Electronic Supplementary Information (ESI)

Identify the origin of the V_{oc} deficit of kesterite solar cells from the two grain growth mechanisms induced by Sn^{2+} and Sn^{4+} precursors in DMSO solution

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EXPERIMENTAL SECTION

Preparation of the molecular precursor solutions

The precursor solutions were prepared in a glovebox with O_2 and H_2O level below 5 ppm at room temperature with reference to our previous report.[1] First, CuCl-thiourea (Cu-Tu) solution was prepared as follow: 1.602 g Tu (99%, Aladdin, recrystallized twice) was added to 4 mL DMSO (99.8%, J&K) under stirring until completely dissolved, then 0.582 g CuCl (99.999%, Alfa) was added to the above solution under stirring to make a clear solution. To make Sn^{2+} precursor solution, 0.903 g $SnCl_2·2H_2O$ (99.99%, Aladdin), 0.567 g $ZnCl_2$ (99.95%, Aladdin) and 4 mL DMSO were subsequently added to the above Cu-Tu solution under stirring until completely dissolved. For Sn^{4+} solution, a second solution (Sn-Zn solution) was made separately as follow: 4 mL DMSO was injected into a sealed vial containing 1.042 g SnCl4 (99.99%, Alfa) (Notice: $SnCl_4$ reacts with DMSO violently and forms white power, sealing the vial is necessary to prevent the evaporation of $SnCl_4$), after the vial cooled down, 0.763 g $Zn(OAc)_2$ (99.99%, Aladdin) was added to the above suspension under stirring to form a clear solution. The Sn-Zn solution was mixed with Cu-Tu solution to form Sn^{4+} precursor solution.

Fabrication of CZTSSe absorber films

The precursor solution was spin-coated on the precleaned Mo-coated soda-lime glass substrate at 1500 rpm for 60 s. The wet film was immediately annealed on a hot plate at 420°C for 1.5 min. The coating-annealing-cooling cycle was repeated seven times to build up a precursor film with a thickness about 1.5 µm. The film was then put into a graphite box with Se tablets (about 500 mg) and placed in Rapid Heating furnace tube for selenization at 1 atmosphere. For the standard device preparation process, the selenization was performed at 550°C for 20 min with Ar flow rate of 20 sccm. For the samples used to investigate the grain growth process, the selenization was interrupted at a certain point as shown in Figure 2 and the furnace (sample) was cooled down naturally. The cooling rate was about 30°C/min from 500°C to 400°C, 20°C /min from 400°C to 300°C, and 8°C/min from 300°C to 100°C.

Fabrication of solar cell devices

The cadmium sulfide buffer layer of thickness 40~50 nm was deposited by the chemical bath deposition (CBD) method. For samples without thermal annealing, a window layer containing 50 nm i-ZnO and 250 nm ITO was directly deposited on top of CdS by RF sputtering at room temperature. For thermal annealing, the samples (MSLG/CZTSSe/CdS) were loaded on sample holder and put into the chamber for sputtering; the chamber was pumped down to vacuum below $2*10^{-3}$ Pa. The sample holder (and samples) was heated to 200°C within 30 min and kept at 200°C for 2 hours. The window layer containing 50 nm i-ZnO and 150 nm ITO were deposited at 200°C right after thermal annealing. Finally, top contact grids of nickel (50 nm) and aluminum (200 nm) were fabricated in a separate thermal deposition system through a shadow mask. The area of the solar cell was defined by mechanical scribing for an area about 0.105 cm^2. The accurate area was measured individually as described in the previous report.[1]

Film characterization

X-ray diffraction (XRD) spectra (2θ scan) were collected by a Siemens D5005 X-ray powder diffraction system using Cu K (λ = 1.5406 Å) X-ray as the source. The Raman spectra were acquired on Renishaw in Via microscope using 532 Laser diode as the excitation source. The film surface morphology image were measured on Hitachi S4800 scanning electron microscope (SEM) with an accelerating voltage of 5 kV .

