Supplementary Material

Solution-Processed Ge (II)-based Chalcogenide Thin Films with Tunable Bandgaps for Photovoltaics

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This file includes Experiment Section, **Figures S1-S11**, and **Tables S1-S2**.

Experimental Section

Materials. All the chemicals were used as received without any further purification. GeO_2 (99.9999%) was purchased from Aladdin. H_3PO_2 (50 wt. % in H_2O) was purchased from Sigma-Aldrich. Thiourea (99%) and selenourea (99.97%) were purchased from Alfa Aesar.

GeS Film Deposition. GeO_2 (0.8 mmol), H_3PO_2 (2 ml), and ultrapure water (10 ml) were added into a 20 ml sample bottle. The mixtures were fully dissolved under magnetic stirring at 95 ^oC for 30 min. Thiourea (0.8 mmol) was then added into this solution, and a clear and transparent solution was obtained. Afterwards, the solution was transferred into a Teflon tank (50 ml) of an autoclave containing 30 ml of ultrapure water, and the FTO substrate was placed in the aqueous solution. The autoclave was then sealed and the hydrothermal deposition was conducted at 160 °C for 4 h. Consequently, the autoclave was naturally cooled to room temperature. The film was taken out, dried by N_2 gas in the ambient air. Afterwards, the film was annealed on a hotplate in a glove box filled with N_2 at 380 ^oC for 5 min. Finally, the film was taken off the hotplate and cooled to room temperature in the glove box.

$GeSe_{1-x}S_x$ Film Deposition. GeO_2 (0.8 mmol), H_3PO_2 (2 mL), and ultrapure water (10 mL) were added into a 20 mL sample bottle. The mixtures were fully dissolved under magnetic stirring at 95 ^oC for 30 min. Thiourea and selenourea mixed in a certain proportion (total 0.8 mmol) was then added into this solution. Afterwards, the solution was transferred into a Teflon tank (50 mL) of an autoclave containing 30 mL of ultrapure water, and the FTO substrate was placed in the aqueous solution. The autoclave was then sealed and the hydrothermal deposition was conducted at 160 °C for 4 h. Consequently, the autoclave was naturally cooled to room temperature. The film was taken out, dried by N_2 gas in the ambient air. Afterwards, the film was annealed on a hotplate in a glove box filled with N_2 at 380 ^oC for 5 min. Finally, the film was taken off the hotplate and cooled to room temperature in the glove box.

GeSe Film Deposition. GeO_2 (0.8 mmol), H_3PO_2 (2 mL), and ultrapure water (10 mL) were added into a 20 mL sample bottle. The mixtures were fully dissolved under magnetic stirring at 95 ^oC for 30 min. Selenourea (0.8 mmol) was then added into this solution. Afterwards, the solution was transferred into a Teflon tank (50 mL) of an

autoclave containing 30 mL of ultrapure water, and the FTO substrate was placed in the aqueous solution. The autoclave was then sealed and the hydrothermal deposition was conducted at 100 °C for 4 h. Consequently, the autoclave was naturally cooled to room temperature. The film was taken out, dried by N_2 gas in the ambient air. Afterwards, the film was annealed on a hotplate in a glove box filled with N_2 at 350 ^oC for 5 min. Finally, the film was taken off the hotplate and cooled to room temperature in the glove box.

Solar Cell Fabrication. The full GeS thin-film solar cell had a structure of glass/FTO/GeS/CdS/i-ZnO/ITO/Ag. The GeS layer was deposited by solution-processed method described above. CdS buffer layer was deposited on the GeS layer by magnetron sputtering according to a previous report.[1] Window layers of i-ZnO and ITO were successively deposited by magnetron sputtering. The top Ag grid electrodes were finally deposited by thermal evaporation. The active area of the devices was 0.23 cm^2 defined by mechanical scribing.

