Supporting Information

Reducing Traps Density and Carriers Concentration by Ge Additive for An Efficient Quasi 2D/3D Perovskite Solar Cell

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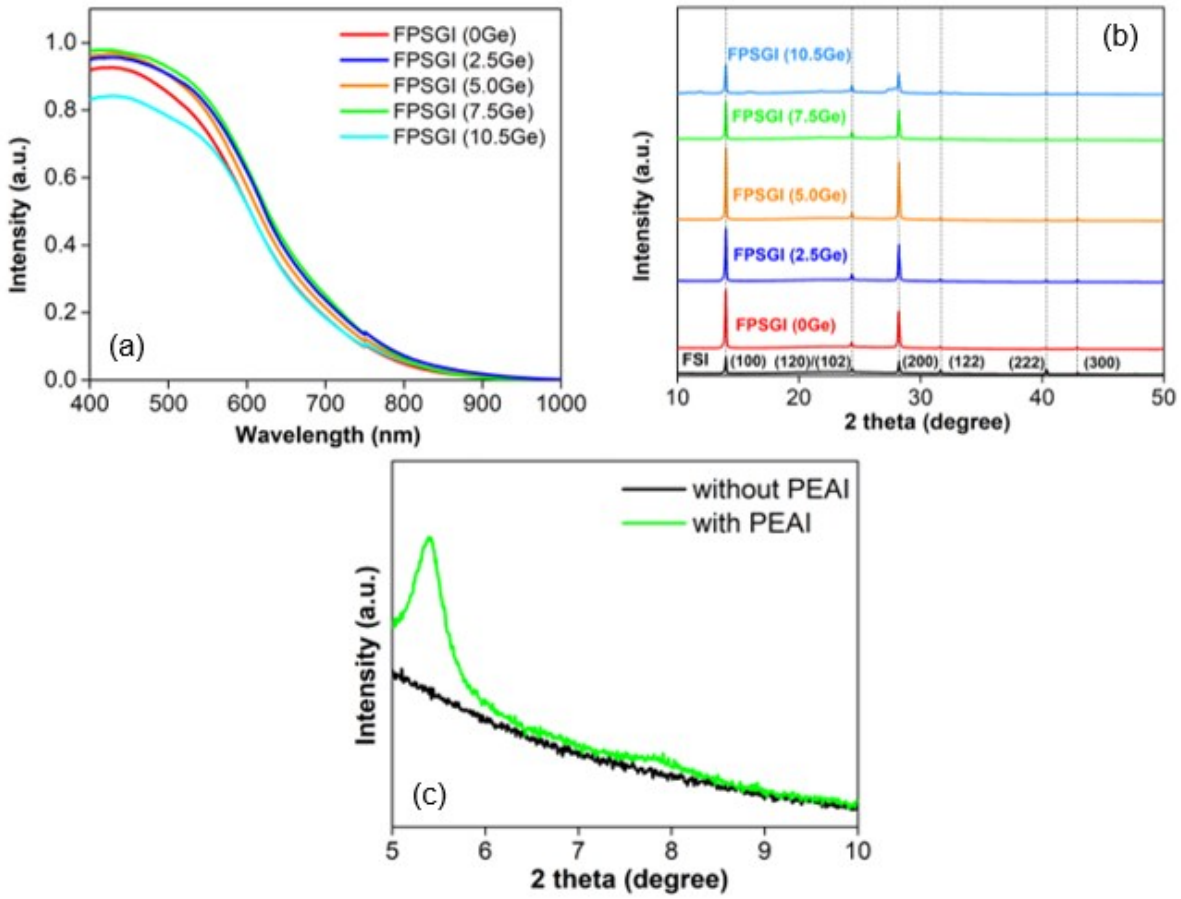

Figure S1. (a) Normalized absorption spectra of $FPS_{1-x}G_xI_3$ perovskite, (b) XRD of $FPS_{1-x}G_xI_3$ perovskite, and (c) magnified XRD patterns of perovskite with and without PEAI additive.

