Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Improving the performance of kesterite solar cells by solution germanium alloying

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Table S1. Elemental analysis of compounds.

Sample	C [wt.%]	H [wt.%]	S [wt.%]
compound	12.34	3.405	15.272
$Ge(DMSO)_2Cl_4$	12.97	3.24	17.297

Table S2. The diffraction angle, FWHM of (112) diffraction peak, and crystalline domain size of samples.

Sample	2-theta (°)	FWHM (°)	Grain Size (nm)
CZTSSe	27.498	0.183	53.6
CZTGSSe-10	27.522	0.219	42.1
CZTGSSe-15	27.579	0.226	40.4
CZTGSSe-20	27.614	0.228	40.0
CZTGSSe-40	27.709	0.255	35.0
CZGSSe	27.947	0.136	88.1

Table S3. Lattice parameters and cell volume of the absorbers.

Sample	a (Å)	c (Å)	vol (Å^3)
CZTS	5.632	11.156	353.835
CZTGSSe-10	5.626	11.150	352.926
CZTGSSe-15	5.615	11.124	350.786
CZTGSSe-20	5.613	11.094	349.491
CZTGSSe-40	5.589	11.076	345.965
CZGSSe	5.544	10.975	337.377

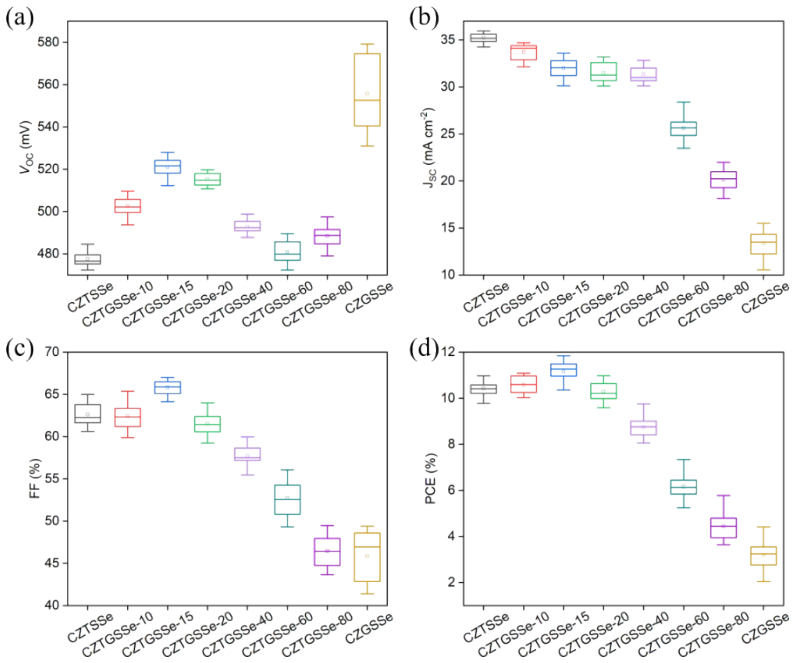

Figure S1. Statistical device parameters of kesterite solar cells with a whole concentration.

Table S4 Device characteristics of CZTSSe, CZTGSSe-n and CZGSSe solar cells.

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	R_S (Ω cm^2)	E_g (eV)	V_{OC}/V_{OC}^{SQ}
CZTS	477.4	35.36	64.99	10.97	2.041	1.081	0.568
CZTGSSe-10	508.8	34.71	62.34	11.01	2.381	1.094	0.597
CZTGSSe-15	519.3	33.05	65.64	11.27	2.248	1.128	0.587
CZTGSSe-20	519.1	33.05	60.72	10.42	2.793	1.132	0.584
CZTGSSe-40	496.7	32.81	58.94	9.61	3.130	1.142	0.553
CZGSSe	577.4	15.48	49.4	4.41	15.510	1.517	0.463

Table S5. Average device characteristics of CZTSSe, CZTGSSe-n and CZGSSe solar cells.

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
CZTS	477.6 ± 3.6	35.21 ± 0.5	62.63 ± 1.3	10.42 ± 0.3
CZTGSSe-10	502.5 ± 4.0	33.71 ± 0.9	62.42 ± 1.5	10.58 ± 0.3
CZTGSSe-15	521.0 ± 4.2	32.00 ± 0.9	65.82 ± 0.8	11.15 ± 0.4
CZTGSSe-20	515.3 ± 3.2	31.50 ± 1.1	61.51 ± 1.2	10.29 ± 0.4
CZTGSSe-40	492.8 ± 2.9	31.34 ± 0.8	57.70 ± 1.1	8.74 ± 0.4
CZGSSe	555.7 ± 16.9	13.39 ± 1.3	45.83 ± 2.8	3.20 ± 0.6

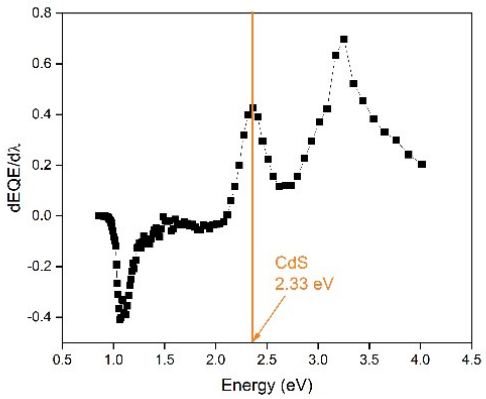

Figure S2. The bandgap of CdS obtained by differentiation based on EQE data.

The bandgap of CdS is estimated by plotting dEQE/dλ versus energy, three peaks represent the absorber, cadmium sulfide (CdS) buffer layer, and window layer respectively, with a bandgap of 2.33eV in the buffer layer.

Table S6. Device characteristics of CZTGSSe-15 and ACZTGSSe-15 solar cells.

Cell	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	R_S (Ω cm^2)	n	J_0 (A cm^{-2})	E_U (meV)	E_g (eV)	V_{OC}/V_{OC}^{SQ}
CZTGSSe-15	522.3	33.24	65.16	11.31	2.253	1.81	4.15×10^{-7}	24.7	1.129	0.589
ACZTGSSe-15	523.8	35.87	65.22	12.25	2.139	1.56	7.40×10^{-8}	23.8	1.131	0.590