Materials and Device Characterization. The crystal structure of GeS films was determined by powder X-ray diffraction (Regaku, D/Max-2500 diffractometer equipped with a Cu $K\alpha_1$ radiation, λ = 1.54056 Å). Raman spectrum (Horiba JobinYvon, LabRAM HR800) was measured under the excitation line of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300 W Al Kα radiation. The surface morphology was obtained using a Hitachi S-4800 scanning electron microscopy (SEM) and the atomic ratio of elements was measured by EDS equipped with SEM. The optical transmittance of GeS film was recorded via UV-vis-near IR spectrophotometer (UH4150, HITACHI). The current density–voltage (J–V) curves of photovoltaic devices were measured by a solar simulator (Newport, USA) equipped with 450 W xenon lamp (OSRAM) and a Keithley-2420 source meter. Light intensity was adjusted using a NREL certified Si solar cell with a KG^{-2} filter for approximating AM 1.5G light (100 mW cm^{-2}). During the test, the scanning range was -1 V~1 V, a total of 100 points were collected, and the scanning speed was 100 mV/s (step size 20 mV, interval time 200 ms). Forward scan is from -1 V to 1 V, and reverse scan is from 1 V to -1 V.

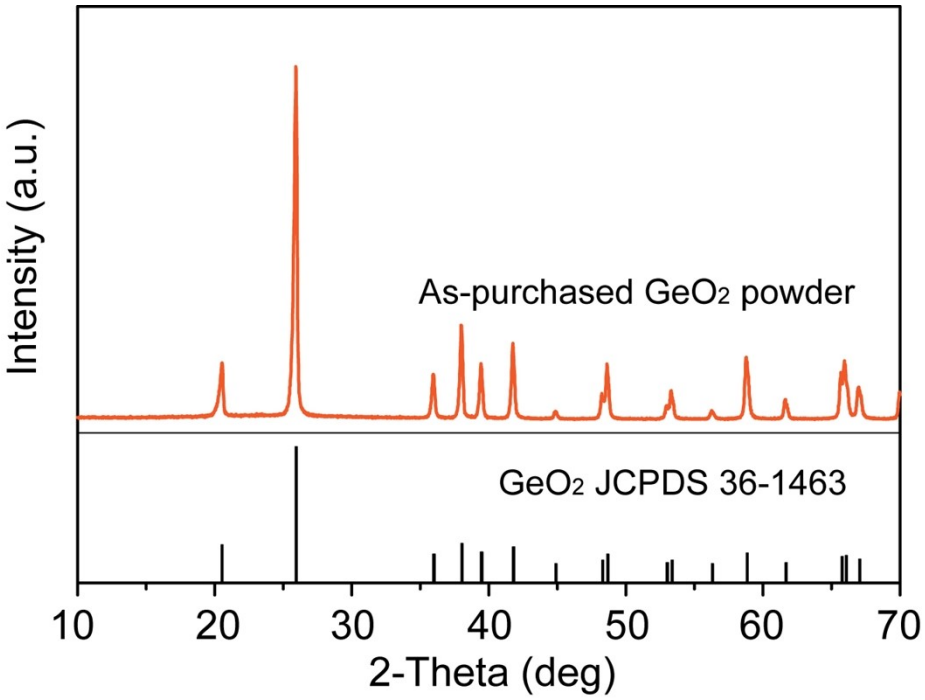

Figure S1. XRD pattern of as-purchased GeO_2 powder.

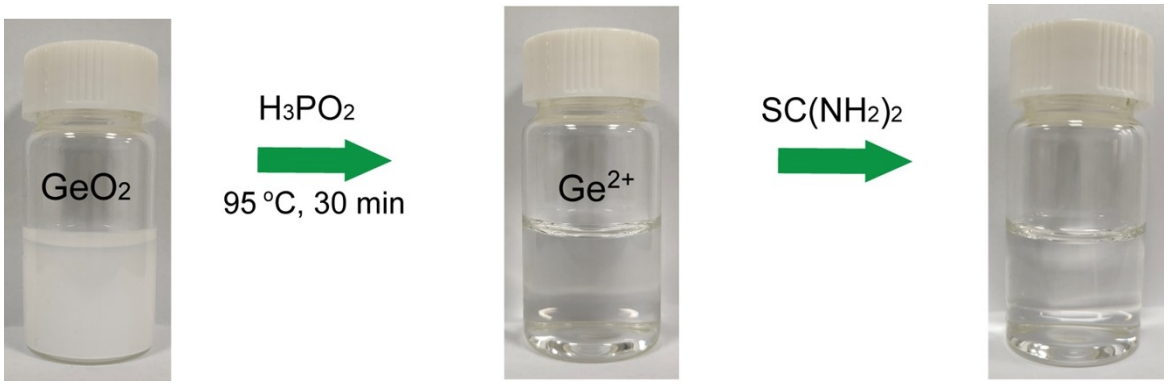

Figure S2. Photographs of GeO_2 powder in water before (left) and after the addition of (middle) H_3PO_2, and (right) thiourea.

