

Supporting Information

Efficient Defect Passivation of Sb₂Se₃ Film by Tellurium Doping for High Performance Solar Cells

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Experimental Section

Preparation of precursor solution

4 mmol Se powder, 2.5 mmol Sb powder and a certain amount of Te powder was dissolved in a mixed solvent of 4 mL ethanediamine and 1 mL 2-mercaptoethanol. The mixture was stirred at 60 °C for 5 h, followed by cooling down to room temperature naturally.

Solar cell fabrication

A CdS thin film was prepared by CBD method at 65 °C for 16 min. Sb₂Se₃ thin films were fabricated by spin-coating Sb₂Se₃ precursor solution at a speed of 6000 rpm for 40 s. The obtained films were annealed on a preheated hotplate with a two-consecutive step program at 200 °C for 1 min and 400 °C for 2 min in N₂-purged glove box. The hole extraction materials Spiro-OMeTAD was prepared according the reported method.^[1] Finally, Au counter electrode was deposited by a thermal evaporator under a pressure of 5.0×10^{-4} Pa. The active area of the device was defined as 0.12 cm².

Characterization and measurements

The crystallinity of the as-prepared films was investigated by X-ray diffraction (XRD) using a Bruker Advance D8 diffractometer equipped with graphite-monochromatized Cu K α radiation ($\lambda=1.5406$ Å). For the XRD characterization, the Sb₂Se₃ films were prepared on glass substrate which have been deposited CdS layer. The surface and cross-section morphologies of the Sb₂Se₃ thin films were characterized by Field emission SEM (Hitachi, SU8220). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCALAB 250Xi system with an Al K α monochromatized source and a multidetection analyzer under 10⁻⁸ Torr. The optical absorption of thin films was measured by UV–vis–NIR 3600 spectrometer. The current–voltage curves were recorded using a Keithley 2400 apparatus under solar-simulated AM 1.5 sunlight (100 mW cm⁻²) with a standard xenon-lamp-based solar simulator (Oriel Sol 3A, Japan). The external quantum efficiency (EQE, Model SPIEQ200) was measured using a single source illumination system (halogen lamp) combined with a monochromator. Electrochemical impedance spectroscopy (EIS) measurements were performed using

the Zahner Mess System PP211 electrochemical workstation at a bias potential of -0.50 V in the dark with the frequency ranging from 100 Hz to 1 MHz. Transient absorption spectroscopy (Time-Tech Spectra, TA100) was pumped by 190 fs duration laser pulses of 580nm wavelength at 10 kHz repetition rate and probed at 720 nm. The DLTS measurements were carried out with a Phystech FT-1230 HERA DLTS system. Temperature scans were made between 120 and 400 K, at a heating rate of 2 K/min. The capacitances of samples were measured using Boonton 7200 capacitance meter. The reverse bias voltage was 0.4 V The pulse height, filling pulse width, and pulse period width were -0.4 V, 10 ms, and 20 ms, respectively. The activation energy, capture cross-section, and concentration of traps were calculated using an Arrhenius plot.

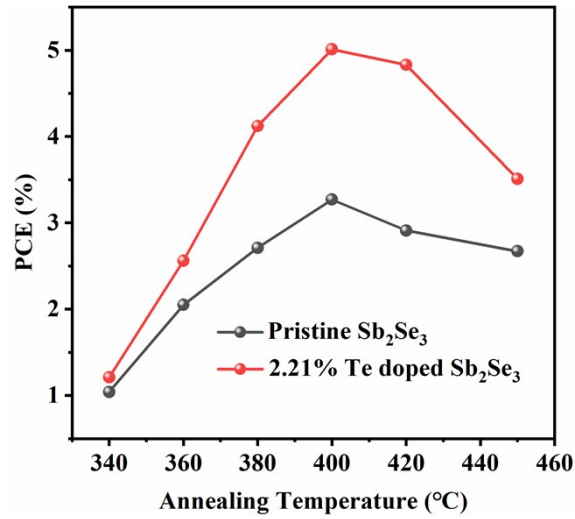


Figure S1 The dependence of device efficiency on the annealing temperature for pristine Sb_2Se_3 -based devices and 2.21% Te-doped Sb_2Se_3 solar cells.