Device characterization

The current density–voltage (J-V) curves were measured using Keithley 2400 Source Meter under simulated AM 1.5 sunlight at 100 mW/cm^2 irradiance generated by an AAA sun simulator (CROWNTECH, Inc.) with the intensity calibrated by an NREL calibrated Si reference cell. The external quantum efficiency (EQE) of the solar cells was measured on Enlitech QE-R3018 using calibrated Si and Ge diodes (Enli technology Co. Ltd.) as references. The FTPS was measured combining a Fourier-transform infrared spectroscopy (FTIR, Vertex 70, Bruker Optics) with a low-noise current amplifier (SR570, Stanford Research Systems). The photocurrent produced by the devices was amplified and fed back into the external detector port of the FTIR. Eu was calculated by the EQE data measured by FTPS, with a fitting error of ±0.1 meV. Capacitance– voltage (C–V) and DLCP were measured by using a Keithley 4200A-SCS system. The C-V measurement was performed using 30 mV, 100 kHz AC excitation with a DC bias from 0 to -5 V and the DLCP was performed using 100 kHz AC excitation with an AC amplitude from 20 to 140 mV and a DC bias from 0 to -2.5 V.

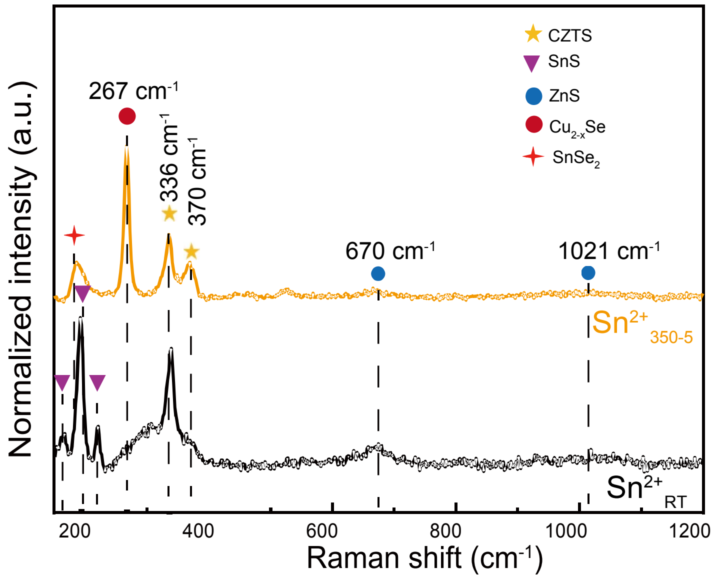


Figure S1. Raman spectra of precursor film of $Sn^{2+}{}_{RT}$ and its selenized film at 350°C for 5 min.

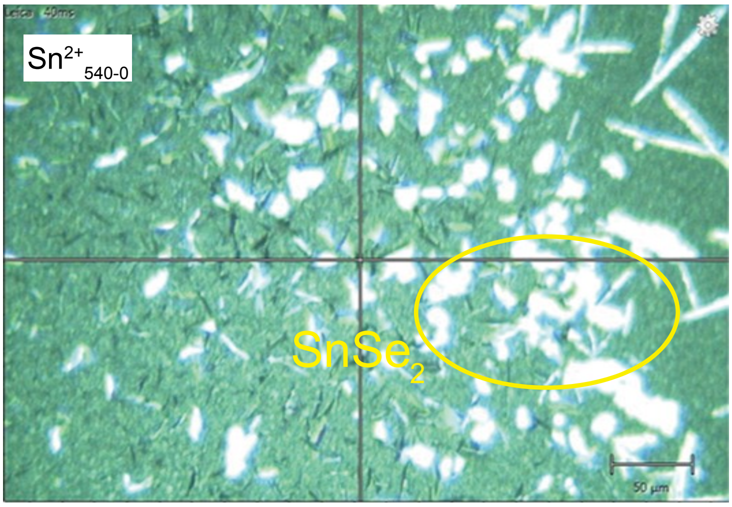


Figure S2. Photograph of $Sn^{2+}{}_{540-0}$ film under microscope.