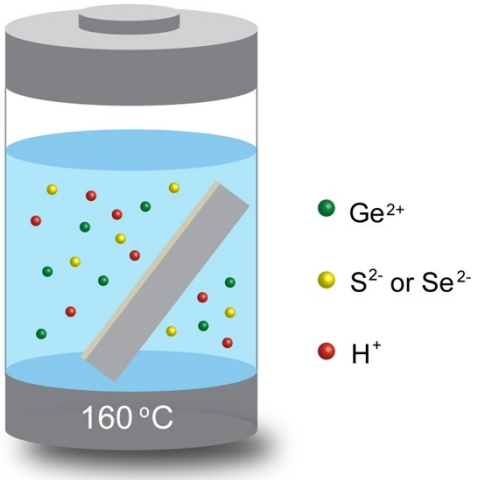

Figure S3. Schematic of the hydrothermal deposition of Ge (II)-based chalcogenide thin films in an autoclave.

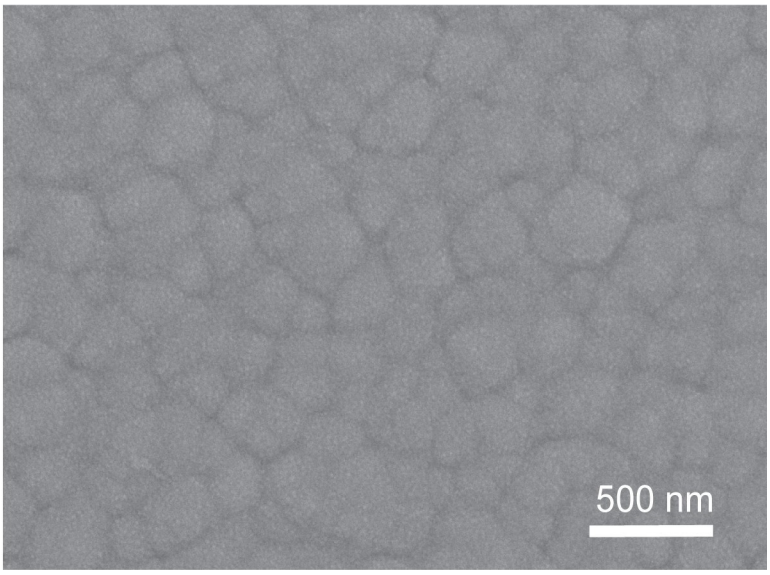

Figure S4. Top-view SEM image of as-deposited amorphous GeS film.

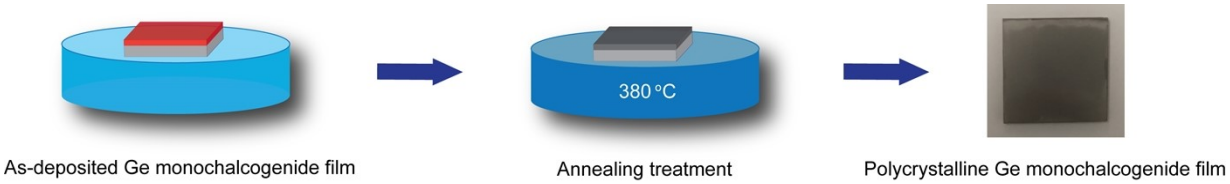

Figure S5. Schematic of the fabrication of polycrystalline Ge monochalcogenide films.