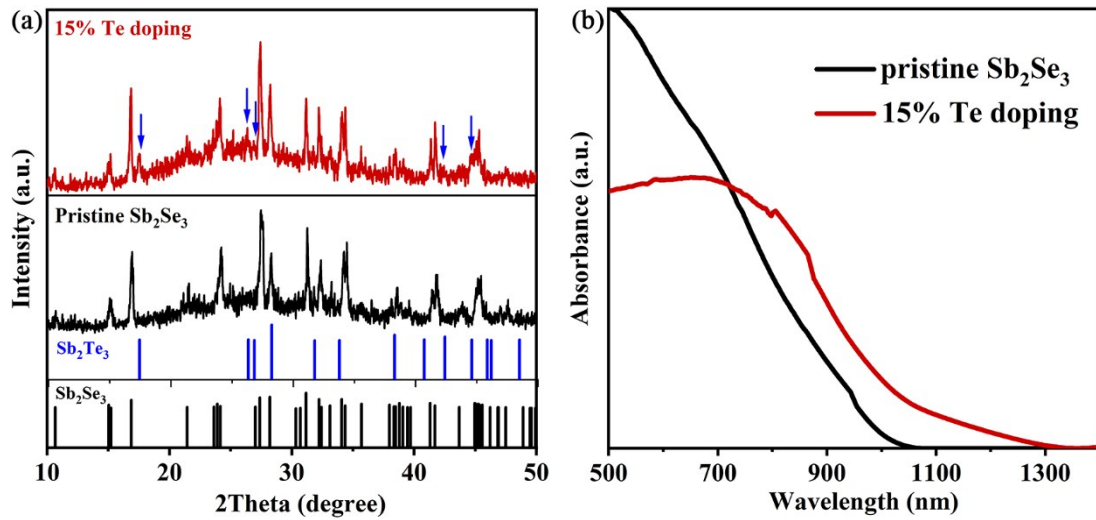


Figure S2 (a) X-ray diffraction patterns and (d) UV-vis absorption spectra of the pristine Sb_2Se_3 film and the film prepared by 15% Te doping in the precursor solution.

