Bypassing Sulfides: Comparing the Morphology and Performance of Solution Processed Cu(In,Ga)Se_2 Films

Prepared via Two Selenide Molecular Precursor Routes

Supporting Information

Robert Spilker Daniel Hayes Shubhanshu Agarwal Kim Kisslinger

Rakesh Agrawal

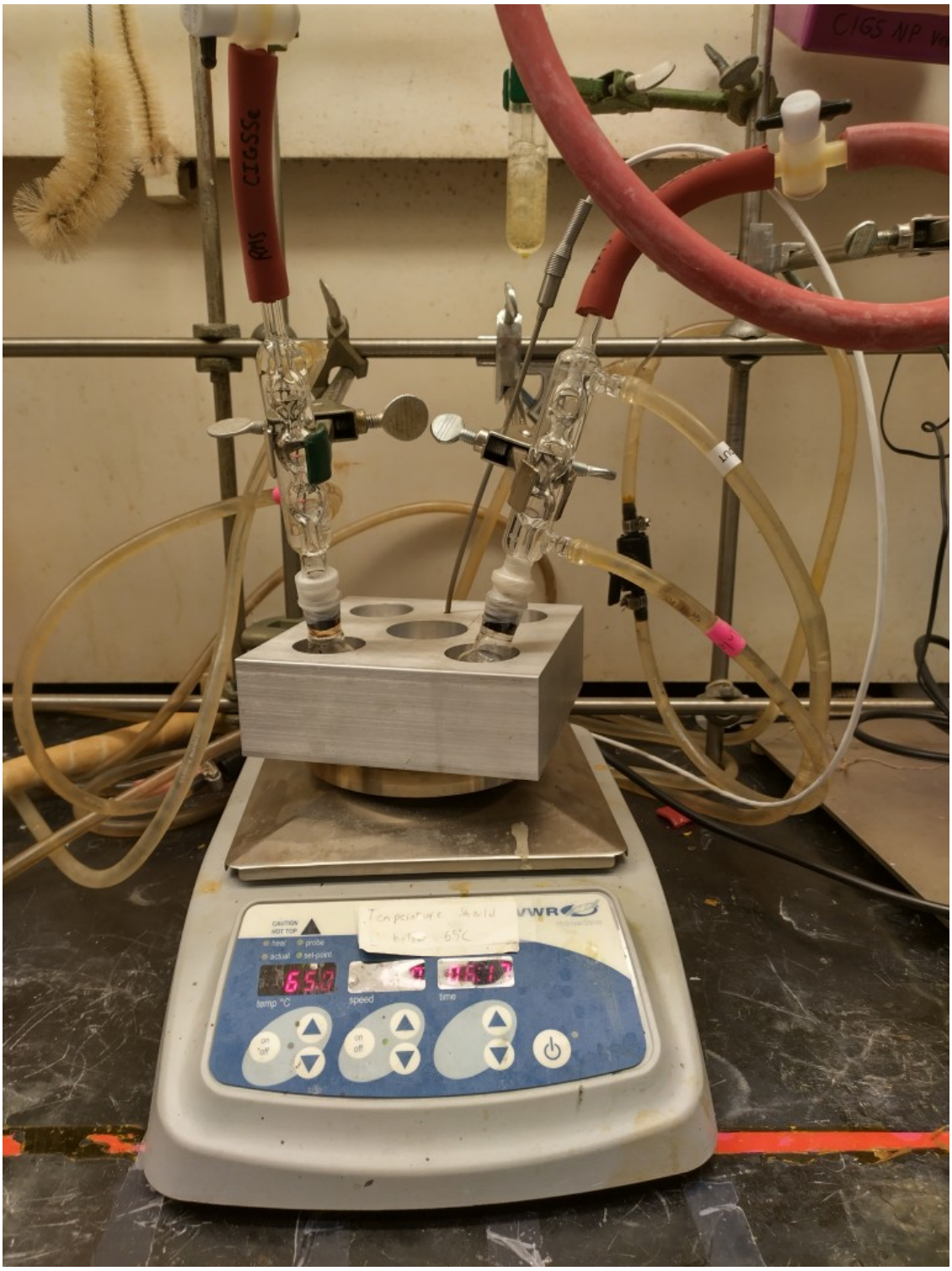

Figure S1: The dissolution setup for Cu_2Se (left) and In (right) in BAPSe. 15 mL round-bottom flasks were situated in a machined aluminum heating block, with the temperature monitored by a plug-in thermocouple probe. In-line cold-water condensers were connected.