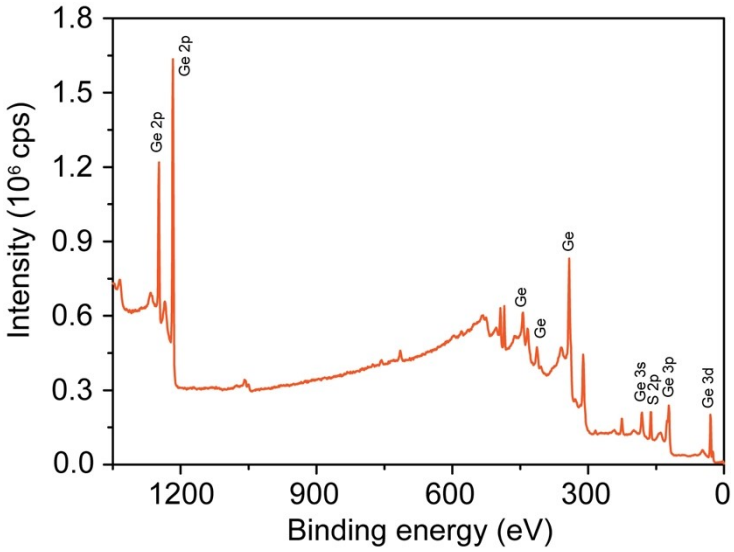

Figure S6. XPS spectrum of as-prepared GeS film.

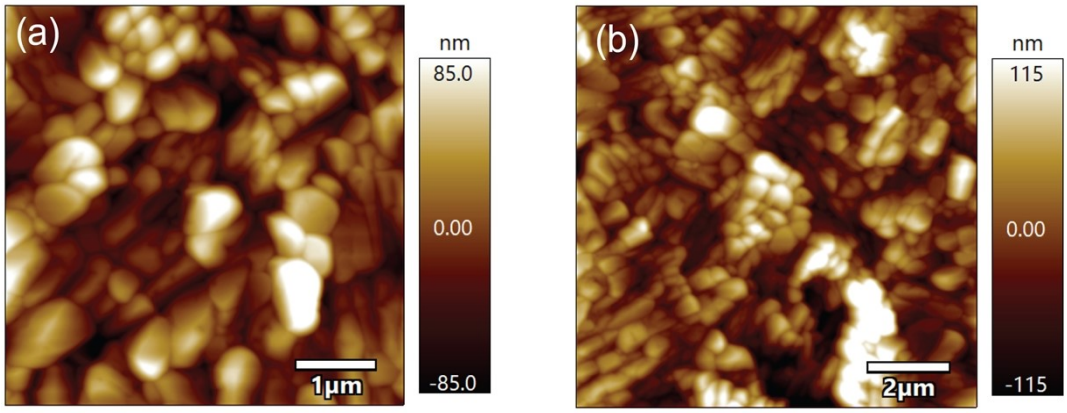

Figure S7. AFM images of (a) GeS film and (b) GeSe film.

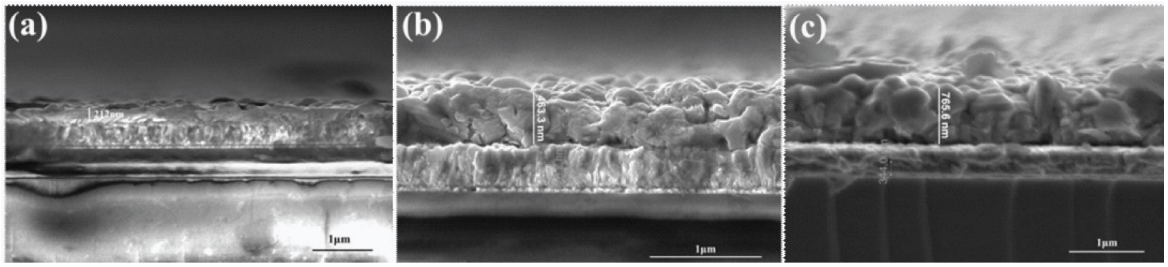

Figure S8. Cross-sectional SEM images of GeS prepared at different deposition times of (a) 1.5 h, (b) 3 h and (c) 6 h.

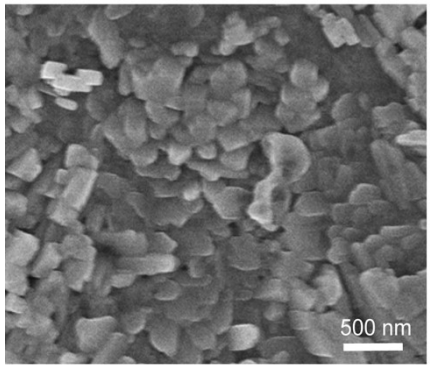

Figure S9. Top-view SEM image of GeSe film.

