Two Birds with One Stone: Dual Grain-Boundary and Interface Passivation Enables > 22% Efficient Inverted Methylammonium-Free Perovskite Solar Cells

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Device and Material Characterization

Current density–voltage (J–V) measurements. The J-V characteristics of the PSCs were measured with a class AAA xenon-lamp solar simulator (Newport Oriel Sol3A) with a scan rate set at 0.6 V/s using a sourcemeter (Keithley 2400) with an air-mass 1.5 global (AM1.5G) spectra (100 mW/cm²). The solar simulator irradiation intensity was calibrated using a certified Si solar cell (Fraunhofer ISE) equipped with a KG5 band pass filter. The stabilized PCE of the PSCs was determined by measuring the photocurrent at the maximum power point (MPP) by using a perturb and observing algorithm under continuous AM 1.5G illumination, while the temperature of the devices was controlled at 25 °C by a Peltier element connected to a microcontroller during the measurements. The measurement was performed in a nitrogen-filled glovebox.

External Quantum Efficiency Measurements (EQE). The EQE was measured using a PVE300 photovoltaic QE system (Bentham EQE system). A chopping frequency of ~570 Hz with an integration time of 500 ms to acquire the spectra in a wavelength range from 300 to 850 nm was used. An illumination spot (1.5mm) was utilized to obtain the average over possible variations in the EQE spectra.

Scanning electron microscopy (SEM). High-resolution field emission cross-sectional and top-view SEM images of the perovskite thin films based grain boundary-incorporation and surface treatment processes were taken using a Zeiss LEO1530 VP scanning electron microscope with an in-lens detector and an aperture size of 20 μ m. The SEM images were captured using a 3-kV acceleration voltage.

X-ray diffraction (XRD). The crystal structure of the perovskite layers was carried out utilizing XRD (Bruker D2Phaser system) with Cu-K_{α} radiation (λ = 1.5405 Å) in Bragg–Brentano configuration using a LynxEye detector. The XRD was taken from the perovskite layer deposited on the ITO/2PAcz substrate to obtain the same perovskite nucleation as well as crystallization as in the solar cells.

UV-Vis Spectrophotometry (UV). Transmittance and reflectance spectra of the perovskite thin films were measured using a Bentham PVE300 spectrophotometry setup equipped with a monochromator and a modulated source. A chopper frequency in the range of 400 Hz was applied.

Cathodoluminescence (CL). Cathodoluminescence (CL) measurement is performed on an FEI Verios scanning electron microscope (SEM) equipped with a GatanMonoCL4 Elite. The measurements are performed at 3 kV / 25 pA. CL images were captured in panchromatic mode with appropriate dichroic filters (band pass filter with 500 \pm 40 nm).

X-ray and Ultraviolet Photoelectron Spectroscopy (XPS and UPS). Photoelectron spectroscopy was performed with a PHI 5000 VersaProbe at the Clustertool at InnovationLab GmbH in Heidelberg. The samples were introduced from the glovebox with exposures to air <1 min. The pressure in the ultra-high vacuum system is around 10⁻⁹ mbar. For XPS, monochromatic Al Kα radiation with an excitation energy of 1486.6 eV was used. UPS was carried out with a He-discharge lamp using the He-I emission with an energy of 21.22 eV. Pass energies of 11.75, 2.95, and 0.59 eV were used for XPS core-level spectra, UPS valence band and UPS secondary electron cutoffs, respectively. For the measurements of the secondary electron cut-off, a bias of -5 V was applied. The takeoff angle for all measurements was 90°. The binding energies of the spectra were calibrated with respect to the Fermi level of an Ar⁺-ion etched silver foil. For the XPS core level spectra shown in this work a background subtraction was performed using a Shirley type or linear background.^{1–3} Stoichiometric ratios were determined using corrected peak areas using CasaXPS software. For the correction of the peak areas, we used calculated photoionization cross-sections by Scofield,⁴ angular distribution correction for a source-analyzer-angle of 45° based on Reilman et al.,⁵ an empirical transmission function determined for the used system, and an escape depth correction with a kinetic energy exponent of 0.7. The peak area correction was verified using the I 3d and I 4d emissions from a survey spectrum. The derived corrected area ratio of I3d/I4d is 1.03 and thereby in good agreement with the expected value of 1. The inelastic mean free path (IMFP) for the calculation of the 2D passivation overlayer thickness was estimated using the TPP-2M equation in the NIST database software.^{6,7} We estimated a IMFP value of 3.1 nm for the photoelectrons of the Pb 4f7/2 emission. This IMFP value and a Lambert-Beer type exponential law were used to calculate the 2D passivation overlayer thickness from the intensity decay of the Pb $4f_{7/2}$ component emitted from the underlying 3D bulk phase (see Fig. S28).