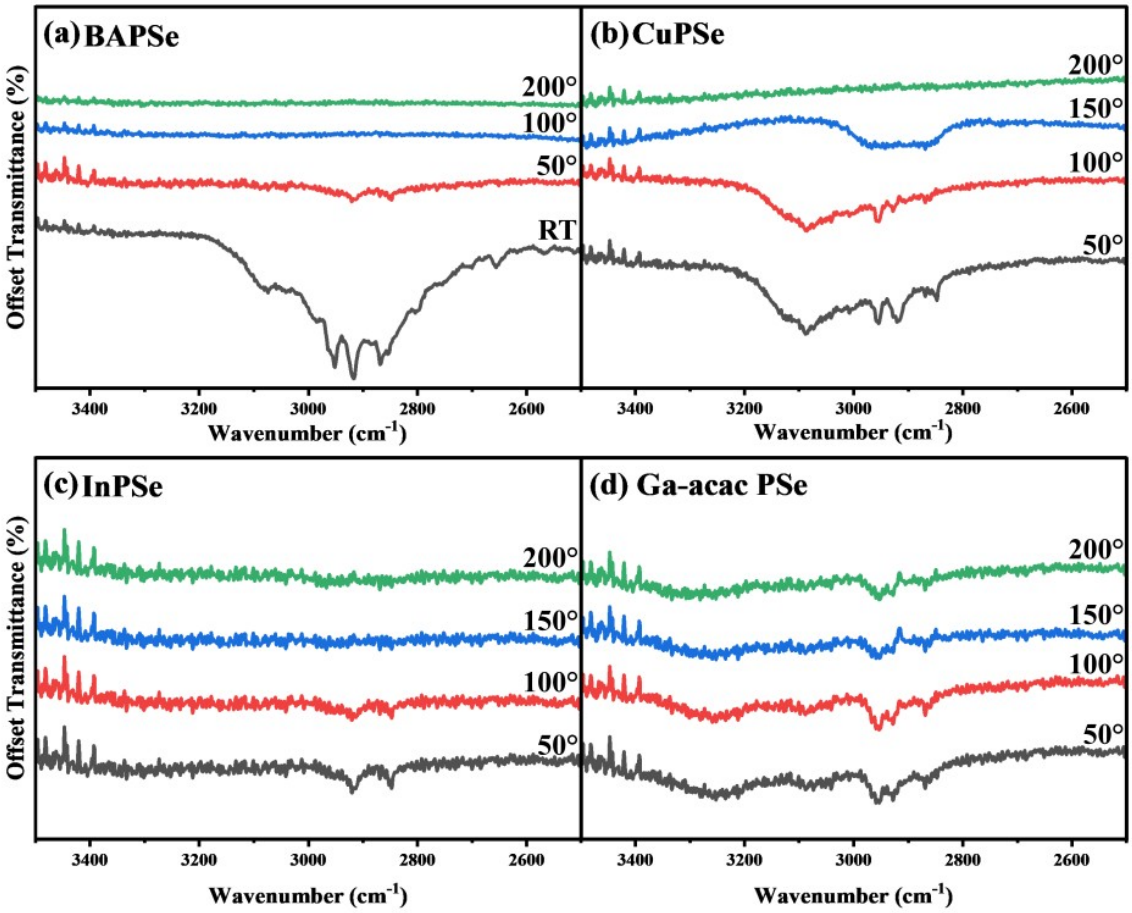

Figure S2: FTIR transmission spectra of coated films of (a) BAPSe and BAPSe facilitated dssolutions of (b) copper(II) selenide, (c) indium metal, and (d) gallium acetylacetonate, dried or annealed at temps from room temperature to 200°C.

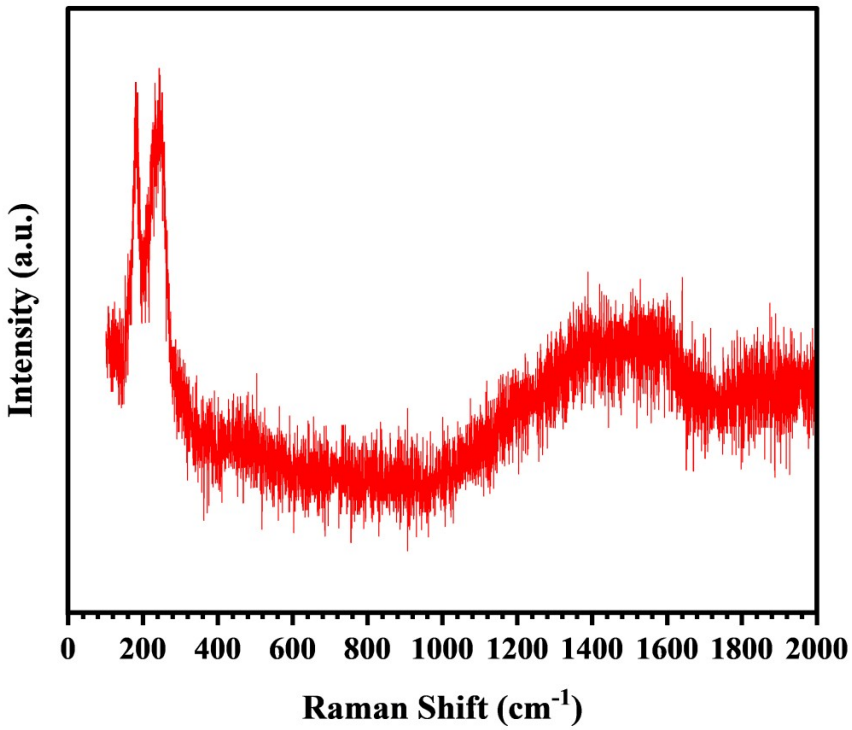

Figure S3: Raman spectra of a CIGSe film coated using a precursor ink of copper(II) selenide, indium metal, and gallium acetylacetonate dissolved separately in BAPSe, combined and coated with an annealing temperature of 350°C. Residual carbon stretching can be observed from 1200-1600 cm^{-1}.

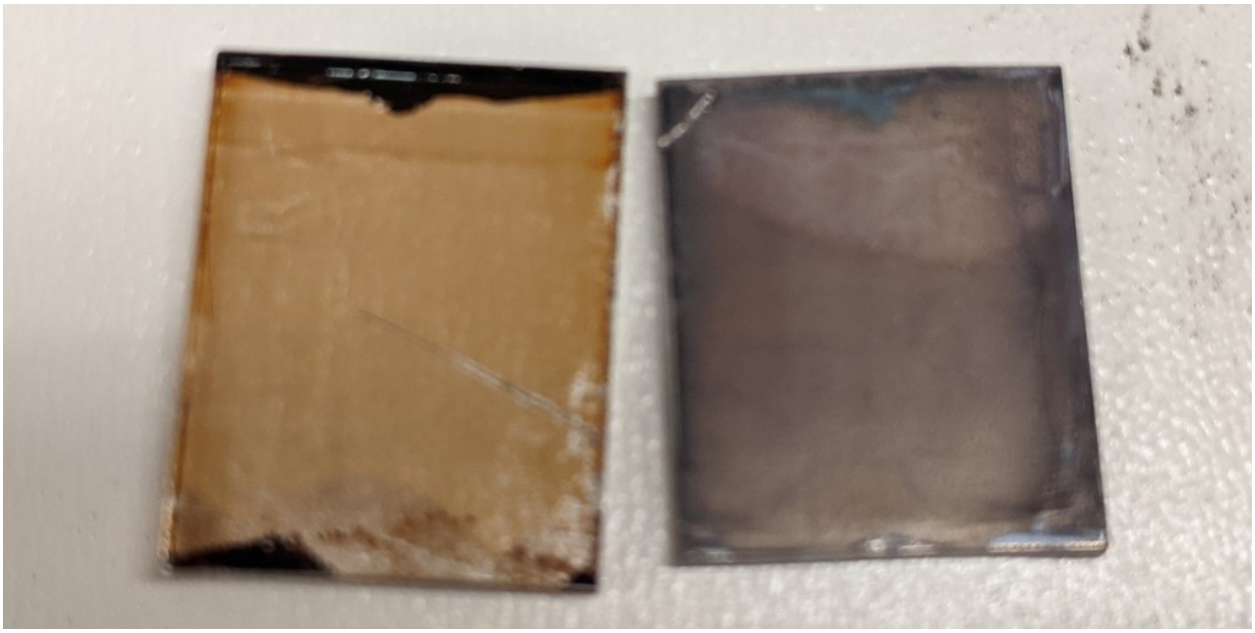

Figure S4: Cu-PSe thin films on coated SLG before (left) and after (right) a 200°C anneal.

