.

Fabrication of CIGSe Thin Film Solar Cells with different Ga gradients

To fabricate photovoltaic devices, CIGSe thin film solar cells with different Ga gradients were fabricated according to the following well-known device structure: Ag/ITO/i-ZnO/CdS/CIGSe/Mo/glass. First, a ~ 70 nm thick cadmium sulfide (CdS) layer was deposited by a chemical bath approach. 12.0 mL of Ammonium hydroxide, 50 mL of cadmium sulfate (0.006 M), and 50 mL of thiourea (0.03 M), and 150 mL of deionized H_2O were mixed in a 65 °C water bath for 13 min.[1, 2, 3] Next, about 50 nm thick i-ZnO (100 W, 0.4 Pa Ar, 5 min) and 200 nm thick ITO layers (90 W, 0.5 Pa Ar, 5 min) were deposited on CdS/CIGSe/Mo/glass layer using magnetron sputtering. Then, 80 nm thick Ag top electrodes were made on the top of the devices using thermal evaporation (thermal evaporation current of 12 A, evaporation time of 2 min). Finally, all CIGSe devices with different Ga gradients owning an active area of 0.21 cm^2 (~ 91% of the total device area, 0.23 cm^2) were separated by mechanical scribing. The digital photographs of the final devices that had different Ga gradients were shown in Fig. S1. No antireflection layer was used in our devices.

Characterizations

The X-ray diffraction (XRD) patterns were taken with a Bruker D8Advance X-ray diffractometer. The scanning electron microscope (SEM) images were collected using a Nova Nano SEM 450 field emission scanning electron microscope (FESEM). Photocurrent density-voltage curves were recorded under the standard AM1.5 illumination (100 mW cm^{-2}) with a Keithley 2400 source meter. The external quantum efficiency (EQE) spectrum was measured using a Zolix SCS100 QE system equipped with a 150-W xenon light source and a lock-in amplifier. The overall composition of each type of ion is measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using Optima 2100DV with spectral region of 165~782nm. The C-V characterizations curves were measured by Deep Level Transient Spectroscopy (HERA-DLTS) system produced by Phys Tech. The depth composition measurements is obtained by Secondary ion mass spectrometry (SIMS) using CAMECA, IMS 7f-Auto and was proved by an energy dispersive X-ray (EDX-line scan) analyzed by Nova Nano SEM 45050/EDAX.

Supporting figures and tables

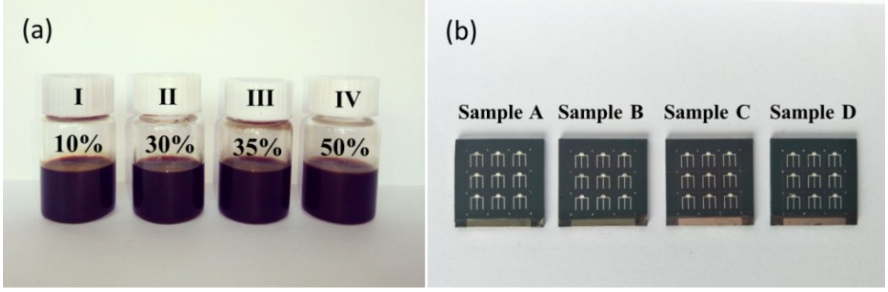

Figure S1. (a) Digital photographs of the four Cu(In,Ga)Se_2 precusor solutions with different Ga ratios. (b) Cu(In,Ga)Se_2 solar cells with different Ga gradients.

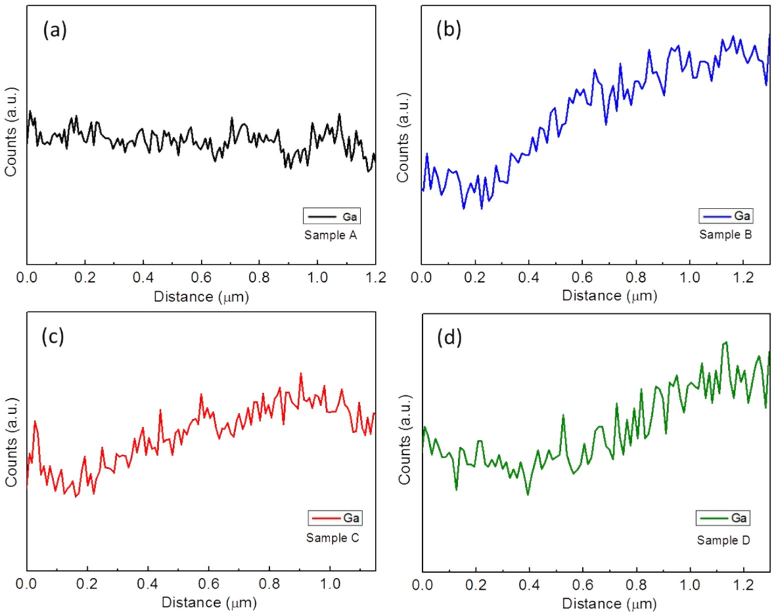

Figure S2. EDS elemental Ga line scan of the Cu(In,Ga)Se_2 selenized films that had different Ga gradients.