Kelvin probe force microscopy (KPFM). KPFM was measured on an Oxford Instruments/Asylum Research MFP-3D AFM in an argon glovebox (level of humidity below 0.2 ppm, level of oxygen below 0.1 ppm) for all experiments. The typical resonance frequency of the cantilevers (Bruker Model: SCM-PIT-V2) was ~65 kHz, spring constant of 2 N/m, a tip radius of 25 nm and a tip height of 10 to 15 μ m. Tip, tip cone and cantilever are coated with PtIr (work function ~5.5 eV)⁸ on both sides. The topography feedback was performed with amplitude modulation (AM) on the first eigenmode and the oscillation amplitude was kept to approximately \approx 20-30 nm for all measurements. To perform the KPFM feedback, we used a Zurich Instruments HF2 Lock-In amplifier for all heterodyne frequency modulation (FM) experiments. The electric drive amplitude of the ω_E signal was 2 V. We grounded the sample via the sample holder with an external wire to ground level of the Zürich Lock-In Amplifier. The compensating U_{DC} was applied to the tip, minimizing electrostatic tip–sample interactions.⁹ In the tip-bias configuration, the measured CPD signal, U_{CPD}, is connected to the work functions of sample, Φ_{sample} , and tip, Φ_{tip} , by

$$U_{CPD} = \frac{1}{e} (\Phi_{tip} - \Phi_{sample})$$

Thus, a lower value of $U_{\mbox{\scriptsize CPD}}$ corresponds to a higher sample work function.

Photoluminescence Quantum Yield (PLQY). PLQY measurements were carried out inside an integrating sphere (LabSphere, 15 cm diameter) in ambient air (relative humidity <30%). A green laser (Coherent or LD-515-10MG from Roithner Lasertechnik) was directed into the sphere *via* a small entrance port. An optical fiber was used to collect the emission from the exit port of the sphere and guide it to the spectrometers (QE65 Pro from Ocean Optics and AvaSpec-ULS2048x64TEC from Avantes). The spectral response was calibrated using a calibration lamp (HL-3plus-INT-Cal from Ocean Optics). Raw measured spectra were recalculated to give power spectra using the integration time. The PLQY was determined using the method described by de Mello *et al.*¹⁰ The samples were placed at an angle of 15° with respect to the laser beam to avoid specular reflectance toward the entrance port. The radiative limit of the *V*_{OC} (V_{OC-rad}), the implied *V*_{OC} (*V*_{OC-imp}) (Fig. 3c) and the pseudo *JV*-curves (Fig. S14) were determined from the (intensity-dependent) PLQY measurements as described by Stolterfoht et al.¹¹ and Kirchartz et al.¹²

Time-resolved photoluminescence (TPRL). Time-resolved photoluminescence (TRPL) measurements were carried out in gated-mode with a pulsed laser of 532 nm. A repetition rate of 1 kHz and a pulse width of 0.8 ns was used for the excitation of the samples. All measurements were performed with a pump fluence of ~20-30 nJ/cm². The photoluminescence was captured using an ACTON spectrometer and a CCD camera PIMAX512 at room temperature. The measurements were carried out in the air.