Solvent	Conc. Factor	Layers	Thickness (μm)	Se/metal	S (at. %)
BA	x2	8	0.225	1.04	5.16
BA	x4	8	0.872	1.16	2.31
HA	x2	8	0.243	1.05	5.89
HA	x4	8	0.641	1.13	3.35
BA	x2	14	0.459	1.15	3.97
BA	x4	18	2.404	1.27	2.27
HA	x2	15	0.617	1.09	2.70
HA	x4	18	1.591	1.19	1.97

Table S1: Summary of the impact of solvent choice and concentration on film thickness, Se/metal ratio, and residual sulfur content as reported by XRF for as-coated CIG-PSe films.

Figure S5: Images of the film surfaces follwoing the coating of 14-18 layers using inks with BA or HA as the solvent at x2-x4 concentration.

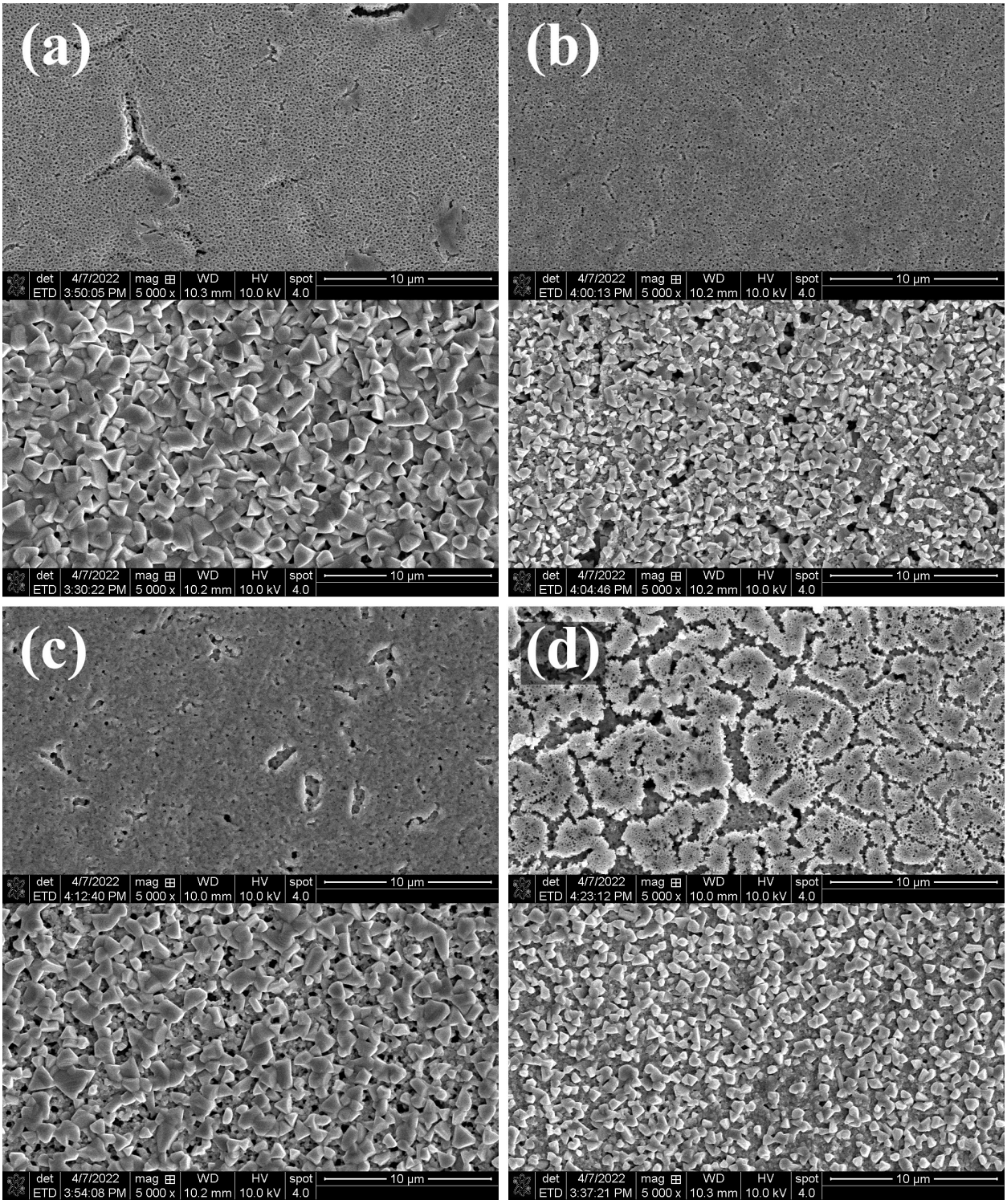

Figure S6: SEM micrographs at x5k magnification of the surfaces of as-coated (top) and selenized (bottom) films from inks using (a) BA at x2 concentration, (b) BA at x4 concentration, (c) HA at x2 concentration, and (d) HA at x4 concentration.