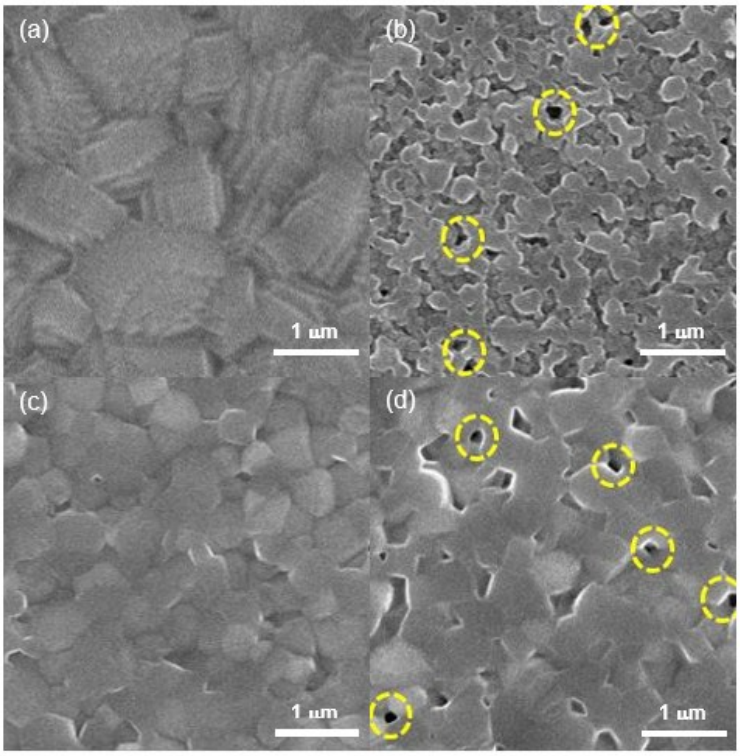

Figure S2. SEM of (a) FSI, (b) FPSI, (c) FPSGI (7.5Ge), and (d) FPSGI (10.5Ge). Pinholes are circled in yellow.

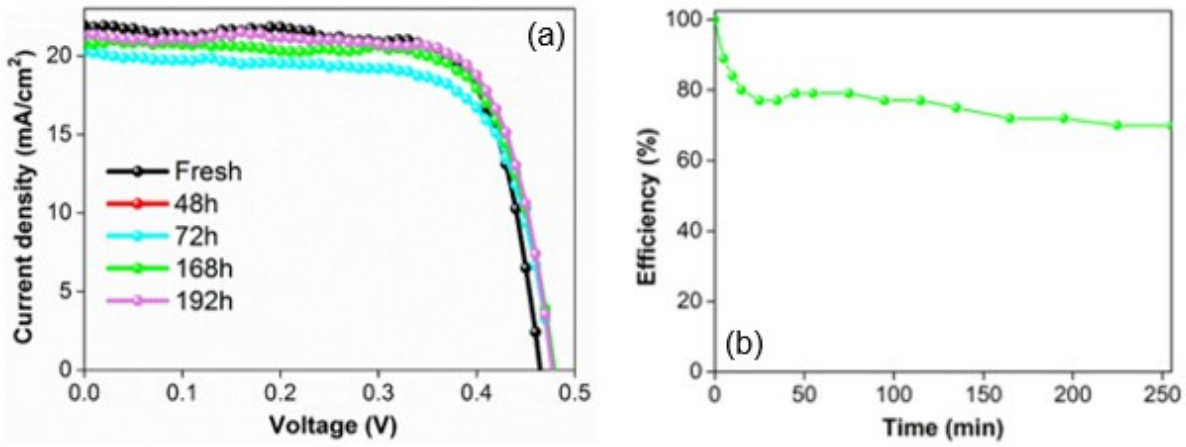

Figure S3. Shelf life of FPSGI (7.5 Ge) perovskite solar cell at (a) nitrogen atmosphere (in the glovebox) and (b) under 3h continuous light exposure at ambient condition.

