Electronic Supplementary Information (ESI)

Crystal Reconstruction and Defects Healing Enabled High-quality Sb_2Se_3 Films for Solar Cell Applications

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Supplementary Note

Note 1

Principles of Deep-level Transient Spectroscopy

We conducted deep-level transient spectroscopy (DLTS) to detect the deep-level defects properties and the defect level is identified from DLTS signal using Fourier deconvolution algorithm. The active energy (E_a, E_C-E_T or E_T-E_V) and capture cross section of electron traps and hole traps can be calculted by the Arrhenius Equations (1) and (2),

$$ln(\tau_e \nu_{th,p} N_V) = \frac{E_T - E_V}{k_B}\frac{1}{T} - \ln(X_p \sigma_p) \#(1)$$

$$ln(\tau_e \nu_{th,n} N_C) = \frac{E_C - E_T}{k_B}\frac{1}{T} - \ln(X_n \sigma_n) \#(2)$$

where τ_e, N_V, N_C, E_T, E_V, and E_C are emission time constant, valence band state density, conduction band state density, trap energy level, valence band, and conduction band, respectively. $v_{th,n/p}$, $X_{n/p}$, and $\sigma_{n/p}$ are thermal velocity, entropy factor, and capture cross-section for electron and hole, respectively. E_a can be obtained from the slope of the corresponding line, and the σ can be obtained from the y-intercept of the lines. The trap concentration (N_T) can be acquired from Equation (3):

$$N_T = 2N_S\frac{\Delta C}{C_R} \#(3)$$

where N_S is the shallow donor concentration, C_R is the capacitance under reverse bias, while ΔC represents the amplitude of transient capacitance.

The product of the capture cross section and the defect density ($\sigma \times N_T$) is considered as an important parameter for the intuitive evaluation of the carrier lifetime, and the relationship follows the following Equation (4):

$$\tau_{trap} = \frac{1}{\upsilon \sigma N_T} \#(4)$$

where υ is the thermal velocity of electric charge.[1, 2]