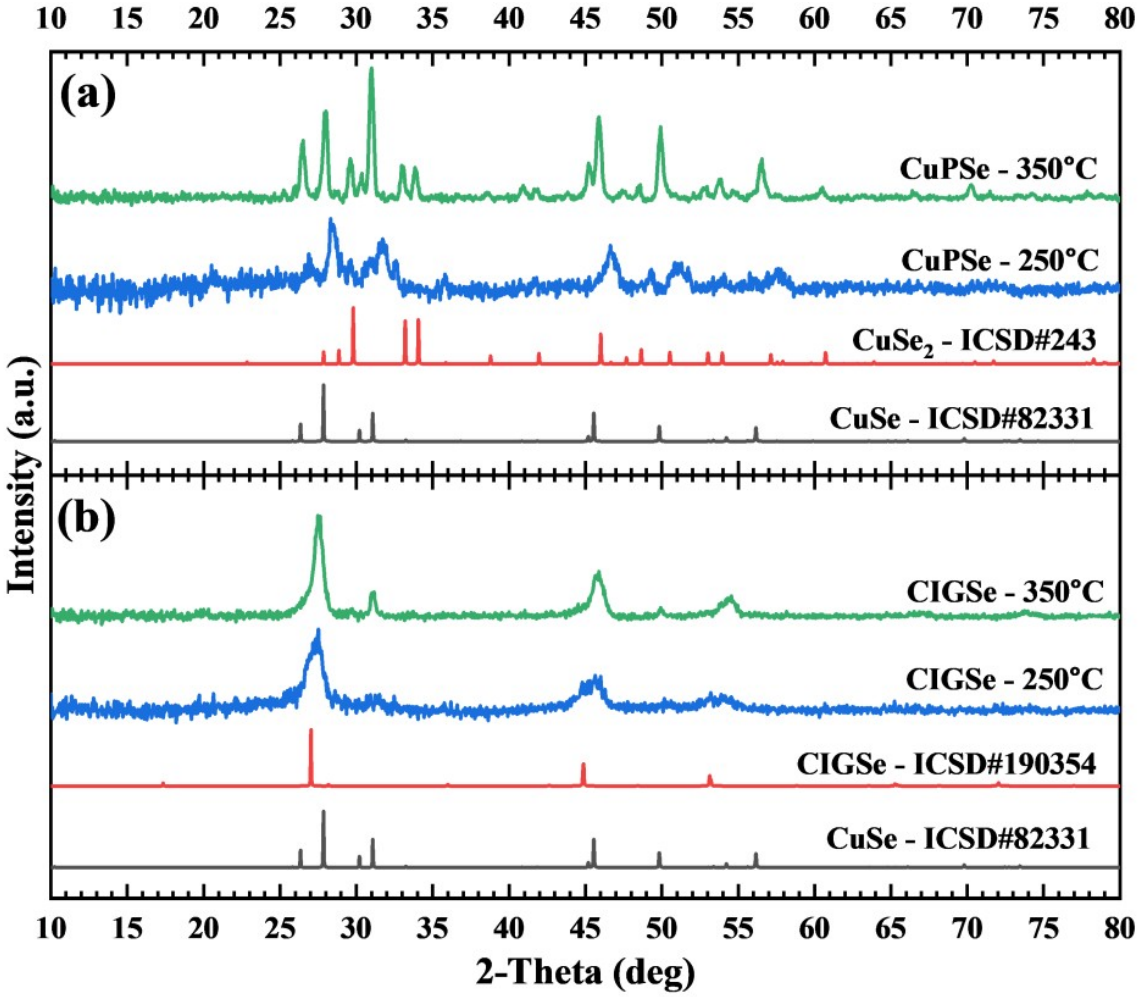

Figure S7: XRD spectra of dropcasts of (a) copper metal dissolved in BAPSe and (b) a CIG-PSe ink (CGI = 0.95) made by mixing Cu-PSe, In-PSe, and a dissolved Ga and Se solution. Dropcasts were allowed to dry and then annealed at 250 and 350°C. Reference spectra were generated from ICSD#243 ($CuSe_2$), ICSD#82331 (CuSe), and ICSD#190354 ($Cu_{0.82}In_{0.61}Ga_{0.39}Se_2$).

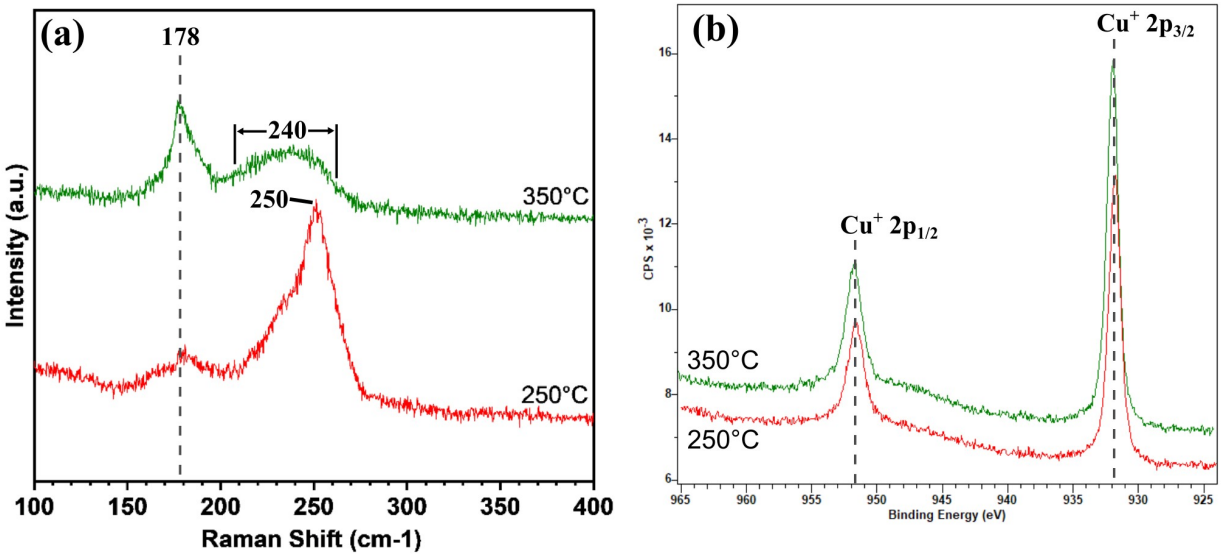

Figure S8: (a) Raman and (b) XPS spectra of films from CIG-PSe inks (CGI = 0.95) annealed at 250 and 350°C for 10 minutes. The CIGSe A_1 peak is seen at 178 cm^{-1}, and the broad peak stretching over 240 cm^{-1} is ascribed to the B_2/E modes of CIGSe.

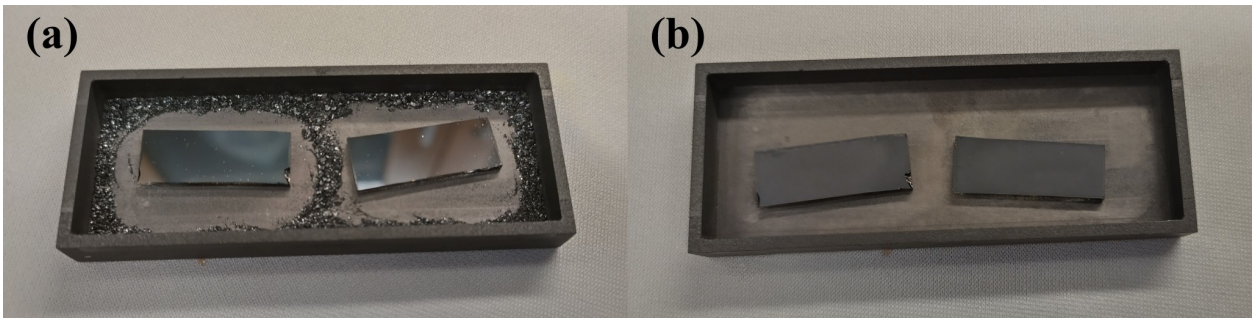

Figure S9: Images of CIG-PSe films (a) prior to selenization, demonstrating their arrangement and surrounding crushed selenium and (b) after selenization but immediately before CdS deposition.