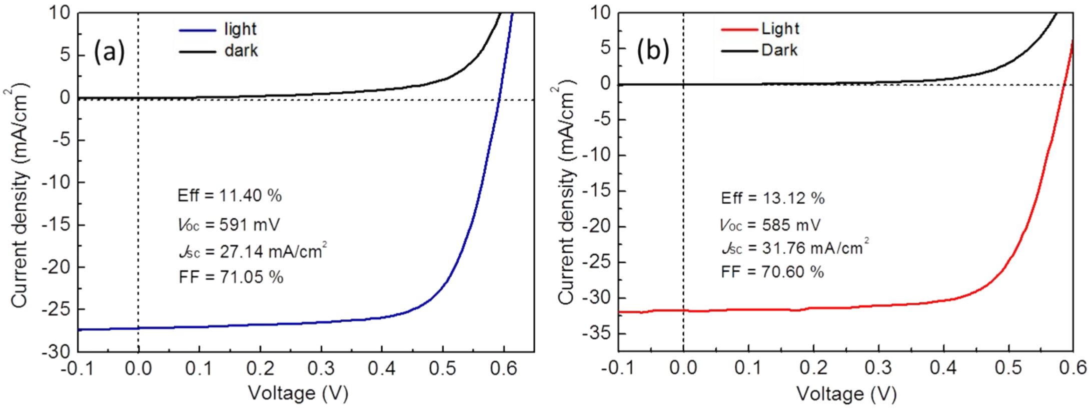

Figure S3. *J*−*V* curves of (a) the best homogeneous Cu(In,Ga)Se$_2$ solar cell and (b) the best graded Cu(In,Ga)Se$_2$ solar cell under AM 1.5G illumination.

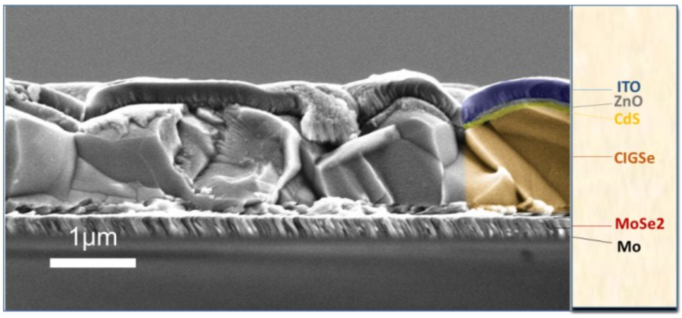

Figure S4. Cross-sectional SEM image of the champion Cu(In,Ga)Se$_2$ solar cell.

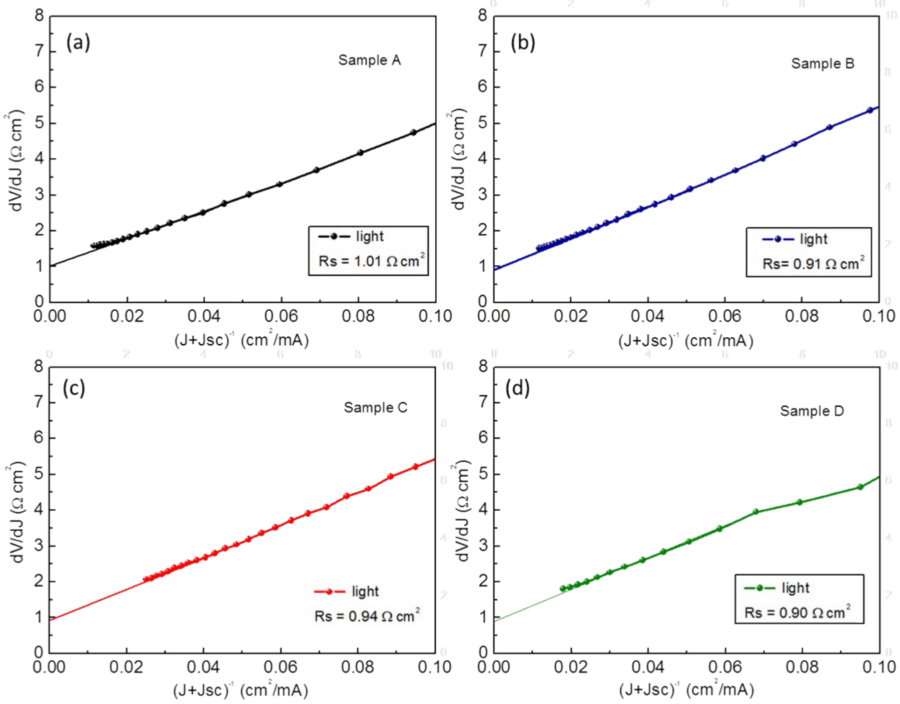

Figure S5. Plots of *dV*/*dJ* vs (J+J_{sc})$^{-1}$ redrawn from the standard light *J-V* curves of the Cu(In,Ga)Se$_2$ solar cells that had different Ga gradients.