Supplementary Figure

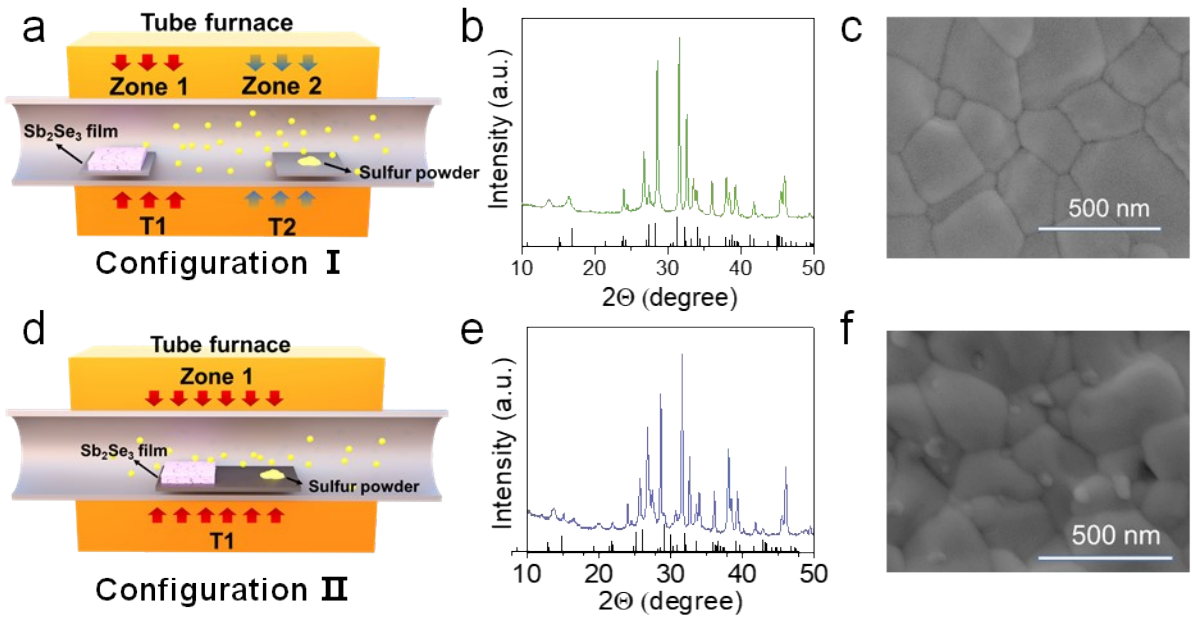

Fig. S1. Characterization of structure and surface morphology of the films. XRD pattern of the Sb_2Se_3 films sulfurized using b) configuration I and e) configuration II; Surface SEM images of the Sb_2Se_3 films sulfurized using b) configuration I and e) configuration II.

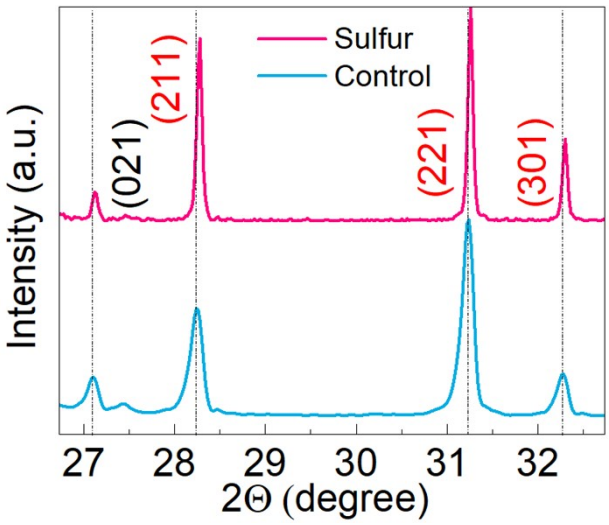

Fig. S2. Magnified view of the (021), (211),(221) and (301) XRD peaks of the films.

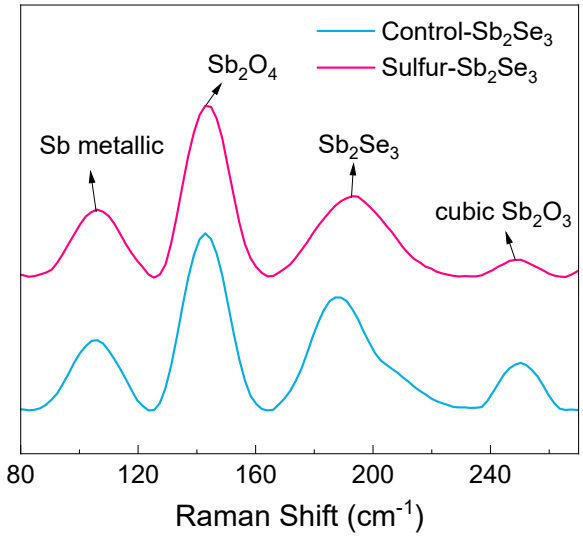

Fig. S3. Raman spectra of the Control-Sb_2Se_3 and Sulfur-Sb_2Se_3 films.