Thermal admittance spectroscopy (TAS). The thermal admittance spectroscopy (TAS) measurements were performed on Paios (Fluxim AG)- platform for all-in-one-characterization of solar cells and OLEDs at short circuit in the dark with the perturbation AC voltage amplitude of 35 mV in a frequency range 0.5 Hz-1M Hz. The temperature was varied between 278 and 318 K using liquid-cooled Peltier cryostat where the sample chamber was filled with nitrogen gas. The theoretical formalism of the TAS can be found in the literature. ^{13–16}

Space charge limited current (SCLC) measurements. Space charge limited current (SCLC) measurements were performed on Paios (Fluxim AG)- platform for all-in-one-characterization of solar cells and OLEDs. The dark *J-V* measurements are plotted on a log-log scale. Generally, three distinct regions are observed in the *J-V* plot: (1) Ohmic region with slope 1, (2) trap filling region with a slope higher than 2 and (3) trap-free SCLC region with a slope of 2. The mobility value is typically extracted by the quadratic region of the *J-V* curve which is governed by the Mott-Gurney equation:

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3}$$

where ε_0 is the permittivity of vacuum, ε is the dielectric constant of the material, μ is the mobility of the charge carrier and d is the thickness of the active layer. The electron mobility is extracted by fitting the above equation. It should be noted that the dielectric constant is taken as 26 which is calculated from the capacitance-frequency measurement. The trap densities for the devices are calculated from the trap-filled-limit voltage:

$$V_{TFL} = \frac{qn_t d^2}{2\varepsilon\varepsilon_0}$$

Where q is the elementary charge, n_t is the trap density and and d is the thickness of the active layer. The trapfilled-limit-voltage V_{TFL} is the voltage at the intersection point of the tangent with slope 1 and tangent with slope higher than 2.^{17,18}

Experimental Section

Materials:

2PACz (TCI, CAS: 20999-38-6), Lead iodide (Pbl₂: TCI, CAS: 10101-63-0), Formamidinium iodide (FAI: Dyenamo, CAS: 879643-71-7), Cesium chloride (abcr, CAS: 7647-17-8), 2-phenylethylammonium chloride (PEACI: Sigma-Aldrich; CAS: 156-28-5), *n*-Octylammonium Chloride (OACI: Greatcell solar materials, CAS: 142-95-0), *n*-Butylammonium Chloride (BACI: TCI, CAS: 3858784, Fullerene-C₆₀ (C₆₀: Sigma-Aldrich, CAS: 99685-96-8), Bathocuproine (BCP: Lumtec, CAS: 4733-39-5), (MgF₂: Sigma-Aldrich , CAS: 7783-40-6) . All solvents including *N*,*N*-dimethylformamide, \geq 99.9% (DMF, CAS: 68-12-2), Dimethyl sulfoxide (DMSO) anhydrous, \geq 99.9% CAS: 67-68-5), Chlorobenzene (CB) anhydrous, 99.8%, CAS: 108-90-7), 2-Propanol, \geq 98%, (IPA, CAS: 67-63-0) were ordered from Sigma-Aldrich. Ethanol absolute 99.8% was ordered from VWR Chemicals.

Perovskite solar cell Fabrication:

The planar p-i-n perovskite solar cells were fabricated with the architecture of: $glass/ITO/2PACz/Cs_{0.18}FA_{0.82}PbI_3/C_{60}/BCP/Ag$.

ITO substrates (sheet resistance 15 Ω /sq, Luminescence Technology, CAS: 50926-11-9) were cut in 0.16 cm × 0.16 cm and cleaned with acetone and isopropanol in an ultrasonic bath for 10 minutes each. The substrates were further treated with oxygen plasma for 3 min before the deposition of the hole transport layer (HTL).

