Electronic supplementary information

Ion Migration in p-Type Perovskite $MAPbI_3$ Films under Electric Field and Thin-Film Transistor Device Failure

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EXPERIMENTAL METHODS

Materials

Methylammonium iodide (MAI, 99.5%), lead(II) iodide (PbI_2, 99.999%) were purchased from Xi'an Yuri Solar Co. Ltd. *N,N*-dimethylfojmrmamide (DMF, anhydrous, 99.9%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), benzenesulfonic acid (BSA,98%), aniline (AN, 99%), and 1-Butyl-4-methylpyridinium iodide (BMPI, 98%) were purchased from Aladdin. Ethyl acetate (EA, 99.5%) was purchased from J&K scientific. Acetone (99.5%) was purchased from Chengdu Chron Chemicals Co. Ltd. Ethanol absolute (99.7%) was purchased from Tianjin ZhiYuan Reagent Co. Ltd. Ultra-pure water (Level 1) was purchased from Guangzhou Howei Pharma Tech Co.Ltd. SiO_2 wafer was purchased from Suzhou Rdmicro Co. Ltd. All the chemicals and solvents were used as received without further purification.

Device fabrication

The perovskite thin-film transistors (TFTs) were fabricated on cleaned Si/SiO_2 substrates using bottom-gate and bottom-contact device configurations. The SiO_2 dielectric layer has a thickness of 300 nm and an areal capacitance of 11.5 nF/cm^2. The Si/SiO_2 substrates were cleaned using standard cleaning procedures, which involved successive sonication in acetone, ethanol absolute and ultra-pure water for 10 minutes, respectively. The cleaned substrates were subsequently placed into a vacuum chamber for the deposition of 5 nm of Cr and 30 nm of Au as the source and drain electrodes. The channel length (L) and width (W) of the electrodes are 50 μm and 3000 μm, respectively. Prior to perovskite film deposition, the substrates with electrodes underwent standard cleaning procedures followed by a UV-ozone treatment for 30 minutes to eliminate organic residues and enhance surface wettability. Following the UV-ozone treatment, the substrates were promptly transferred into a glove box for perovskite film deposition.

The perovskite precursor solution for depositing the $MAPbI_3$ thin films was

prepared by co-dissolving 318.0 mg of MAI and 922.0 mg of PbI_2 in a mixed solvent of DMF/DMSO (4:1 in volume ratio) to obtain a perovskite precursor solution with a molar concentration of 1 M. Subsequently, the additive solutions were prepared by dissolving different additives, including BA, AN, and BMPI, into a DMF/DMSO solvent mixture (4:1 in volume ratio), respectively. The resulting solutions had the additives with a molar concentration of 0.1 M. The resulting solution was stirred at a temperature of 70 ℃ for four hours until it achieved clarity and homogeneity. Afterward, the perovskite precursor solution was filtered using PTFE filters with a pore size of 0.4 μm. The perovskite precursor solution with an additive to $MAPbI_3$ molar ratio of 0.1% was prepared by incorporating additive solution. The $MAPbI_3$ film-based devices were fabricated by spin-coating the solutions of $MAPbI_3$ onto the substrates at 3000 rpm for 25 seconds, while EA was gently deposited onto the substrates at the 10^{th} second. The resulting devices were subjected to annealing at a temperature of 120 °C for 10 minutes, followed by encapsulation using glass and silicone. The film thickness measures approximately 40 nm. It should be noted that the entire experimental procedures, including the solution preparation and the device fabrication, were carried out in a nitrogen glove box with oxygen and water concentrations below 0.5 ppm.

Device characterization

The optical images of the films were recorded using a microscope (FJ-3A, Shenzhen Finial Technology Ltd., Co). The film thickness was measured using a mechanical profilometer (Bruker, Dektak XT stylus profilometer). The transfer curves and the bias stress stability tests were conducted by Keithley 4200 source meter in dark conditions and at room temperature. The measurement speed is normal with a holding time of 0 second, and the gate voltage step is 2V. Each transfer curve test lasted approximately 15 seconds. The claimed field effect mobilities μ claimed were extracted from the saturated regions ($|V_{SD}| > |V_{GS} - V_{th}|$) from the forward transfer curves as follows:

$$\mu_{\text{Claimed}} = \frac{2L}{WC_{\text{i}}}\left(\frac{\partial\sqrt{I_{\text{SD}}}}{\partial V_{\text{GS}}}\right)^2 \tag{1}$$

