## **Supplementary Information**

## Reforming material chemistry of CIGS solar cells via a precise Ag doping strategy

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Fig. S1 XRD ( $\theta$ -2 $\theta$  scan) patterns of CIGS and ACIGS films. The Ag incorporation was found to weaken (220)/(204) preferred orientation. The ACIGS films showed (112) preferred orientation similar to the powder pattern of chalcopyrite.



**Fig. S2** (112) XRD ( $\theta$ -2 $\theta$  scan) patterns of CIGS films. The CIGS film (i.e., control) shows broad (112) reflections that originate from relatively inhomogeneous Ga/(Ga+In) compositional depth profiles and the ACIGS film (Ag incorporation in the second stage) appeared to exhibit a slightly higher Ga/(Ga+In) ratio than the others, which is verified by the SIMS analyses.



**Fig. S3** Further APT results of CIGS without and with Ag incorporation: 3D atom maps of (a) CIGS and (b) ACIGS specimens; 1D concentration profiles of matrix elements: (c) without and (d) with Ag incorporation; and 1D concentration profiles of alkali (Na and K) elements: (e) without and (f) with Ag incorporation.



Fig. S4 Box plot of the extracted  $\triangle CPD_{GB}$  values ( $\triangle CPD_{GB}$ =  $CPD_{GB}$ - $CPD_{IG}$ ). The CIGS sample with Ag incorporation in the first stage showed the highest average of  $\triangle CPD_{GB}$  and that of the CIGS sample without Ag was the lowest. The CIGS sample with Ag incorporation in the second stage showed a relatively wide range of  $\triangle CPD_{GB}$  values indicating inhomogeneous CPD value distribution.



**Fig. S5** Illuminated JV (a) and external quantum efficiency (EQE) (b) curves of the best CIGS solar cells in each case.

	Eff (%)	FF (%)	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA/cm^2})$
(a) wo Ag	16.7	75.1	0.686	32.5
(b) Ag – 1st	17.6	79.2	0.712	31.2
(c) Ag – 2nd	17.0	73.8	0.705	32.7

Table S1. Illuminated JV characteristics of CIGS solar cells of Fig. S5.



**Fig. S6** Drive-level capacitance profiling (DLCP) curves of CIGS solar cells: (a) control, (b) Ag incorporation in the first stage, and (c) Ag incorporation in the second stage.

	Temperature	<x> nm</x>	$N_{DLCP} (10^{15}/cm^3)$
Without Ag (control)	80 K	714.40	1.82
	100 K	690.40	1.49
	200 K	431.01	1.79
	300 K	301.12	2.87
Ag - first stage —	80 K	651.06	1.17
	100 K	619.27	1.13
	200 K	394.02	1.98
	300 K	369.66	1.85
Ag - second stage	80 K	758.85	1.11
	100 K	715.24	1.02
	200 K	483.38	1.56
	300 K	334.22	1.49

**Table S2**. Moment of charge response ( $\langle x \rangle$ ) and drive-level density (N<sub>DLCP</sub>) values derived from Fig. S6.