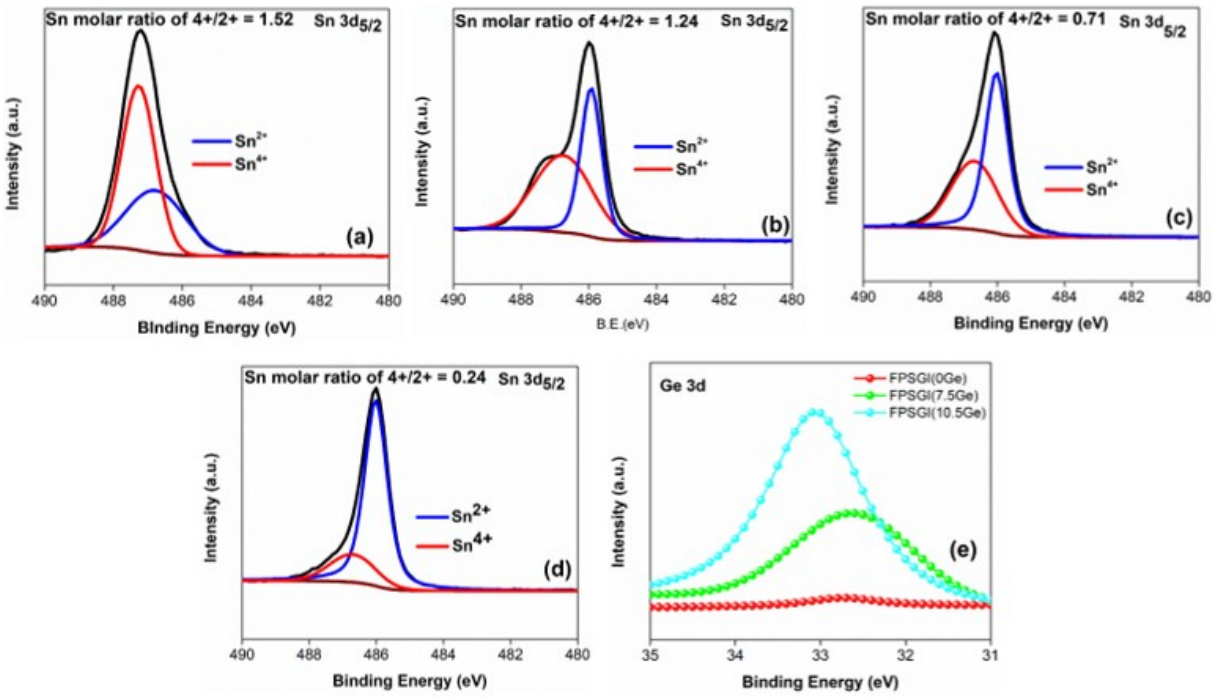

Figure S4. Sn^{4+}/Sn^{2+} molar ratios of (a) FSI, (b) FPSGI (0Ge), (c) FPSGI (7.5Ge), and (d) FPSGI (10.5Ge), and (e) intensity of GeO_x of $FPS_{1-x}G_xI_3$ with and without Ge.

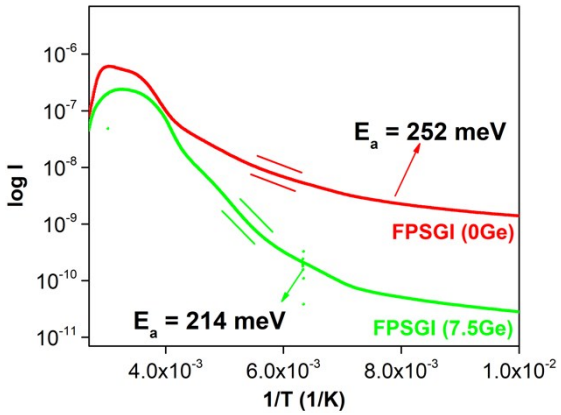

Figure S5. Activation energy, E_a of the trap states of perovskite with (green) and without Ge (red).