Where, W and L are the width and length of the channel of the transistor. C_{i} is the unit capacitance of the dielectric layer. I_{SD} and V_{GS} are the source-drain current and gate-source voltage, respectively. The reliability factor (r_{Sat}) and effective mobility (μ_{Eff}) were calculated as follows:

$$r_{\text{Sat}} = \left(\frac{\sqrt{\left|I_{\text{SD}}\right|^{\max}} - \sqrt{\left|I_{\text{SD}}^{0}\right|}}{\left|V_{\text{GS}}\right|^{\max}}\right)^2 \Big/ \left(\frac{\partial\sqrt{\left|I_{\text{SD}}\right|}}{\partial V_{\text{GS}}}\right)^2_{\text{Claimed}} \tag{2}$$

$$\mu_{\text{Eff}} \equiv r_{\text{Sat}} \times \mu_{\text{Claimed}} \tag{3}$$

FIGURES & TABLES

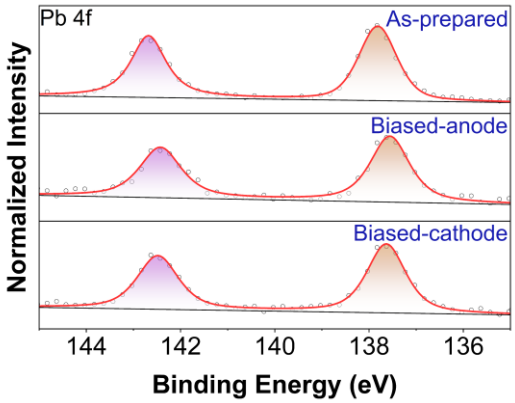

Figure S1. Pb 4f XPS spectra acquired from the as-prepared $MAPbI_3$ film and at the anode and cathode following voltage bias.

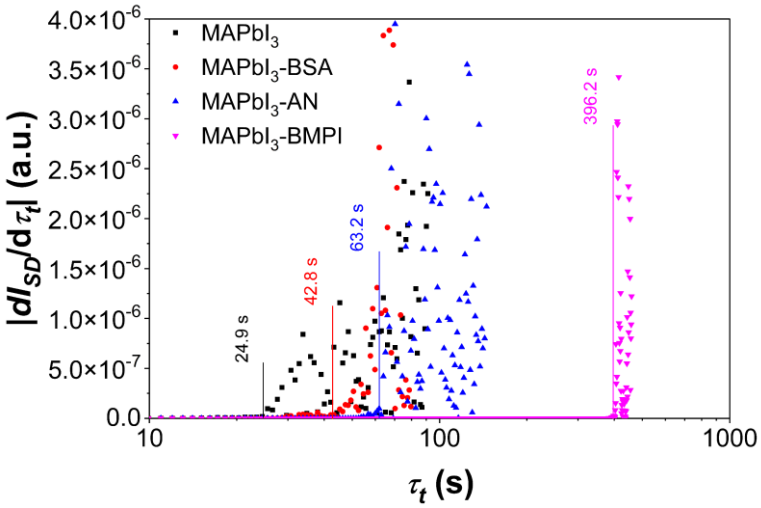

Figure S2. Derivative of I_{SD} divided by bias time t.

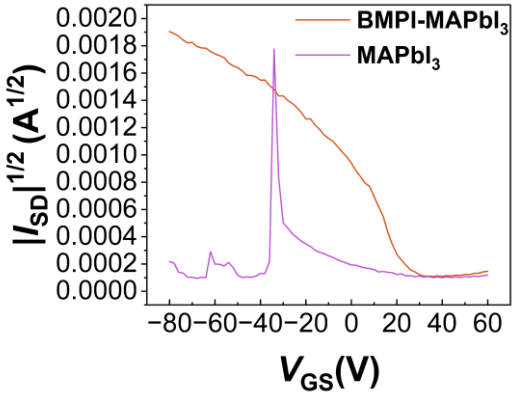

Figure S3. Plots of $I_{SD}^{1/2}$ versus V_{GS} of the TFTs fabricated with $MAPbI_3$ and BMPI-$MAPbI_3$ at a V_{DS} of −60V at room temperature.

Table S1. Atom ratios of elements in the $MAPbI_3$ films before and after voltage bias (unit: a.u.)

	N/Pb	I/Pb	N/I
As-prepared (anode)	1.41	3.59	0.39
As-prepared (cathode)	1.51	3.73	0.40
Biased-anode	3.53	2.92	1.21
Biased-cathode	3.06	3.10	0.99