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Electronic supplementary information

Chemical origin of the p-type and n-type doping effects in the hybrid methylammonium-lead iodide (MAPbI$_3$) perovskite solar cells

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1. Fabrication of the bottom-contact lateral devices

The glass slides were cleaned by sonication in a base piranha solution (a mixture of hydrogen peroxide and ammonia, both obtained from ChimMed, Russia), rinsed with deionized water and dried in an oven at 60°C for 30 min. Gold electrodes (100 nm) were deposited directly on glass by thermal evaporation in vacuum ($2\ x{\cdot}10^{-6}$ mbar) through a shadow mask. Two laterally arranged electrodes formed a channel with the length (L) of 70-90 μm and width of 2 mm. A 35 wt% solution of CH_3NH_3I and PbI_2 (1:1 molar ratio) in anhydrous DMF was spin-coated above the gold electrodes at 6000 rpm for 50 s inside a nitrogen glove box. The deposited films were annealed at 100°C for 15 min under inert atmosphere to produce a black hybrid perovskite ($CH_3NH_3PbI_3$) layer. Outlying edges of the contacts were cleaned from the perovskite film using dried cotton tips dipped into anhydrous acetone.

2. Fabrication of the top-contact lateral devices

The glass slides were cleaned by sonication in a base piranha solution (a mixture of hydrogen peroxide and ammonia, both obtained from ChimMed, Russia), rinsed with deionized water and dried in an oven at 60°C for 30 min. Afterwards, they were treated with oxygen plasma (150 W) for 10 min. A 35 wt% solution of CH_3NH_3I and PbI_2 (1:1 molar ratio) in anhydrous DMF was spin-coated onto the cleaned glass slides at the frequency of 3000 rpm for 50 s inside a nitrogen glove box (MBraun Unilab). The deposited films were annealed at 100°C for 15 min under inert atmosphere to produce a black hybrid perovskite ($CH_3NH_3PbI_3$) layer. Gold electrodes (100 nm) were evaporated above the perovskite layer in vacuum through a shadow mask. The device channel length (L) and width (W) were 70-90 μm and 2 mm, respectively.

3. Polarization of the devices under constant bias voltage

These experiments were performed using double-channel Keithley 2612A source-measurement unit and a custom-made probe station installed inside MBraun glove box under nitrogen atmosphere. Initially the current-voltage characteristics of the device were measured several times between -100 V and +100 V in order to prove the quality of the contacts with the perovskite active layer. In particular, we registered I-V curves in dark, under ambient light provided by two 36W fluorescent lamps installed in the glove box (0.35 mW/cm^2) and using monochromatic green light (37 mW/cm^2, λ=532 nm). All I-V curves were scanned in the forward and backward directions with the scanning rate of ~15 V/s in order to reveal any possible hysteresis effects.

Afterwards, a constant bias voltage of 100 V was applied between the electrodes of the device in the dark and the evolution of the current flowing through the channel was monitored within 2h. Performing such polarization experiment with the same device several times one just after another or with some delays (1-12 h) produced very similar results.

It was also noticed that applying different bias potentials between 50 and 150 V for polarization of the lateral devices produced essentially the same results. Higher potentials induce stronger field which results in a faster evolution of the system and *vice versa*.

4. Measuring photoresponse of the devices

A lateral device (no differences observed for top-contact and bottom-contact architectures) was biased at 100 V for 10 min and the current flowing between the electrodes was monitored using Keithley 2612A source-measurement unit. Two minutes after applying the bias voltage a violet diode laser (~40 mW, λ=405 nm) was switched on for 5 min. This experiment was performed several times with the same device to reveal possible degradation effects. The obtained profiles are shown in Fig. S1.