A thin layer of 2PACz HTL was deposited on the ITO substrate by spin-coating at 3000 rpm for 30 s and subsequently annealed at 100 °C for 10 min. The 2PACz precursor solution was prepared by dissolving 2PACz in anhydrous Ethanol with a concentration of 1 mmol/l. The prepared solution was put in an ultrasonic bath for 15 min before it was used. The reference double cation perovskite Cs0.18FA0.82Pbl3 precursor solution was prepared by mixing PbI₂ (507 mg: 10% excess of PbI₂), CsCl (30 mg) and FAI (172 mg) in 1 mL solvent mixture of DMF:DMSO 4:1 volume ratio.¹⁷ The reference perovskite film was deposited on the substrate at 1000 rpm (acceleration 2000 rpm s⁻¹) for 10 s and 5000 rpm (acceleration rate 2000 rpm s⁻¹) for 30 s. 20 s after the start of the second step spin-coating, 150 µL Chlorobenzene was quickly dropped on the spinning substrate. The samples were then annealed at 150 °C for 30 min in an inert atmosphere. For preparing surface passivation (SP) perovskite layer, PEACI dissolved in IPA with different concentrations (1.5 and 3mg) was dynamically spin-coated on top of the reference perovskite film at 5000 rpm (acceleration 2000 rpm s⁻¹) for 30 s, followed by annealing at 100 °C for 5 min. For preparing the grain boundary passivation (GBP) perovskite layer, 25 µL of PbCl₂:PEACl solution with a molar ratio of 1:1 dissolved in 1 mL DMSO was added in the reference perovskite precursor solution and then was heated at 150 °C for 30 min. In the case of preparing the grain boundary perovskite layer based on other chloride-based long-chain organic alkylammonium salts BACI and OACI, the same procedure was applied. Finally, for preparing grain boundary passivation & surface passivation (GBP&SP) perovskite layer, the PEACI interlayer was spin-coated on top of the GBP perovskite film, followed by annealing at 100 °C for 5 min. The electron transport layer, 23 nm C₆₀ and 3 nm BCP, were thermally evaporated at an evaporation rate of 0.1-0.2 Å/s at a pressure of around 10⁻⁶ mbar. Afterwards, 100 nm Ag was thermally evaporated using a shadow mask with an active area of 0.12 mm² to complete the perovskite solar cells with 4 pixels per substrate. It should be noted that in order to reduce the reflection in perovskite solar cell, 125 nm MgF₂ as an antireflection layer was evaporated on top of the Ag.

Table S1: Photovoltaic parameters in reverse (BW) and forward (FW) bias of perovskite solar cells based on the reference (Ref), grain boundary passivation (GBP), surface passivation (SP), and combination of grain boundary & surface passivation (GBP&SP) processes.

	V _{oc} (V)	J _{sc} (mA/cm²)	FF	PCE (%)
BW	1.086	23.9	78.6	20.4
FW	1.08	23.6	75.6	19.3
BW	1.114	23.5	79.3	20.8
FW	1.11	23.6	77.9	20.4
BW	1.131	23.7	82.3	22.1
FW	1.131	23.6	79.9	21.3
BW	1.162	23.5	83.2	22.7
	1.153	23.6	80.6	22.0
	BW FW BW FW BW FW BW FW	BW 1.086 FW 1.08 BW 1.114 FW 1.111 BW 1.131 FW 1.131 BW 1.131 FW 1.131 FW 1.153	BW 1.086 23.9 FW 1.08 23.6 BW 1.114 23.5 FW 1.111 23.6 BW 1.131 23.7 FW 1.131 23.6 BW 1.131 23.7 FW 1.131 23.6 FW 1.131 23.6 FW 1.162 23.5 FW 1.153 23.6	BW 1.086 23.9 78.6 FW 1.08 23.6 75.6 BW 1.114 23.5 79.3 FW 1.11 23.6 77.9 BW 1.131 23.7 82.3 FW 1.131 23.6 79.9 BW 1.131 23.6 79.9 FW 1.131 23.6 79.9 FW 1.131 23.6 80.6

Table S2: The calculated electron mobilities and trap densities for the perovskite solar cells based on the reference (Ref), surface passivation (SP), grain boundary passivation (GBP), and combination of grain boundary & surface passivation (GBP&SP) processes.

Device	Electron mobility (cm ² V ⁻¹ s ⁻¹)	n _t (cm⁻³)
Ref	4.9 x10 ⁻³	9.2 x10 ¹⁵
GBP	7.2 x10 ⁻³	6.5 x10 ¹⁵
SP	6.3 x10 ⁻³	5.4 x10 ¹⁵
GBP&SP	10.0 x10 ⁻³	3.7 x10 ¹⁵

Table S3: The calculated hole mobilities and trap densities for the perovskite solar cells based on the reference (Ref), surface passivation (SP), grain boundary passivation (GBP), and combination of grain boundary & surface passivation (GBP&SP) processes.