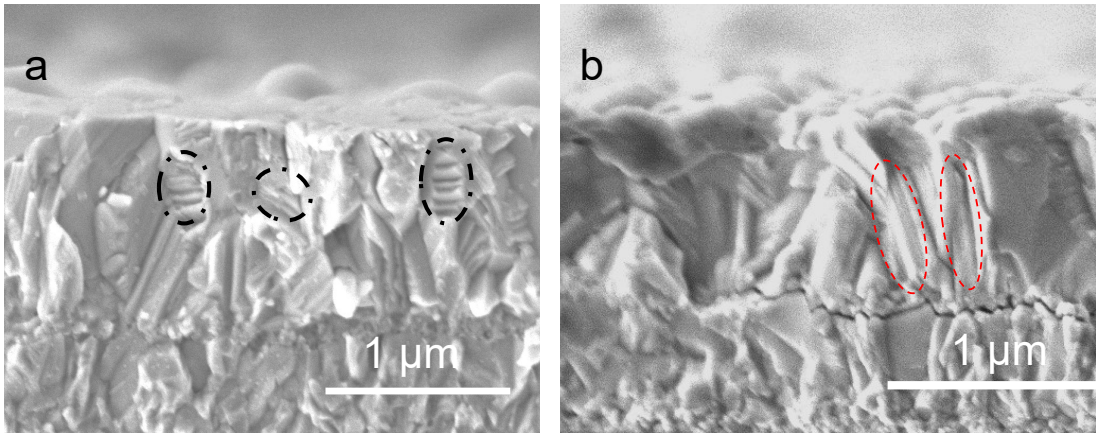

Fig. S4. The cross-sectional SEM image of the films. a) Control-Sb_2Se_3 films, b) Sulfur-Sb_2Se_3 films.

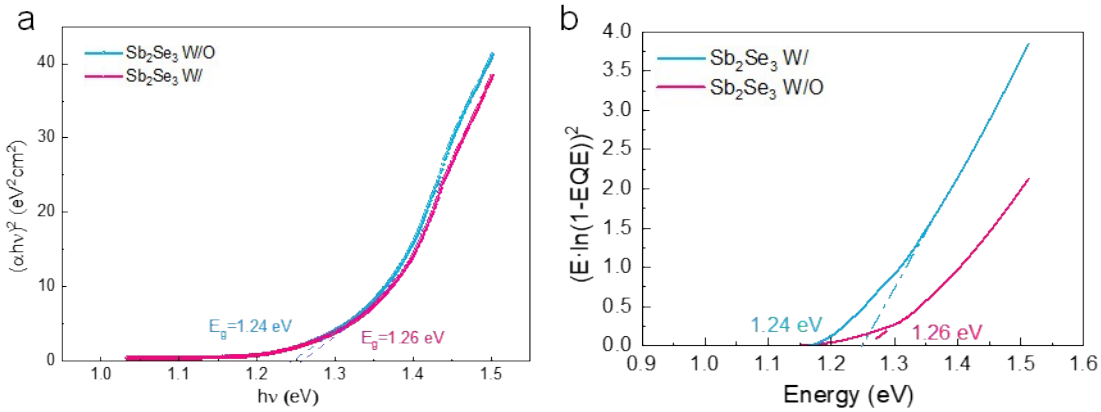

Fig. S5. UV-visible absorption characterization of the films. a) plot of $(\alpha h\nu)^2$ versus $(h\nu)$ of Sb_2Se_3 films. b) Bandgap value extracted from EQE spectra.

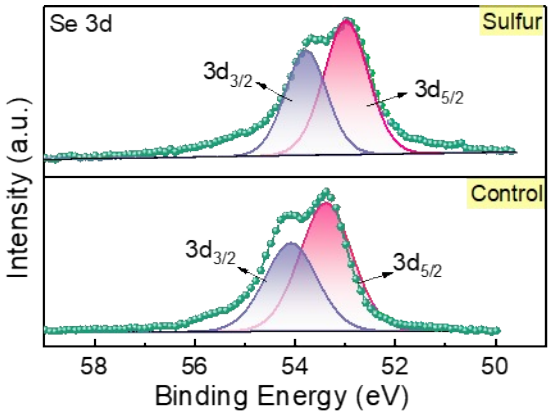

Fig. S6. Surface composition of the films. Analysis of the surface chemical states of Control-Sb_2Se_3 and Sulfur-Sb_2Se_3 films for Se 3d XPS peaks.