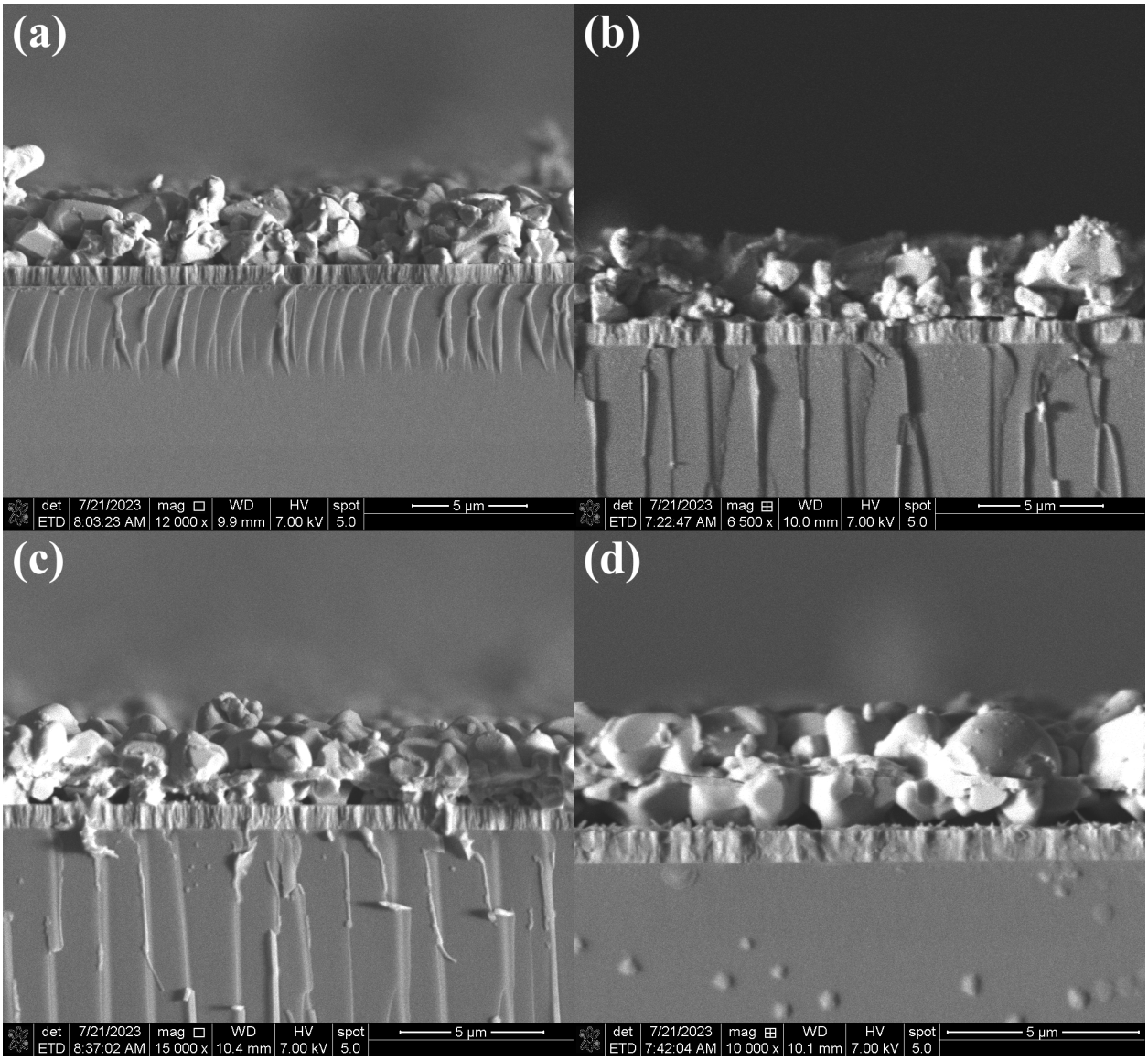

Figure S10: SEM micrographs showing cleaved cross sections of the final (a) CISSe, (b) CIGSSe, (c) CI-PSe, and (d) CIG-PSe devices.