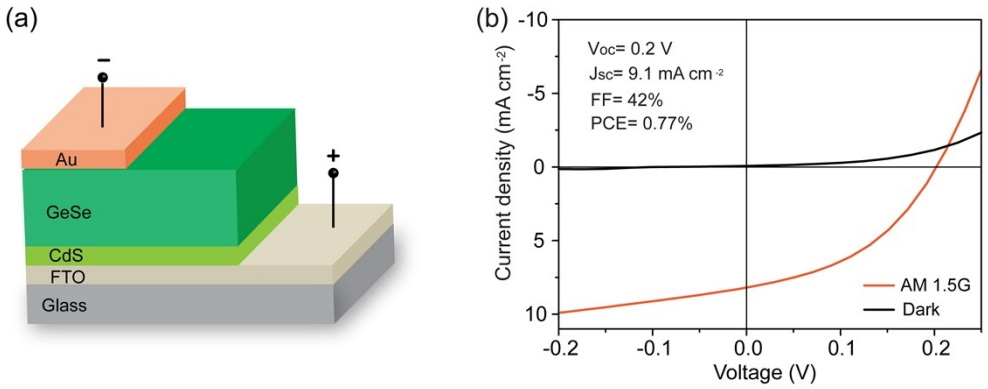

Figure S10. (a) Schematic of solution-processed GeSe solar cell. (b) J-V curves of GeSe solar cell in the dark and under 100 mW cm^{-2} simulated AM 1.5G irradiation, respectively.

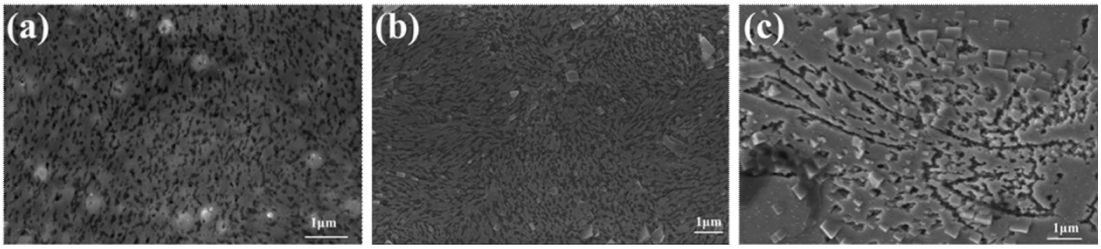

Figure S11. Top-view SEM images of (a) $GeSe_{0.25}S_{0.75}$ film, (b) $GeSe_{0.56}S_{0.44}$ film, (c) $GeSe_{0.72}S_{0.28}$ film.

Table S1. Standard potentials in the fabrication of Ge (II)-based chalcogenide thin films.[2]

Half reaction	Standard potential (V)
GeO_2 (hex) + $4H^+$ + $2e^-$ = Ge^{2+} + $2H_2O$	-0.132
H_3PO_3 + $2H^+$ + $2e^-$ = H_3PO_2 + H_2O	-0.499

Table S2. Result summary for the composition of $GeSe_{1-x}S_x$ films measured by EDS and XRD. The EDS results were measured at three randomly selected areas of the film.

Composition measured by EDS (Se/S atom ratio %)	Composition measured by XRD (Se/S atom ratio %)	Stoichiometry	Eg (eV)
0:1	0:1	GeS	1.71
0.2432:0.7568 0.2491:0.7509 0.2505:0.7495	0.25:0.75	$GeSe_{0.25}S_{0.75}$	1.53
0.5588:0.4412 0.5701:0.4299 0.5575:0.4425	0.56:0.44	$GeSe_{0.56}S_{0.44}$	1.35
0.7169:0.2831 0.7301:0.2699 0.7182:0.2818	0.72:0.28	$GeSe_{0.72}S_{0.28}$	1.28
1:0	1:0	GeSe	1.14

References

1. Liu, S.-C.; Li, Z.; Wu, J.; Zhang, X.; Feng, M.; Xue, D.-J.; Hu, J.-S., Boosting the efficiency of GeSe solar cells by low-temperature treatment of p-n junction. *Sci. China Mater.* **2021**, 64, 2118-2126.

2. Speight, J. G. A. *Lange's Handbook of Chemistry*, McGraw Hill Book Co.: New York, **2005**.