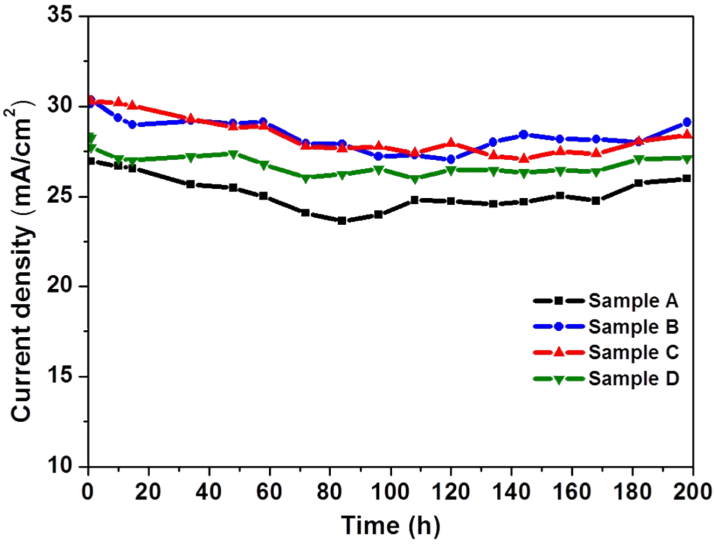

Figure S6. Stability of the current-density curves for Cu(In,Ga)Se_2 solar cells stored in air for 200 hours.

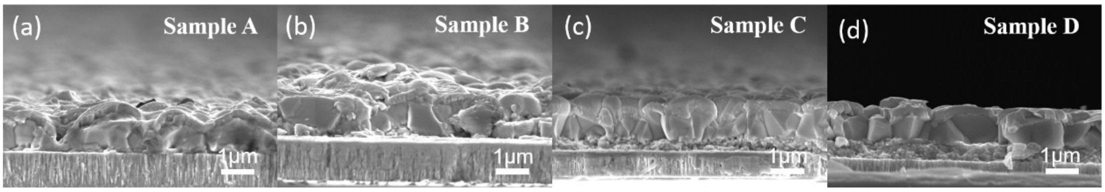

Figure S7. SEM images of the Cu(In,Ga)Se_2 solar cells with different Ga gradients after I-T test.

Table S1. Thickness of Stages 1-4 in Fabricating Cu(In,Ga)Se_2 Absorber Layers that had Different Ga Gradients.

Sample	Stage- 1 (nm)	Stage- 2 (nm)	Stage- 3 (nm)	Stage- 4 (nm)	Total (nm)
A	1730	---	---	---	1730
B	310	783	480	185	1758
C	294	580	483	390	1747
D	312	376	492	570	1750

Table S2. Summary of ICP-AES Results for the Cu(In,Ga)Se_2 Solar Cells that had Different Ga Gradients.

ICP-AES	Cu/(Ga+In)	Ga/(Ga+In)	Cu (%)	In (%)	Ga (%)	Se (%)
Sample 1	0.90	0.29	20.4	16.1	6.6	56.8
Sample 2	0.89	0.29	22.1	17.6	7.3	54.0
Sample 3	0.91	0.26	21.8	17.7	6.3	54.1
Sample 4	0.90	0.28	22.4	18.1	6.9	52.5

Table S3. Values of charge density and depletion region width of the $Cu(In,Ga)Se_2$ devices that had different Ga gradients.

Sample	**Charge Density (cm^{-3})**	**Depletion region width (μm)**
A	3.42×10^{16}	0.264
B	5.53×10^{15}	0.544
C	2.12×10^{16}	0.358
D	4.88×10^{16}	0.280

Table S4. Summary of the detailed amounts of starting materials dissolved in four precursor solutions that had different Ga ratios.

No.	**[Ga]/([In]+[Ga])**	**Ga (x mmol)**	**In_2Se_3 ((1.09-x)/2 mmol)**	**Cu_2S (mmol)**	**Se (mmol)**
I	10%	**0.11**	**0.49**	0.50	2.20
II	30%	**0.33**	**0.38**	0.50	2.20
III	35%	**0.38**	**0.36**	0.50	2.20
IV	50%	**0.56**	**0.27**	0.50	2.20

References

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2 Q. Tian, G. Wang, W. Zhao, Y. Chen, Y. Yang, L. Huang and D. Pan, *Chem. Mater.*, 2014, **26**, 3098-3103.

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