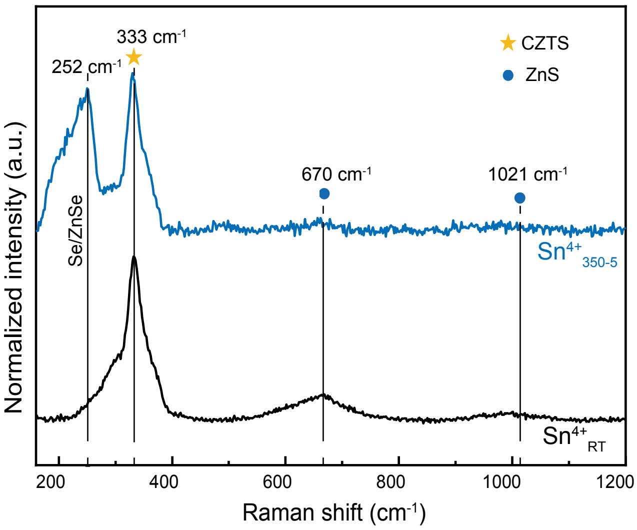
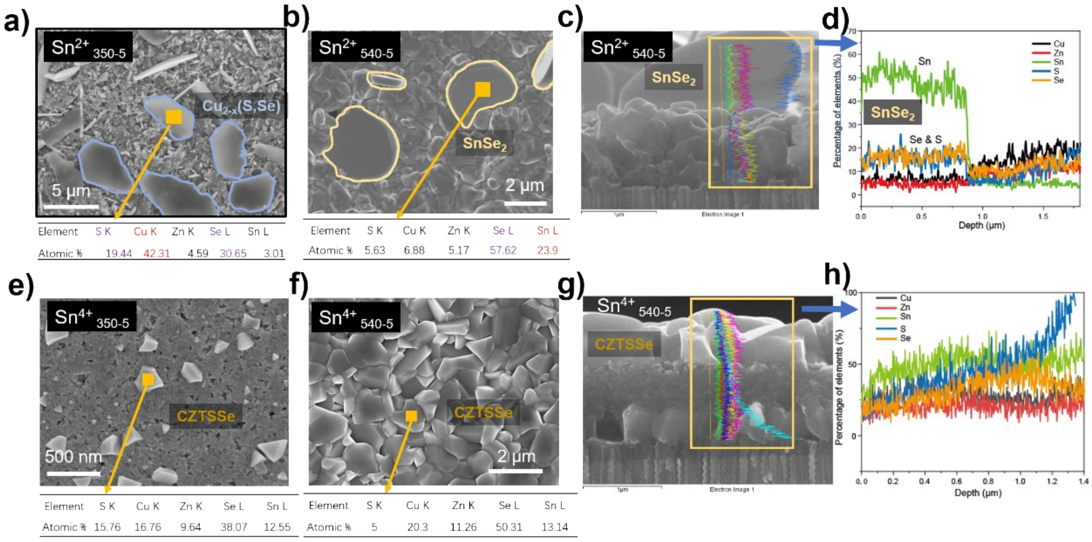


Figure S3. Raman spectra of precursor film of Sn^{4+}_{RT} and its selenized film at 350°C for 5 min.



Element	S K	Cu K	Zn K	Se L	Sn L
Atomic %	19.44	42.31	4.59	30.65	3.01

Element	S K	Cu K	Zn K	Se L	Sn L
Atomic %	5.63	6.88	5.17	57.62	23.9

Element	S K	Cu K	Zn K	Se L	Sn L
Atomic %	15.76	16.76	9.64	38.07	12.55

Element	S K	Cu K	Zn K	Se L	Sn L
Atomic %	5	20.3	11.26	50.31	13.14

Figure S4. The SEM images and EDX results of the Sn^{2+} (a, b, c, d) and Sn^{4+} (e, f, g, h) absorber films at different selenization stage.

Identification of film components were performed by a combination of SEM and EDX and the results are shown in Figure S4. EDX in Figure S4(a) shows the angular polygonal crystals in $Sn^{2+}_{350\text{-}5}$ are $Cu_{2\text{-}x}(S,Se)$ and the high S/(S+Se) ratio (>30%) of these crystals confirms $Cu_{2\text{-}x}(S,Se)$ is the intermediate of the transition from pure sulphide ($Cu_{2\text{-}x}S$) to selenide. From Figure S4 (b and c), $SnSe_2$ was identified as an elliptical in $Sn^{2+}_{540\text{-}5}$. For Sn^{4+} films, no angular polygonal ($Cu_{2\text{-}x}(S,Se)$) and elliptical shaped crystal ($SnSe_2$) were observed in all stages. The EDX in Figure S4(e) clearly shows the metal composition of the small crystals in $Sn^{4+}_{350\text{-}5}$ are similar to the large grains in $Sn^{4+}_{540\text{-}5}$ (Figure S4(f)), both close that to that of kesterite, confirming the kesterite structure of the small crystals. The EDX also shows the small crystal has a high S content with S/(S+Se) ratio close to 30%, similar to that of $Cu_{2\text{-}x}(S,Se)$ in Figure S4(a), which further confirms that CZTSSe is the intermediate of the transition from pure sulphide kesterite to near pure selenide kesterite, in consistent to the XRD and Raman data shown in Figure 3.

