## Supporting Information

## Efficiency Enhancement and Doping Type Inversion in Cu<sub>2</sub>CdSnS<sub>4</sub> Solar Cells by Ag Substitution

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## **Experimental Section**

*Substrate Cleaning*: Commercial Mo-coated soda-lime glass (SLG) substrates were washed using water and soap, then subsequently subjected to ultrasonic bath cleaning of soapy water, ethanol, and deionized water, each for 5 minutes.

Absorber Preparation: Cu<sub>2</sub>CdSnS<sub>4</sub> sol-gel solution was prepared by dissolving 0.52 mol L<sup>-1</sup> copper(II) acetate dihydrate Cu(CH<sub>3</sub>COO)<sub>2</sub>· 2H<sub>2</sub>O (ACS reagent,  $\geq$ 98%), 0.33 mol L<sup>-1</sup> cadmium acetate dihydrate Cd(CH<sub>3</sub>COO)<sub>2</sub>· 2H<sub>2</sub>O (reagent grade, 98%), 0.27 mol L<sup>-1</sup> tin(II) chloride dihydrate SnCl<sub>2</sub>· 2H<sub>2</sub>O (ACS reagent, 98%) and 2.06 mol L<sup>-1</sup> thiourea SC(NH<sub>2</sub>)<sub>2</sub> (ReagentPlus<sup>®</sup>,  $\geq$ 99.0%) in 2-methoxyethanol (anhydrous, 99.8%) and stirred for 2 hours at 50°C. Silver nitrate AgNO<sub>3</sub> (ACS reagent,  $\geq$ 99.0%) was also added for Ag incorporation, and the concentration was adjusted to the desired concentration relative to copper content (e.g., Ag/(Ag+Cu)) = 0.05 for 5% Ag). Ethanolamine (ACS reagent,  $\geq$ 99.0%) and triethylamine ( $\geq$ 99%) were also added as stabilizers. The (Cu+Ag)/(Cd/Sn) ratio was maintained at around 0.86, and Cd/Sn was about 1.25. All chemical reagents were purchased from Sigma-Aldrich without further purification.

*Device Fabrication*: The Cu<sub>2</sub>CdSnS<sub>4</sub> solution was spin-coated onto the Mo-SLG substrate for 20 s at 4000 rpm and subsequently annealed in air for 2 minutes at 280°C. These subsequent steps were repeated 12 times. The deposited thin films were then annealed in argon and sulfur atmosphere for 40 minutes at 580°C in a two-zone furnace and were naturally cooled at room temperature. The cadmium sulfide buffer layer was deposited by chemical-bath deposition (CBD). The bath was prepared by mixing 20 mL cadmium sulfate (0.015M, ACS reagent,  $\geq$ 99.0%, Sigma-Aldrich), 20 mL 28-30% ammonium hydroxide solution (Thermo Scientific), 20 mL thiourea (0.75M, ReagentPlus<sup>®</sup>,  $\geq$ 99.0%, Sigma-Aldrich) in 140 mL deionized water. The bath was continuously stirred throughout the CBD process for 8 minutes at 80°C. Finally, the indium-tin oxide layer was deposited by DC magnetron sputtering. The samples were delineated to form approximately 0.15 cm<sup>2</sup> device (active area) by mechanical scribing. Silver electrodes were then pasted to complete the device.

*Characterization*: X-ray diffraction patterns were acquired using Shimadzu XRD-6000. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) data were obtained using JEOL JSM-7600F field emission SEM (FESEM). Photoluminescence (PL) spectra were acquired using a Horiba/Jobin-Yvon LabRAM HR800 confocal microscope setup equipped with an InGaAs detector through a 10x objective lens using a He:Ne laser (632.8 nm excitation wavelength). Raman measurement was conducted using Renishaw's inVia Qontor, equipped with 2400 lines/mm visible grating and Leica DM2700 M microscope with 50x objective. The devices' current density-voltage (J-V) was measured by Keithley 2612A and VS-0852 light source to simulate AM1.5 and 100 mW cm<sup>-2</sup>, calibrated by a certified Si reference cell. External quantum efficiency (EQE) measurement was obtained using a Bentham PVE300 system, and certified standard Si and Ge cell references were used for calibration. The voltage-biased EQE data was taken using an in-house built instrument with a preamplifier and lock-in amplifier for signal processing with a chopper frequency of 160 Hz. Capacitance-voltage (C-V) data were obtained using Autolab PGSTAT302N. Hall measurements were conducted using a parallel dipole line system on exfoliated absorber films.<sup>1–3</sup>





Figure S1 Refinement plot for  $(Cu_{1-x}Ag_x)_2CdSnS_4$  samples with x = a) 5%, b) 10%, c) 20%, d) 40%, e) 60%, and f) 80%.