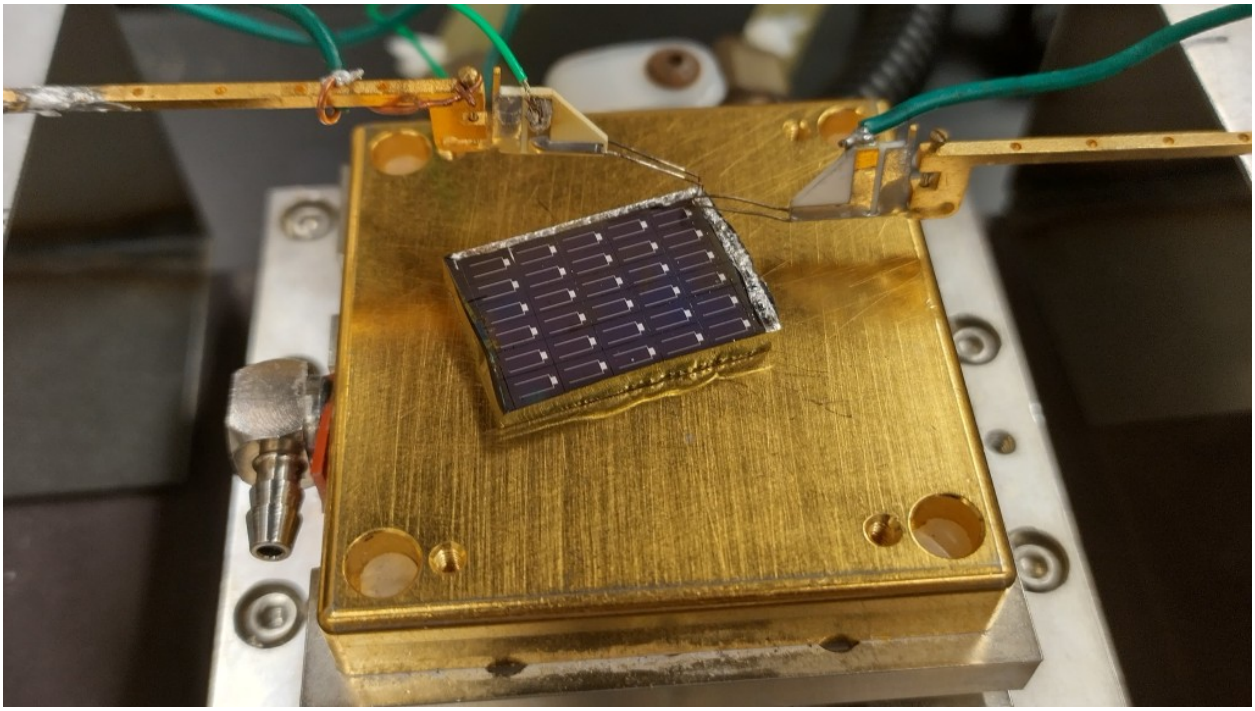

Figure S11: An example device and measurement set-up. After deposition, the device is mechanically scribed to separate grids into individual cells with an active area of $\sim$0.09 cm^2. Each cell's active area is measured individually.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	3.84	0.30	31.8	40.2	B1	1.38	0.14	33.3	29.6
A2	2.15	0.27	25.5	31.2	B2	1.42	0.14	34.1	29.9
A3	1.84	0.25	24.4	30.2	B3	1.74	0.17	32.9	31.0
A4	2.61	0.24	30.9	35.1	B4	1.33	0.12	35.8	31.0
A5	4.01	0.30	33.0	40.4	B5	1.97	0.16	38.5	32.0
A6	4.86	0.34	32.4	44.1	B6	1.25	0.12	33.0	31.5
A7	5.09	0.36	30.5	46.4	B7	1.69	0.15	35.0	32.1
A8	3.81	0.29	32.9	40.0	B8	0.84	0.10	30.4	27.4
A9	3.76	0.30	31.9	39.3	B9	0.72	0.09	29.4	27.2
A10	3.86	0.31	31.7	39.3	B10	0.62	0.08	26.8	29.0
A11	3.39	0.30	29.0	39.0	B11	0.88	0.10	28.9	30.4
A12	3.11	0.30	28.4	36.5	B12	0.50	0.07	25.8	27.8
A13	2.56	0.26	29.3	33.5	B13	0.49	0.07	27.3	25.3
A14	2.60	0.26	28.9	34.6	B14	0.42	0.06	25.1	27.8
A15	0.74	0.13	22.3	25.5	B15	0.61	0.08	26.6	28.8
A16	0.97	0.16	22.0	27.6	B16	0.36	0.06	23.1	26.2
A17	1.29	0.17	26.1	29.1					

Table S2: Current-voltage measurement results for $CuInSe_2$ solar cells from sulfoselenide inks.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	5.62	0.33	37.6	45.3	A18	4.15	0.3	33.8	27.4
A2	5.94	0.34	39.5	44.2	A19	4.28	0.3	33.6	42.4
A3	5.78	0.35	35.2	47.0	A20	5.23	0.34	33.0	46.6
A4	5.85	0.36	33.4	48.6	B1	2.67	0.23	33.5	34.7
A5	5.77	0.33	38.9	45.0	B2	2.08	0.19	35.8	30.6
A6	5.74	0.33	39.5	44.0	B3	1.39	0.15	31.2	29.8
A7	5.61	0.33	37.6	45.2	B4	1.26	0.15	27.9	30.1
A8	5.23	0.34	33.2	46.3	B5	2.11	0.21	31.9	31.4
A9	4.04	0.27	37.5	39.9	B6	0.61	0.09	27.6	24.9
A10	4.49	0.29	37.8	41.0	B7	0.45	0.07	24.2	26.0
A11	4.09	0.28	35.5	41.1	B8	0.36	0.06	22.5	26.5
A12	3.66	0.28	31.9	41.0	B9	1.21	0.15	28.3	28.4
A13	4.12	0.28	35.6	41.3	B10	0.20	0.04	19.8	26.0
A14	4.06	0.28	35.9	40.4	B11	0.17	0.04	18.0	22.9
A15	3.77	0.28	34.2	39.3	B12	0.20	0.04	20.0	26.1
A16	4.39	0.32	32.4	36.4	B13	0.13	0.03	15.9	28.5
A17	5.14	0.31	35.6	29.7	B14	0.31	0.06	20.2	25.0

Table S3: Current-voltage measurement results for $CuInSe_2$ solar cells from sulfoselenide inks with NaF deposited prior to selenization.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	8.11	0.50	29.6	54.9	B1	7.93	0.50	31.4	50.4
A2	7.13	0.50	29.1	49.0	B2	7.51	0.50	30.9	48.6
A3	6.83	0.49	27.6	50.5	B3	7.27	0.49	29.1	50.9
A4	6.41	0.49	26.8	48.8	B4	7.94	0.48	29.2	56.7
A5	7.21	0.50	28.2	51.1	B5	8.49	0.51	31.7	52.5
A6	5.67	0.49	26.2	44.0	B6	7.60	0.50	29.5	51.5
A7	6.88	0.49	28.2	49.7	B7	6.79	0.48	29.9	47.2
A8	8.65	0.50	29.1	59.3	B8	7.71	0.50	29.4	52.5
A9	7.11	0.49	28.7	50.6	B9	5.78	0.50	26.0	44.4
A10	7.84	0.49	28.6	56.0	B10	6.55	0.50	26.8	49.0
A11	7.41	0.49	26.9	56.4	B11	7.75	0.49	28.5	55.6

Table S4: Current-voltage measurement results for $Cu(In,Ga)Se_2$ solar cells from sulfoselenide inks.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	2.81	0.42	20.2	33.1	B1	0.32	0.37	3.0	28.1
A2	3.41	0.44	23.0	33.7	B2	1.06	0.42	8.1	31.3
A3	3.65	0.44	22.9	36.1	B3	1.53	0.44	11.5	30.3
A4	3.03	0.41	20.2	36.5	B4	1.84	0.44	13.4	31.1
A5	1.76	0.40	13.3	33.0	B5	1.68	0.36	16.0	29.1
A6	0.56	0.40	5.1	27.8	B6	2.79	0.39	17.3	41.3
A7	0.89	0.42	7.3	28.9	B7	0.72	0.24	9.6	31.4
A8	2.33	0.41	16.7	34.1	B8	0.88	0.35	8.0	31.6
A9	1.30	0.41	10.4	30.6	B9	0.41	0.30	4.5	30.7
A10	0.45	0.33	4.8	28.4	B10	1.08	0.40	8.3	32.7
A11	0.55	0.26	6.9	30.4	B11	1.10	0.34	10.1	31.8
A12	1.28	0.38	11.0	30.5	B12	0.59	0.33	6.0	29.6

Table S5: Current-voltage measurement results for $Cu(In,Ga)Se_2$ solar cells from sulfoselenide inks with NaF deposited prior to selenization.