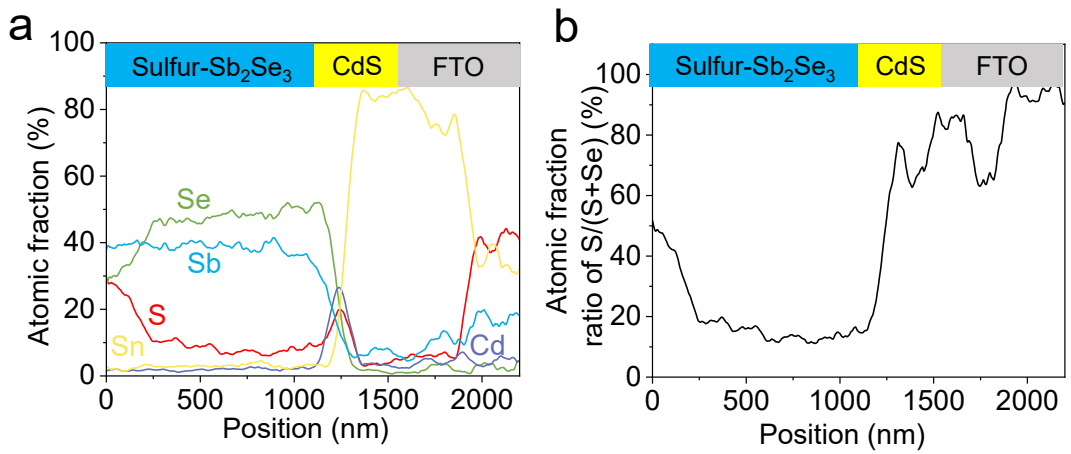

Fig. S7. Elementary composition of the films. a) EDX line scan of Sulfur-Sb_2Se_3; b) Atomic fraction ratio of S/(S+Se) in Sb_2Se_3 films.

Table S1 Effect of annealing temperature on device performance

Temperature/ °C	V_{OC}/V	J_{SC}/mA cm^{-2}	FF/%	PCE/%
370	0.43	28.21	52.75	6.45
360	0.43	27.56	53.81	6.43
350	0.43	27.21	55.36	6.50

Table S2 Effect of annealing time on device performance

Time/min	V_{OC}/V	J_{SC}/mA cm^{-2}	FF/%	PCE/%

10	0.43	27.12	55.36	6.50
20	0.46	29.70	48.98	6.66
30	0.41	29.57	38.05	4.60

Table S3 Effect of the amount of sulfur on device performance

Amount/g	V_{OC}/V	J_{SC}/mA cm^{-2}	FF/%	PCE/%
0.025	0.41	29.95	54.75	6.71
0.05	0.40	31.31	53.16	6.71
0.1	0.45	30.06	56.23	7.63
0.2	0.44	31.15	54.99	7.53
0.3	0.42	31.48	53.68	7.12
0.4	0.40	30.15	53.76	6.43

Table S4 Effect of the thickness on device performance

Thickness/nm	V_{OC}/V	J_{SC}/mA cm-^{2}	FF/%	PCE/%
400	0.42	28.81	52.55	6.38
1000	0.45	30.06	56.23	7.63
1200	0.40	31.47	56.41	7.05
1500	0.42	29.75	57.63	7.12

Table S5 Effect of the temperature of sulfur on device performance

Temperature/ °C	V_{OC}/V	J_{SC}/mA cm^{-2}	FF/%	PCE/%
250	0.45	30.06	56.23	7.63
275	0.40	32.19	54.02	6.90
300	0.38	30.60	56.88	6.59

Table S6 The element proportion of Sulfur-Sb_2Se_3 and Control-Sb_2Se_3

Sb_2Se_3 films	Se (at.%)	S (at.%)	Sb (at.%)	(Se+S)/Sb	S/(Se+S)
Sulfur-Sb_2Se_3	33.0	8.6	21.5	1.93	0.21
Control-Sb_2Se_3	47.5	0	26.3	1.81	0

Table S7 Parameters fitted from electrochemical impedance spectra of devices

Sample	R_S(Ω)	R_{REC}(Ω)
Control-Sb_2Se_3	54.2	15411
Sulfur-Sb_2Se_3	77.74	3046

References

1. Y. Zhao, S. Wang, C. Li, B. Che, X. Chen, H. Chen, R. Tang, X. Wang, G. Chen, T. Wang, J. Gong, T. Chen, X. Xiao and J. Li, *Energy & Environmental Science*, 2022, **15**, 5118-5128.
2. S. Wang, Y. Zhao, B. Che, C. Li, X. Chen, R. Tang, J. Gong, X. Wang, G. Chen, T. Chen,

J. Li and X. Xiao, *Adv Mater*, 2022, **34**, e2206242.