Device	Hole mobility (cm ² V ⁻¹ s ⁻¹)	n _t (cm ⁻³)
Ref	4.0 x10 ⁻⁴	4.2 x10 ¹⁵
GBP	6.2 x10 ⁻⁴	3.4 x10 ¹⁵
SP	5.3 x10 ⁻⁴	3.0 x10 ¹⁵
GBP&SP	7.9 x10 ⁻⁴	2.9 x10 ¹⁵

Table S4: The atomic ratio of CI/Pb, Cl/Pb, Cs/Pb, FA/Pb, and I Cl/Pb for the reference (Ref) and grain boundary (GBP) perovskite films treated with different concentration of PEACI (1.5, 3 and 10 mg/ml) as a surface passivation layer (referred to as: SP(1.5), SP(3), SP(10), GBP&SP(1.5), GBP&SP(3) and GBP&SP(10), respectively.

Atomic ratio	I / Pb	Cl / Pb	I+Cl/ Pb	Cs / Pb	FA / Pb
Ref	3.06	0.00	3.06	0.11	0.55
SP(1.5)	2.95	0.31	3.26	0.14	0.43
SP(3)	2.64	0.90	3.55	0.11	0.27
SP(10)	1.41	3.30	4.71	0.00	0.00
GBP	2.67	0.22	2.89	0.16	0.43
GBP&SP(1.5)	1.87	1.15	3.02	0.29	0.24
GBP&SP(3)	1.49	1.79	3.28	0.24	0.17
GBP&SP(10)	1.07	4.07	5.14	0.00	0.00

Table S5: Estimation for the 2D RP passivation layer thickness, the atomic ratio of PEA to the 2D Pb (II) phase and the corresponding calculated n.

	estimated 2D thickness	PEA / Pb II	calculated n
Ref	0.00	0.00	0.00
SP(1.5)	0.75	1.68	1.19
SP(3)	2.38	1.19	1.69
SP(10)	-	1.74	1.15
GBP	0.00	0.41	4.85
GBP&SP(1.5)	1.53	0.77	2.59
GBP&SP(3)	4.30	0.85	2.35
GBP&SP(10)	-	2.10	0.95



Fig. S1: Reported champion power conversion efficiencies (PCEs) measured in the *J*-*V*-scan for *n*-*i*-*p* vs. *p*-*i*-*n* perovskite solar cells compared to the champion PCE of 22.7% reported in this work.



Fig. S2: (a) Reported champion open-circuit voltage (V_{OC}) with respect to the Shockley-Queisser (S-Q) limit for the respective bandgap for *n-i-p* vs. *p-i-n* perovskite solar cells (PSCs). The bandgap of all PSCs was determined from the inflection point of the external quantum efficiency spectra extracted from literature as suggested by Kirchartz *et al.*¹² (b) Reported champion V_{OC} x fill factor (FF) product of *n-i-p* vs. *p-i-n* PSCs with respect to the S-Q limit. We note that the highest reported value in 2019 was based on a PSC with PCE <21% given the rather low J_{SC} .²⁰



Fig. S3: Comparison of photovoltaic parameters (extracted from the reverse scan of the J-V curves) of reference (Ref) and grain boundary passivation perovskite solar cells prepared with various amounts of PEACI:PbCl₂ solution added into the Ref perovskite solution (10, 25 and 40 μ L, referred to as GBP(10), GBP(25) and GBP(40), respectively). (a) Power conversion efficiency (PCE), (b) open-circuit voltage (V_{OC}), (c) short-circuit current density (J_{SC}), and (d) fill factor (FF).



Fig. S4: The effect of the PEACl concentration (1.5 mg/ml and 3 mg/mL) as a surface passivation interlayer on photovoltaic parameters of reference (Ref) and grain boundary passivation (GBP) perovskite solar cells (referred to as: SP(1.5), SP(3), GBP&SP(1.5) and GBP&SP(3) respectively. (a) Power conversion efficiency (PCE), (b) opencircuit voltage (V_{oc}), (c) short-circuit current density (J_{sc}), and (d) fill factor (FF).