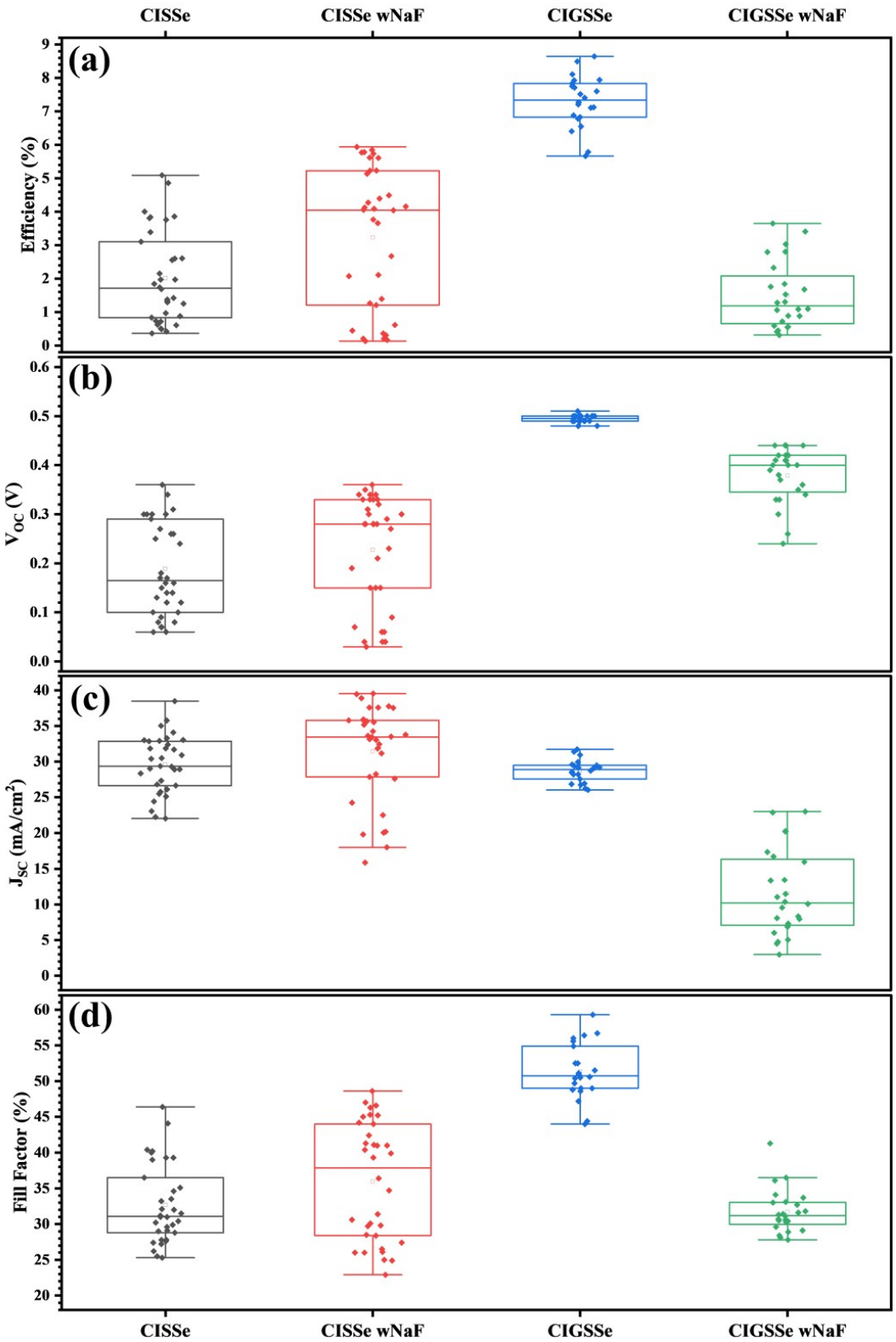

Figure S12: (a) Efficiency, (b) open-circuit voltage, (c) short-circuit current, and (d) fill factor distributions of all solar cells fabricated using sulfoselenide inks.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	6.81	0.40	35.9	47.5	A12	6.54	0.38	31.7	54.4
A2	7.25	0.38	37.4	50.8	B1	5.80	0.39	33.2	44.8
A3	6.39	0.37	35.6	48.4	B2	5.28	0.37	31.3	45.6
A4	6.51	0.38	32.0	53.5	B3	5.24	0.37	28.0	50.6
A5	7.02	0.38	34.5	53.5	B4	6.94	0.38	33.3	54.8
A6	7.23	0.38	35.3	53.9	B5	6.72	0.38	33.7	52.4
A7	7.11	0.37	34.0	56.4	B6	7.01	0.37	33.0	57.4
A8	5.79	0.37	30.1	51.9	B7	6.35	0.38	32.4	51.4
A9	6.93	0.38	34.4	53.1	B8	5.99	0.37	31.6	51.3
A10	6.61	0.38	34.0	51.1	B9	6.67	0.37	30.9	58.3
A11	7.06	0.38	34.9	53.2	B10	5.81	0.36	31.1	51.9

Table S6: Current-voltage measurement results for $CuInSe_2$ solar cells from polyselenide inks.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	5.60	0.40	30.5	46.0	B2	5.62	0.37	33.7	45.0
A2	6.17	0.40	32.8	47.1	B3	4.69	0.38	28.9	42.6
A3	5.43	0.40	27.9	48.7	B4	4.72	0.36	28.4	45.1
A4	5.36	0.39	29.2	47.1	B5	4.97	0.36	29.4	47.1
A5	4.65	0.38	29.0	42.2	B6	5.43	0.36	30.6	49.4
A6	5.35	0.38	27.9	50.4	B7	4.83	0.37	28.9	45.1
A7	3.04	0.31	26.7	36.7	B8	4.50	0.35	27.7	46.4
A8	5.39	0.37	29.6	49.2	B9	4.72	0.35	28.2	47.8
A9	3.65	0.34	27.8	38.6	B10	4.24	0.33	27.8	46.2
A10	5.61	0.37	29.8	50.7	B11	4.31	0.33	26.8	48.8
A11	4.46	0.36	25.4	48.8	B12	4.48	0.36	27.9	44.6
B1	5.07	0.37	31.1	44.0	B13	4.18	0.33	28.2	44.9