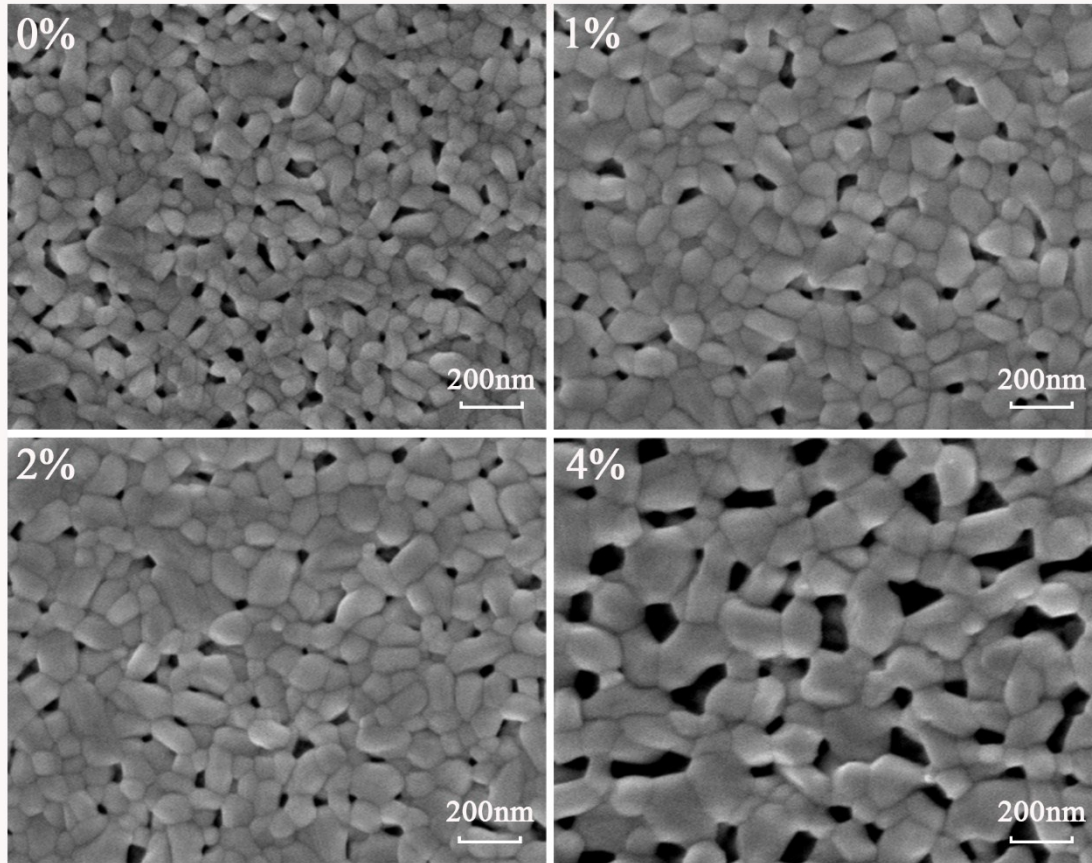


Figure S3 SEM images of the as-prepared pristine Sb₂Se₃ film and Sb₂Se₃ with different Te doping concentrations.

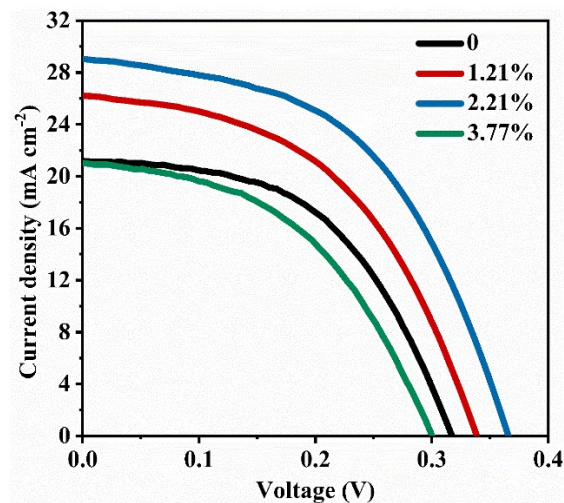


Figure S4 Current density–voltage curves of the devices with Te doping concentration of 0%, 1.21%, 2.21% and 3.77% in the Sb₂Se₃ films.

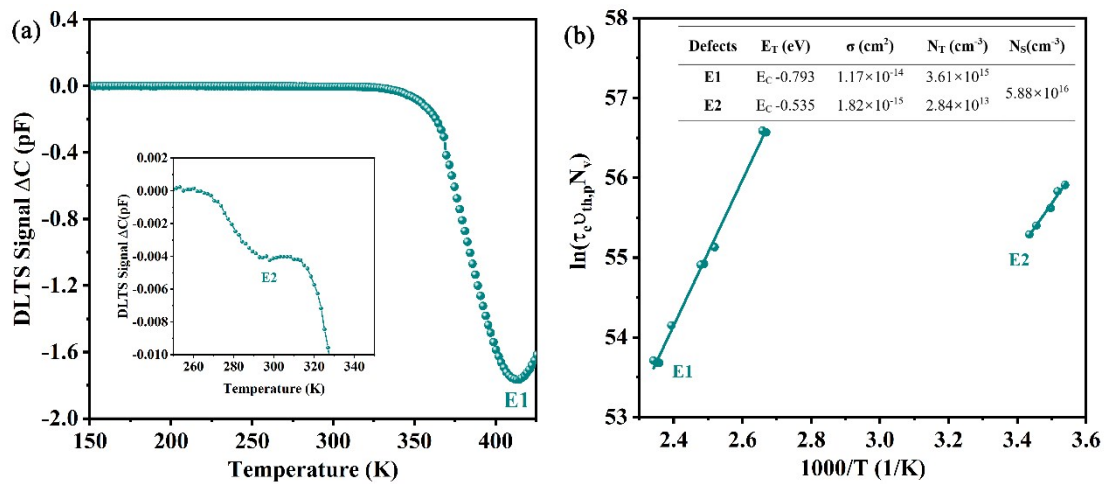


Figure S5 (a) DLTS signals and (b) corresponding Arrhenius plots of 3.77% Te-doped Sb_2Se_3 solar cell.