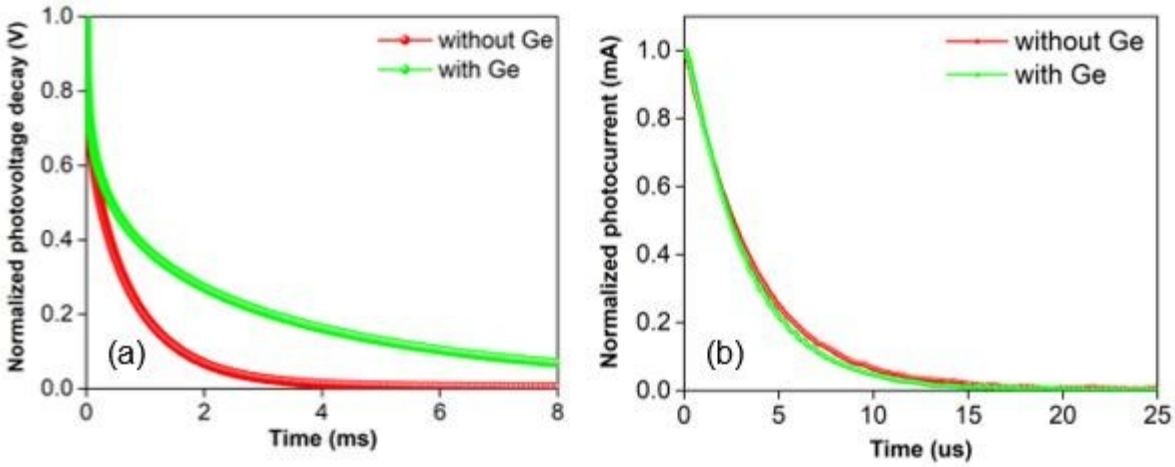

Figure S6. (a) Transient photovoltage and (b) transient photocurrent of $FPS_{1-x}G_xI_3$ perovskite solar cells either with or without Ge addition.

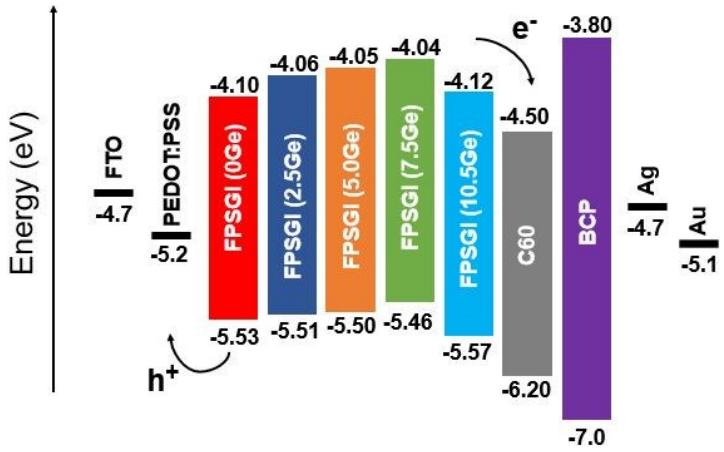

Figure S7. Energy level diagram of $FPS_{1-x}G_xI_3$ perovskites.

Table S1. Photovoltaic performances of mixed 2D-3D SnGe perovskite solar cells at different Ge concentrations after 192h.

Perovskites	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
FPSGI (0 Ge)	13.94	0.38	0.71	3.78
FPSGI (2.5 Ge)	19.97	0.41	0.69	5.70
FPSGI (5.0 Ge)	19.64	0.47	0.66	6.10
FPSGI (7.5 Ge)	21.28	0.48	0.75	7.57
FPSGI (10.5 Ge)	15.57	0.30	0.36	1.68

Table S2. Reproducibility of $FPS_{1-x}G_xI_3$ perovskite solar cells with 25 devices.

FPSGI (7.5Ge) no.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	21.17	0.46	0.72	7.08
2	20.67	0.46	0.73	7.03
3	21.92	0.46	0.73	7.45
4	21.62	0.46	0.72	7.20
5	21.48	0.47	0.73	7.39
6	21.36	0.47	0.72	7.24
7	20.48	0.47	0.70	6.73
8	20.13	0.47	0.72	6.71
9	20.47	0.47	0.73	6.99
10	20.47	0.47	0.73	6.97
11	20.25	0.48	0.70	6.74
12	20.28	0.47	0.68	6.55
13	19.81	0.48	0.69	6.49
14	19.82	0.47	0.70	6.56
15	19.09	0.48	0.70	6.34
16	19.77	0.47	0.75	7.02
17	20.75	0.48	0.73	7.29
18	20.82	0.47	0.73	7.16
19	21.37	0.47	0.62	6.25
20	21.16	0.47	0.69	6.91
21	21.12	0.47	0.63	6.31
22	19.83	0.48	0.72	6.90
23	19.75	0.48	0.69	6.54
24	20.32	0.48	0.72	7.05
25	20.73	0.48	0.71	7.02

FPSGI (0Ge) no.	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1	15.56	0.33	0.69	3.61
2	15.93	0.35	0.62	3.48
3	16.27	0.36	0.68	3.92
4	16.17	0.35	0.68	3.85
5	13.14	0.42	0.70	3.89
6	13.15	0.42	0.71	3.91
7	13.45	0.41	0.68	3.81
8	13.08	0.41	0.69	3.72
9	12.91	0.42	0.68	3.71
10	12.61	0.42	0.69	3.62
11	15.46	0.35	0.68	3.69
12	15.12	0.34	0.69	3.56
13	12.05	0.47	0.60	3.40
14	11.72	0.45	0.59	3.15
15	11.72	0.44	0.50	2.57
16	10.71	0.46	0.57	2.86
17	17.35	0.32	0.67	3.70
18	17.24	0.31	0.65	3.51
19	12.39	0.39	0.70	3.42
20	12.37	0.39	0.70	3.36
21	14.15	0.33	0.72	3.40
22	14.31	0.38	0.69	3.77