Table S7: Current-voltage measurement results for $CuInSe_2$ solar cells from polyselenide inks with NaF deposited prior to selenization.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	9.74	0.55	29.8	59.5	A14	8.60	0.54	26.5	60.2
A2	9.36	0.55	28.2	60.3	A15	8.89	0.54	26.3	62.8
A3	9.18	0.54	27.2	62.4	B1	9.09	0.54	30.0	56.0
A4	10.80	0.55	32.9	60.0	B2	8.28	0.54	30.6	50.1
A5	11.10	0.55	32.4	62.2	B3	7.86	0.54	28.6	50.9
A6	11.02	0.55	31.0	64.7	B4	7.44	0.54	24.8	55.6
A7	10.36	0.54	29.5	65.2	B5	7.81	0.54	28.3	51.1
A8	10.31	0.55	31.3	59.9	B6	8.58	0.54	28.6	55.4
A9	10.24	0.55	30.4	61.3	B7	8.63	0.55	26.7	58.6
A10	10.25	0.55	28.9	64.7	B8	6.96	0.59	24.0	49.1
A11	9.51	0.54	26.8	65.6	B9	9.00	0.54	29.3	56.7
A12	7.25	0.52	26.5	52.6	B10	9.39	0.55	30.1	56.7
A13	8.81	0.54	27.9	58.3	B11	7.05	0.55	25.2	50.8

Table S8: Current-voltage measurement results for Cu(In,Ga)Se_2 solar cells from polyselenide inks.

Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)	Cell	PCE (%)	V_{OC}	J_{SC} (mA/cm^2)	FF (%)
A1	7.96	0.52	31.3	48.8	B1	9.06	0.56	29.2	55.3
A2	11.20	0.54	32.3	64.3	B2	10.27	0.56	30.6	60.0
A3	10.19	0.54	31.7	59.8	B3	9.42	0.56	27.1	62.0
A4	8.18	0.53	28.2	54.8	B4	8.63	0.54	26.3	60.9
A5	8.25	0.53	26.4	59.0	B5	7.67	0.52	30.3	48.7
A6	10.09	0.54	30.7	60.7	B6	5.78	0.46	28.3	44.3
A7	9.36	0.54	30.6	56.8	B7	7.48	0.51	26.8	54.7
A8	10.06	0.55	28.8	63.3	B8	6.55	0.47	25.3	55.2
A9	8.90	0.54	26.1	63.3	B9	7.55	0.50	26.5	57.1

Table S9: Current-voltage measurement results for Cu(In,Ga)Se_2 solar cells from polyselenide inks with NaF deposited prior to selenization.

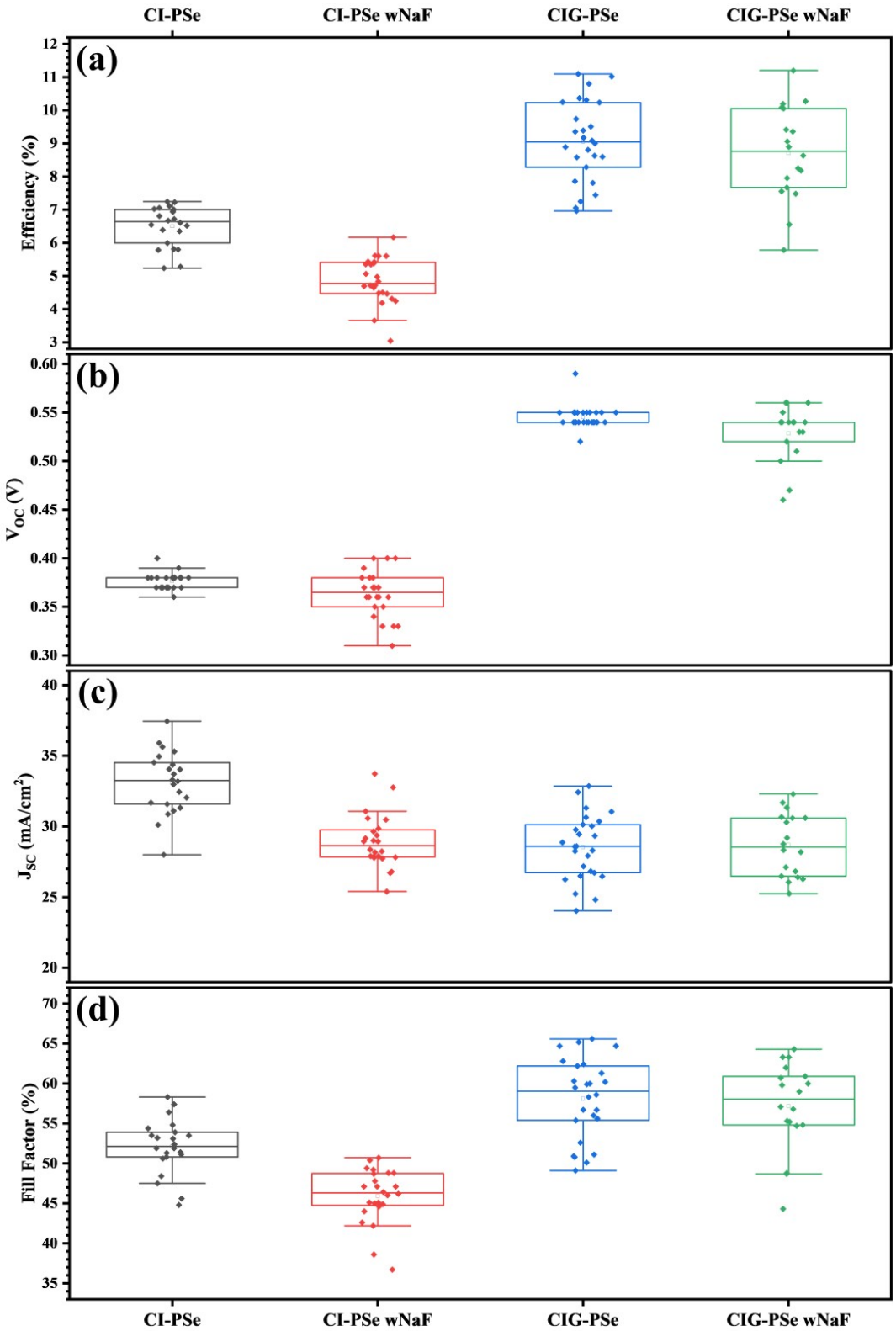

Figure S13: (a) Efficiency, (b) open-circuit voltage, (c) short-circuit current, and (d) fill factor distributions of all solar cells fabricated using polyselenide inks.