Figure S2 Line-scan EDS for  $(Cu_{1-x}Ag_x)_2CdSnS_4$  where a) x = 5% and b) x = 30%



Figure S3 Tauc plot of  $(ahv)^2$  as a function of hv for  $(Cu_{1-x}Ag_x)_2CdSnS_4$  films. Extracted bandgaps are included in the legend



Figure S4 Photoluminescence spectra of Cu2CdSnS4 films with various Ag concentrations

Film	Ag/(Cu+Ag)	(Cu+Ag)/(Cd+Sn)	Cd/Sn
$Cu_2CdSnS_4$	N/A	0.87	1.18
5% Ag	0.03	0.88	1.20
10% Ag	0.08	0.87	1.17
20% Ag	0.18	0.87	1.18
30% Ag	0.35	0.88	1.16
40% Ag	0.44	0.89	1.19
60% Ag	0.56	0.86	1.15
80% Ag	0.72	0.86	1.10
Ag <sub>2</sub> CdSnS <sub>4</sub>	N/A	0.85	1.34

Table S1. Summary of elemental ratio obtained from EDS for various Ag concentrations



Figure S5 Apparent carrier concentration extracted from C-V measurement for Cu<sub>2</sub>CdSnS<sub>4</sub> and 5% Ag device

**Table S2.** Apparent carrier concentration extracted from C-V device measurement ( $N_{C-V}$ ) and Hall film measurement ( $P_{Hall}$ )for Cu<sub>2</sub>CdSnS<sub>4</sub> and 5% Ag

<b>F</b> !1	N <sub>C-V</sub>	P <sub>Hall</sub>	
Film	[cm- <sup>3</sup> ]	[cm- <sup>3</sup> ]	
$Cu_2CdSnS_4$	$2.0  imes 10^{17}$	$2.9  imes 10^{16}$	
5% Ag	$1.8  imes 10^{17}$	$3.0  imes 10^{16}$	

Table S3. Device parameters of the best (Cu<sub>1-x</sub>Ag<sub>x</sub>)<sub>2</sub>CdSnS<sub>4</sub> devices for various Ag concentrations up to 60%

Device	Voc	$J_{SC}$	FF	η	$E_g$	Voc,sq-Voc
	[mV]	$[mA cm^{-2}]$	[%]	[%]	[eV]	[mV]
$Cu_2CdSnS_4$	549	21.89	57.16	6.87	1.39	560
5% Ag	550	24.23	57.89	7.72	1.41	577
10% Ag	566	22.69	58.09	7.46	1.41	559
20% Ag	477	20.50	49.22	4.82	1.41	650
30% Ag	441	14.30	32.98	2.08	1.45	723
40% Ag	280	9.29	33.88	0.88	1.51	941
60% Ag	161	8.87	25.30	0.36	1.63	1172



Figure S6 Extracted derivative from the EQE spectrum onset of CCTS, 5% Ag-CCTS, and CZTS (in-house) solar cell devices. The 13.8% CZTSSe EQE was extracted from the available source data in the literature.<sup>4</sup>

## References

- 1 US Patents, US9041389B2, 2014, 0028306.
- 2 US Patents, US9772385B2, 2017.
- 3 O. Gunawan, Y. Virgus and K. F. Tai, A parallel dipole line system, *Appl. Phys. Lett.*, 2015, **106**, 062407
- J. Zhou, X. Xu, H. Wu, J. Wang, L. Lou, K. Yin, Y. Gong, J. Shi, Y. Luo, D. Li, H. Xin and Q. Meng, Control of the phase evolution of kesterite by tuning of the selenium partial pressure for solar cells with 13.8% certified efficiency, *Nat. Energy*, 2023, 8, 526–535.