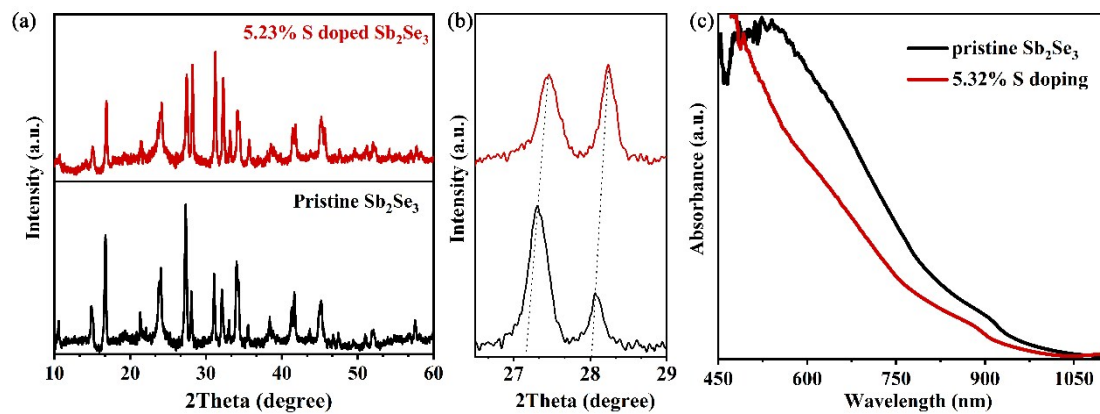


Figure S6 (a) X-ray diffraction patterns of the pristine Sb_2Se_3 film and 5.23% S doped Sb_2Se_3 film and (b) the corresponding enlarged XRD patterns. (c) UV-Vis absorption spectra of the pristine Sb_2Se_3 film and 5.23% S-doped Sb_2Se_3 film.

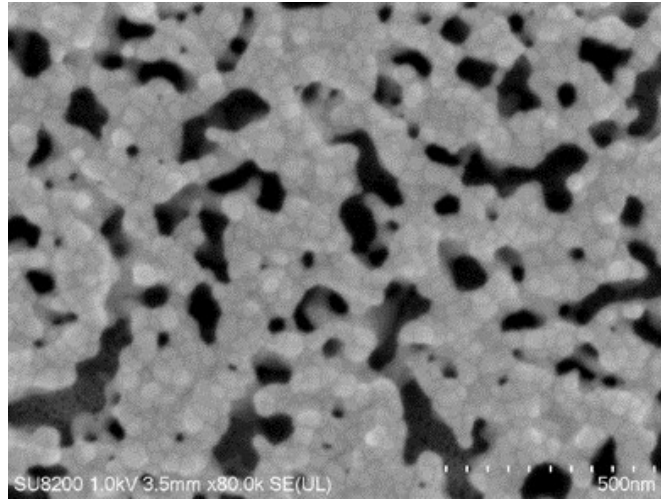


Figure S7 SEM image of surface morphology of S-doped Sb₂Se₃ film (5.23% molar ratio).

Table S1 Elemental composition of Sb₂Se₃ films with Te doping concentration of 1.0%, 2.0%, and 4.0%, determined by XRF characterization.