23	13.24	0.39	0.68	3.52
24	13.05	0.39	0.69	3.50
25	15.70	0.29	0.64	2.89

Table S3. The role of Ge in terms of shunt and series resistances.

Perovskites	Shunt resistance, R_{sh} (kΩ)	Series resistance, R_s (Ω)
$FASnI_3$ (FSI)	2.68	33.53
FPSGI (0Ge)	19.16	24.69
FPSGI (7.5 Ge)	33.78	18.56

Experimental section

Materials: All materials were used without any purification. Tin (II) iodide (SnI_2, 99.99%), tin (II) fluoride (SnF_2, 99%), germanium (II) iodide (GeI_2, >99.8%), N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, ≥99.9%), chlorobenzene (anhydrous, 99.8%), and bathocuproine (BCP) were purchased from Sigma-Aldrich. Formamidinium iodide (FAI, >98%) and 2-phenylethylamine hydroiodide (PEAI, 98%) were obtained from TCI. Acetone and isopropanol were obtained from Wako, Japan. The aqueous poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) was purchased from Clevious PVP AI 4083).

Perovskite Film Fabrication: The quasi-2D $FAPEASn_{1-x}Ge_xI_3$ ($FPS_{1-x}G_xI$) perovskite solution was prepared by dissolving 0.92 M FAI, 0.08 M PEAI, (1-x M) SnI_2, x M GeI_2, and 0.1 M SnF_2 into DMF:DMSO in a 4:1 ratio. 40 µl of the perovskite precursor solution was spin coated on the TSC substrate at 5000 rpm for 50 s. 175 µl of chlorobenzene was casted after 13-15 s and the film was completed by annealing at 70 ºC for 10 min. For TSC measurement, the TSC film was coated with PMMA spun at the condition of 3000 rpm for 60s.

Film Characterization: The Hall measurement was performed using ECOPIA Hall effect measurement system (HMS-3000 VER 3.52). The X-ray photoelectron spectroscopy (XPS) analysis was performed using Shimadzu Kratos Axis-Nova spectrometer where Al Kα excitation source was used at pass energy of 80 eV with an energy resolution of 1000 meV. The UV-Vis measurements were performed via JASCO V-670 Spectrophotometer. The valence band of perovskite and density of states (DOS) were determined using photoelectron yield spectroscopy (PYS) by Bunkoukeiki KV205-HK ionization energy measurement system with an applied voltage of -5.0 V. The X-ray diffraction (XRD) measurement was performed using RINT-ULTIMA III, Rigaku, Japan. The EIS and Mott Schottky were performed via PAIOS, Fluxim. The morphological structure of the perovskites was captured using SEM (JEOL JSM-6340). Transient photovoltage and photocurrent were measured through PAIOS, Fluxim where the illumination was provided by a 60 mW white LED. The TSC measurements were conducted via Rigaku thermally stimulated femtoampere electron trap tracer. Generally, the temperature dependence trap depth and density evaluations are kick started when the carrier traps were filled by the carriers generated from the electrodes in a liquid nitrogen filled condition under a small forward bias of 10 V. Subsequently, the trapped carriers were released along the increasing temperature (constant rate of 2 °C/min) under a small reverse bias, which gave rise to TSC curve.[1] The photovoltaic measurement of the solar cell was performed using a Keithley 4200 source meter and a 100 mW/cm^2 AM 1.5G solar simulator (Bunkouki CEP-2000SRR), while the IPCE spectrum was measured using a monochromatic Xenon lamp (Bunkouki CEP-2000SRR). The measured area was fixed to be 0.1 cm^2 non-reflective metal mask.

Reference

[1] C. H. Ng, K. Nishimura, N. Ito, K. Hamada, D. Hirotani, Z. Wang, F. Yang, S. Likubo, Q. Shen, K. Yoshino, T. Minemoto and S. Hayase, *Nano Energy,* 2019, **58**, 130-137.