Fig. S5: Absorptance spectra of double-cation $Cs_{0.18}FA_{0.82}PbI_3$ perovskite films deposited on the glass substrates prepared without any modification (Ref) as well as with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP).



Fig. S6: Optical bandgap extracted from (a) the Tauc plot assuming a direct bandgap and (b) the inflection point of the external quantum efficiency (EQE) spectra of double-cation $Cs_{0.18}FA_{0.82}PbI_3$ perovskite films prepared without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP) and grain boundary & surface passivation (GBP&SP).



Fig. S7: External quantum efficiency (EQE) and corresponding integrated short-circuit current density (J_{SC}) of the best-performing perovskite solar cells prepared without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP). The inset shows the respective integrated J_{SC} .



Fig. S8: Comparison of the open-circuit voltage (V_{OC}) of dual passivated perovskite solar cells based on the incorporation of PEAI:PbCl₂, PEABr:PbCl₂ and PEACI:PbCl₂ in the precursor solution, as well as surface treatment with PEAI, PEABr and PEACI solution, respectively (referred to as: Ph-Cl/PEAI, Ph-Br/PEABr and Ph-Cl/PEACI).



Fig. S9: Photovoltaic parameters of the perovskite solar cells without any modification (Ref) and with surface passivation process, treated with OACl, BACl and PEACl solution on top of the reference perovskite layer respectively. (a) Power conversion efficiency (PCE), (b) open-circuit voltage (V_{OC}), (c) fill factor (FF), (d) short-circuit current density (J_{SC}).



Fig. S10: Photovoltaic parameters of the perovskite solar cells without any modification (Ref) and with combined grain boundary & surface passivation processes based on the incorporation of OACI:PbCl₂ (Oc-Cl), BACI:PbCl₂ (Bu-Cl) and PEACI:PbCl₂ (Ph-Cl) in the precursor solution, as well as surface treatment with OACI, BACI and PEACI solution, respectively (referred to as: Oc-Cl/OACI, Bu-Cl/BACI and Ph-Cl/PEACI). (a) Power conversion efficiency (PCE), (b) open-circuit voltage (*V*_{OC}), (c) fill factor (FF), (d) short-circuit current density (*J*_{SC}).



Fig. S11. Photoluminescence quantum yield (PLQY) and the obtained implied V_{OC-imp}) of perovskite films prepared on ITO/2PACz substrates without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP) processes.



Fig. S12. The effect of PEACI concentration (1.5 mg/ml and 3 mg/ml) as a surface passivation interlayer on (a) photoluminescence quantum yield (PLQY) and (b) the obtained implied V_{OC} (V_{OC-imp}) of the reference (Ref) and grain boundary passivation (GBP) perovskite solar cells (referred to as: SP(1.5), SP(3), GBP&SP(1.5) and GBP&SP(1.5), respectively.



Fig. S13: Time-resolved photoluminescence (TRPL) for perovskite films prepared on ITO/2PACz substrates without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP) and grain boundary & surface passivation (GBP&SP).



Fig S14: The J-V characteristics (log-log plot) of electron-only devices demonstrating three different regimes, marked with ohmic, trap-filled, and trap-free space charge limited current (SCLC) regime measured in the dark for (a) reference (Ref), (b) grain boundary passivation (GBP), (c) surface passivation (SP), and (d) grain boundary & surface passivation (GBP&SP) films. The electron trap density (nt) could be determined by the trap-filled limited voltage (VTFL) from electron-only devices.



Fig S15. The J-V characteristics (log-log plot) of hole-only devices demonstrating three different regimes, marked with Ohmic, trap-filled, and trap-free space charge limit current regime measured in the dark for (a) reference (Ref), (b) grain boundary passivation (GBP), (c) surface passivation (SP), and (d) grain boundary & sur-face passivation (GBP&SP) films. The insert shows the device configuration: ITO/2PACz/Perovskite/Spiro-MeOTAD/Ag.



Fig. S16: Ideality factor (n_{id}) extracted from a fit to the implied V_{OC} (V_{OC-imp}) (derived from intensity-dependent photoluminescence quantum yield measurements) for perovskite films prepared on ITO/2PACz substrates without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP) and grain boundary & surface passivation (GBP&SP).