Table S1 The device parameters of CZTSSe solar cells extracted from Sn^{2+} and Sn^{4+} devices with different selenization time.

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
Sn$^{2+}_{540\text{-}5}$	0.270±0.052	25.63±5.32	33.58±3.86	2.42±1.02
Sn$^{2+}_{540\text{-}10}$	0.340±0.038	28.39±1.66	40.08±3.57	3.92±0.87
Sn$^{2+}_{540\text{-}15}$	0.346±0.035	30.00±2.63	36.49±2.49	3.83±0.77
Sn$^{2+}_{540\text{-}20}$	0.399±0.021	31.69±1.69	44.65±3.87	5.69±0.93
Sn$^{2+}_{540\text{-}25}$	0.362±0.037	29.32±2.48	38.43±3.34	4.13±0.89
Sn$^{4+}_{540\text{-}5}$	-	-	-	-
Sn$^{4+}_{540\text{-}10}$	0.071±0.062	0.03±0.04	24.80±1.14	0.00±0.00
Sn$^{4+}_{540\text{-}15}$	0.275±0.076	0.90±0.73	21.25±1.41	0.05±0.05
Sn$^{4+}_{540\text{-}20}$	0.435±0.008	33.55±1.31	63.49±1.26	9.27±0.43
Sn$^{4+}_{540\text{-}5}$	0.419±0.008	31.45±1.36	55.09±4.28	7.25±0.62

The average and standard deviation are calculated on the top 10 devices of each condition.

"-" means the corresponding parameter is almost 0.

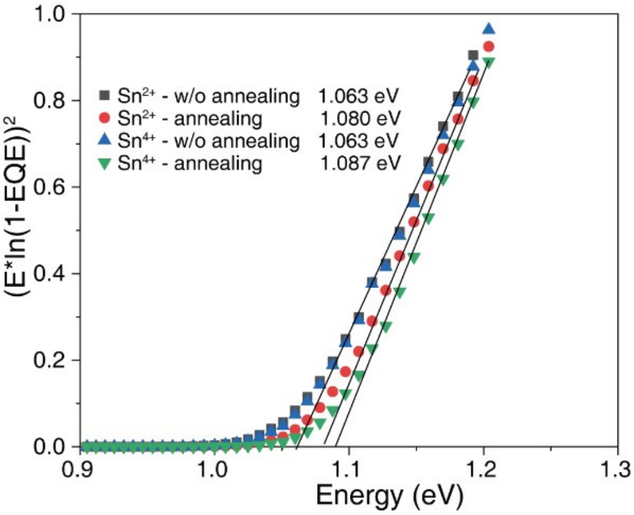


Figure S5. Bandgap extraction from the EQE spectra in Figure 6b.

Table S2. Summary of the carrier density of Sn^{2+} and Sn^{4+} devices derived from the C-V and DLCP measurements.

Device	N_{CV} (cm^{-3})	N_{DLCP} (cm^{-3})	N_{IT} (cm^{-3})	X_d (nm)
Sn^{2+}	1.96 x 10^{16}	1.68 x 10^{16}	2.76 x 10^{15}	114
Sn^{4+}	9.49 x 10^{15}	8.32 x 10^{15}	1.17 x 10^{15}	184

Table S3. Summary of the device parameters of the high performance Sn^{4+} solar cells with thermal annealing.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	n	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	J_0 (A cm^{-2})	$V_{oc\text{-}def}$ (V)	V_{oc}/V_{oc}^{SQ}	E_g (eV)
1#	0.506	33.2	72.3	12.1	1.38	0.30	1402	2.16E-08	0.317	61.5	1.062
2#	0.499	36.4	68.0	12.4	1.65	0.39	626.5	2.77E-07	0.305	62.0	1.042

Reference

1. Y. Gong, Y. Zhang, E. Jedlicka, R. Giridharagopal, J. A. Clark, W. Yan, C. Niu, R. Qiu, J. Jiang, S. Yu, S. Wu, H. W. Hillhouse, D. S. Ginger, W. Huang and H. Xin, *Sci. China Mater.*, 2021, **64**, 52-60.