Sample	molar ratio of Te/(Te+Se) in precursor solutions	molar ratio of Te/(Te+Se) in films	molar ratio of Se/Sb	molar ratio of (Te+Se)/Sb
1	0%	0%	1.578	1.578
2	1.0%	1.21%	1.569	1.588
3	2.0%	2.21%	1.537	1.572
4	4.0%	3.77%	1.465	1.523

Table S2 Photovoltaic parameters of the Sb₂Se₃ solar cells prepared with different Te doping concentrations.

Te doping concentration %	Voc (mV)	Jsc (mA.cm ⁻²)	FF (%)	PCE (%)	R _s (Ω.cm ²)	R _{SH} (Ω.cm ²)
0	312	21.6	48.2	3.3	5.2	65.9
1.21	330	25.1	50.9	4.2	4.4	143.8
2.21	360	29.0	51.5	5.4	4.2	147.6
3.77	294	20.8	47.1	2.9	5.0	105.0

Table S3 Defect energy level (E_T), cross section (σ), concentration (N_T) and shallow dopant concentration (N_S) of the pristine Sb₂Se₃ device, 2.21% Te-doped Sb₂Se₃ device and 5.23% S-doped Sb₂Se₃ device.

	Defects	E _T (eV)	σ (cm ²)	N _T (cm ⁻³)	N _S (cm ⁻³)
Pristine Sb₂Se₃	H1	E _V +0.479	2.07 × 10 ⁻¹⁶	6.10 × 10 ¹⁴	6.41 × 10 ¹⁶
	H2	E _V +0.713	1.53 × 10 ⁻¹⁴	1.00 × 10 ¹⁵	
	E1	E _C -0.628	7.05 × 10 ⁻¹⁷	6.49 × 10 ¹⁴	
2.21% Te-doped Sb₂Se₃	H1	E _V +0.478	2.71 × 10 ⁻¹⁵	5.34 × 10 ¹³	1.02 × 10 ¹⁷
	E1	E _C -0.637	9.48 × 10 ⁻¹⁶	3.32 × 10 ¹⁴	
5.23% S-doped Sb₂Se₃	H1	E _V +0.500	6.80 × 10 ⁻¹⁴	6.93 × 10 ¹⁴	4.44 × 10 ¹⁶
	H2	E _V +0.721	8.19 × 10 ⁻¹⁴	1.43 × 10 ¹⁵	
	E1	E _C -0.633	2.54 × 10 ⁻¹⁶	6.60 × 10 ¹⁴	

Table S4 Photovoltaic parameters, defect energy level (E_T) and concentration (N_T) of Device-1(pristine-Sb₂Se₃ device) and Device-2 (undoped Sb₂Se₃ device with a Se/Sb atom ratio of 1.532).

Devices	Voc (mV)	Jsc (mA.cm ⁻²)	FF (%)	PCE (%)	Defects	E _T (eV)	N _T (cm ⁻³)
Device-1	312	21.6	48.2	3.3	H1	E _V +0.479	6.10 × 10 ¹⁴
					H2	E _V +0.713	1.00 × 10 ¹⁵
					E1	E _C -0.628	6.49 × 10 ¹⁴
Device-2	306	25.0	46.7	3.6	H1	E _V +0.485	1.57 × 10 ¹⁴
					H2	E _V +0.720	8.24 × 10 ¹⁴
					E1	E _C -0.628	4.31 × 10 ¹⁴

Table S5 Results of biexponential fit to 720 nm bleach decay of glass/Sb₂Se₃ films. Average lifetime $\langle\tau\rangle$ is calculated by the equation: $\langle\tau\rangle = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Sample	A1	τ_1 (ps)	A2	τ_2 (ps)	$\langle\tau\rangle$ (ps)
Sb ₂ Se ₃	52.1%	10.1 ± 0.4	47.9%	5253.7 ± 231.2	5242.7
2.21% Te: Sb ₂ Se ₃	34.7%	34.5 ± 3.5	65.3%	6253.2 ± 404.8	6235.0

References

- [1] R. Tang, X. Wang, C. Jiang, S. Li, W. Liu, H. Ju, S. Yang, C. Zhu, T. Chen, *ACS Appl Mater Interfaces* **2018**, *10*, 30314–30321.