Fig. S17: The effect of PEACl concentration (1.5 mg/ml and 3 mg/ml) as a surface passivation interlayer (referred to as: SP(1.5) and SP(3)) on the ideality factor (n_{id}) extracted from a fit to the implied V_{OC} (V_{OC-ipm}) of the reference (Ref) and grain boundary passivation (GBP) perovskite solar cells (referred as: SP(1.5), SP(3), GBP&SP(1.5) and GBP&SP(1.5), respectively.



Fig. S18: The *JV*-curves of (a) the best GBP&SP PSC and (b) the best Ref PSC are compared to pseudo-*JV* curves calculated from the intensity-dependent PLQY data for perovskite films prepared on ITO/2Pacz with (w) and without (wo) a C₆₀ layer on top as well as to an ideal device ($n_{id} = 1$) that has the same J_{SC} as the best PSC, as described by Stolterfoht et al.¹¹



Fig. S19: Top-view scanning electron microscopy (SEM) images of double-cation $Cs_{0.18}FA_{0.82}PbI_3$ perovskite films prepare (a) without any modification and with (b) surface passivation (c) grain boundary passivation, and (d) grain boundary & surface passivation processes. The insets show higher magnification images.



Fig. S20: Top-view scanning electron microscopy (SEM) images of double-cation $Cs_{0.18}FA_{0.82}PbI_3$ perovskite film treated with a high-concentration of PEACI (3 mg/ml) on top of the (a) reference and (b) grain boundary passivated perovskite layers.



Fig. S21: Atomic force microscopy (AFM) analysis of double-cation Cs_{0.18}FA_{0.82}Pbl₃ perovskite films prepared (a) without any modification and with (b) surface passivation (c) grain boundary passivation, and (d) grain boundary & surface passivation processes. The surface roughness of each perovskite film is noted as the root-mean-square (RMS) value.



Fig. S22: Cathodoluminescence (CL) spectra of the reference perovskite film at two different spots.



Fig S23: Top-view scanning electron microscopy (SEM) images of grain boundary passivated perovskite films. The insets show higher magnification images of the large bright grains related to PbI₂-rich crystallites.



Fig. S24: Left: Cross-sectional scanning electron microscopy (SEM) images of grain boundary passivated perovskite films with the configuration of ITO/2PACz/perovskite. Right: The magnified image of a large bright grain - related to a PbI2-rich crystallite as identified by cathodoluminescence and top-view SEM (see Figs. S4 and S22-S23) - indicates that these are situated on top of 3D perovskite grains.



Fig. S25: Cathodoluminescence (CL) spectra of perovskite films prepared without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP). The left panel is a magnified view of the same CL spectra in the visible range of 400 to 700 nm.



Fig. S26: Steady-state photoluminescence (PL) of the perovskite films prepared on ITO/2PACz substrates for the reference (Ref), surface passivation with different PEACI concentrations (SP(1.5), SP(3)), grain boundary passivation (GBP), and grain boundary passivated films treated with different PEACI concentrations (GBP&SP(1.5), GBP&SP(3)) in the visible range of 560-700 nm.



Fig. S27: (a) X-ray diffraction (XRD) pattern of perovskite films prepared without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP). (b) Calculated intensity ratios of the various crystal planes.



Fig. S28: XRD patterns of grain boundary & surface (GBP&SP) perovskite films treated with a high concentration of PEACI (4.5 mg/ml and 10 mg/ml). The red stars denote the diffraction peaks resulting from a pure (n = 1) 2D Ruddlesden-Popper (PEA)₂Pb($I_{1-y}CI_y$)₄ phase with a superlattice spacing of ~1.7 nm.



Fig. S29: X-ray photoelectron spectroscopy (XPS) spectra of (a) N 1s, (b) Cs $3d_{5/2}$, and (c) $I 3d_{5/2}$ core-levels for perovskite films prepared on ITO/2PACz substrates without any modification (Ref) and with surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP).



Fig. S30: Normalized X-ray photoelectron spectroscopy (XPS) spectra of the Pb 4f core levels (same data as in Fig. 5 a) including perovskite films with a PEACI concentration of 3 mg/ml (SP (3) and GBP&SP(3)) (left) and a higher magnification of the Pb $4f_{7/2}$ peak.



Fig. S31: X-ray photoelectron spectroscopy (XPS) spectra of the denoted core levels for reference (Ref) and grain boundary passivated perovskite films treated with a PEACI concentration of 10 mg/ml (SP (10) and GBP&SP(10)) and comparison to the data for the reference perovskite film.



Fig. S32: The atomic ratio of CI/Pb, Cl/Pb, Cs/Pb, FA/Pb, and I+Cl/Pb for the reference (Ref) and grain boundary (GBP) perovskite films treated with different concentration of PEACI (1.5, 3 and 10 mg/ml).



Fig. S33: Additional XRD measurements of grain boundary & surface passivated films (GBP&SP) employing various concentrations of PEACL for surface treatment (3, 3.5, 4 and 4.5 mg/ml). The data is plotted relative to the (100) peak of a GBP reference sample in order to study the trend when going from rather thin to thicker passivation layers. The peaks at ~5.1° and ~10.2° correlate to an n = 1 2D RP phase with superlattice spacing of ~1.7 nm and the peak at ~3.8° correlates to n = 2 with a superlattice spacing of ~2.34 nm.



Fig. S34: (a) Fit to Pb4f core levels of the reference perovskite film, which yields peak positions of ~138.7 eV and ~143.5 eV with a FWHM of 0.8. For (b), (c) and (d), the peak position and FWHM for the 3D perovskite peak are fixed (blue area) and the second component is fixed to 139.1 eV (green area).



Fig. S35: Secondary electron cut-off spectra from ultraviolet photoelectron spectroscopy (UPS) were used to determine the work function of the perovskite films.



Fig. S36: Proposed energy band diagrams from ultraviolet photoelectron spectroscopy (UPS) measurements. Same data as in Fig. 5d, but including data for films with a higher PEACI concentration (SP(3) and GBP&SP(3)).



Fig. S37: Visualization of random grain boundary regions demonstrated by blue and pink lines in contact potential difference (CPD) map to determine the CPD offset and CPD profile lines between grain boundary and grain interior for (a) reference (Ref) and (b) grain boundary passivation (GBP) perovskite films.



Fig. S38: (a) Visualization of ~60 different grain boundary regions to estimate the average contact potential difference (CPD) offset between grain boundary and grain interior for (a) reference (Ref) and (b) grain boundary passivated (GBP) perovskite films. (c) Respective histogram of the extracted ΔCPD_{GB} (CPD_{grain boundary} – CPD_{grain}).



Fig. S39: Contact potential difference (CPD) images and CPD variation recorded in dark for (a), (b) reference (Ref) and (c), (d) grain boundary & surface passivation (GBP&SP) films. The line profiles were analyzed along the blue line and red line indicated in the CPD maps for Ref and GBP&SP films, respectively.



Fig. S40: (a, b, c, d) Capacitance (C) versus angular frequency (ω) spectra and (e, f, g, h) corresponding logarithmic derivative of the reference (Ref), surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP) perovskite solar cells respectively, measured in a temperature range of 278 to 318 K.



Fig. S41: Arrhenius plots of $\ln(\omega_{peak}T^2)$ versus $1/k_BT$ extracted from the derivative of admittance spectra to determine the activation energy (E_a) for reference (Ref), surface passivation (SP), grain boundary passivation (GBP), and grain boundary & surface passivation (GBP&SP) perovskite solar cells.



Fig. S42: Comparison of maximum power point (MPP) tracking of the grain boundary & surface passivation (GBP&SP) and LiF-based perovskite solar cell measured during continuous AM 1.5G illumination at room temperature in a nitrogen-filled glovebox.



Fig. S43. (a) The ultraviolet-visible absorption spectra of grain boundary & surface (GBP&SP) passivation and reference (Ref) perovskite films after 1 day of their exposure to the 50% humidity. Contact angle measurements with a water droplet on top of the (b) Ref (c) GBP&SP perovskite films.

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