ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for *Adv. Funct. Mater.*, DOI 10.1002/adfm.202305211

Role of Metal Contacts on Halide Perovskite Memristors

*José Carlos Pérez-Martínez, Mariana Berruet, Cedric Gonzales, Saeed Salehpour, Ali Bahari, Belén Arredondo and Antonio Guerrero**

Supporting Information

Role of Metal Contacts on Halide Perovskite Memristors

José Carlos Pérez-Martínez,[1,3] Mariana Berruet,[1,2] Cedric Gonzales,[1] Saeed Salehpour,[4,1] Ali Bahari,[4] Belén Arredondo,[3] Antonio Guerrero*[1]

[1]Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain.
[2]División Electroquímica Aplicada, INTEMA, CONICET-Universidad Nacional de Mar del Plata, B7606BWV Mar del Plata, Argentina.
[3] Electronic Technology Area, Universidad Rey Juan Carlos, 28933 Móstoles, Spain
[4] Department of Physics, Faculty of Basic Sciences, University of Mazandaran, Babolsar, Iran, 4741695447

Corresponding author A. Guerrero (aguerrer@uji.es)

Materials and perovskite precursor solution

All materials and solvents were used as received. FTO glass (Pilkington TEC 15), PEDOT:PSS (Heraeus CLEVIOS™ P VP AI 4083), CH_3NH_3I (MAI, Greatcellsolar), PbI_2 (TCI, 99.99%), DMF (Sigma Aldrich, anhydrous 99.8%), DMSO (Sigma Aldrich, anhydrous 99.9%), chlorobenzene (Sigma Aldrich, 99.8%).

The $MAPbI_3$ precursor solution was prepared by preparation of DMF solutions (50 wt %) containing MAI and PbI_2 (1:1 mol %) and MAI, PbI_2 and DMSO (1:1:1 mol %) as reported previously.[1] Briefly, MAI (235 mg) and PbI_2 (681.5 mg) were mixed in DMF (1 mL) and DMSO (95 µL).

Device Fabrication

The devices were prepared in the configuration of glass/FTO/PEDOT:PSS/$MAPbI_3$/Metal. FTO glass substrates were etched with zinc powder and HCl (2M) followed by cleaning with Hellmanex solution and rinsed with Milli-Q water. Afterward, the substrates were sonicated for 15 min in acetone and mixed 50:50 ethanol-isopropanol and dried with nitrogen.

Previous next step, the substrates were treated in a UV−O_3 chamber for 15 min. PEDOT:PSS solution was filtered using PTFE 0.45 µm syringe filter and a thin layer was spin-coated on substrate at 3000 rpm for 30 s followed by annealing at 120ºC for 10 min. Immediately, the samples were transfer inside of a glovebox and heated at 100°C for 5 min to evaporate residual humidity on the surface. The perovskite precursor solution was spin-coated at 4000 rpm for 50 s. During this step, DMF was selectively washed with

chlorobenzene just before the white solid begins to crystallize in the substrate. Afterward the substrate was annealed at 100 °C for 10 min. Finally, metal contacts were performed by thermal evaporation using a mask on the top of the MAPbI3 layer to define an active area of 0.125 cm^2. Devices with AgI ultrathin film (~ 5nm) were performed using pressed powder of AgI (Sigma Aldrich, 99%). Then, a 15 nm thick copper, silver or aluminum layer was followed by 85 nm thick gold electrode. For platinum deposition a 6 nm thick layer was sputtered.

	Work function (eV)	**Atomic Radio (pm)**	**Crystal Ionic radius (pm)**
Pt	5.12 – 5.93	135	71-94
Au	5.10 – 5.47	135	71-151
Cu	4.53 – 5.10	135	54-77
Ag	4.26 – 4.74	160	75-115
Al	4.06 – 4.26	125	67.5

Table. S1. Parameters for different metal used in the manuscript as metal electrodes in perovskite memristors [1].

I-V Characteristics of $MAPbI_3$/Au Devices

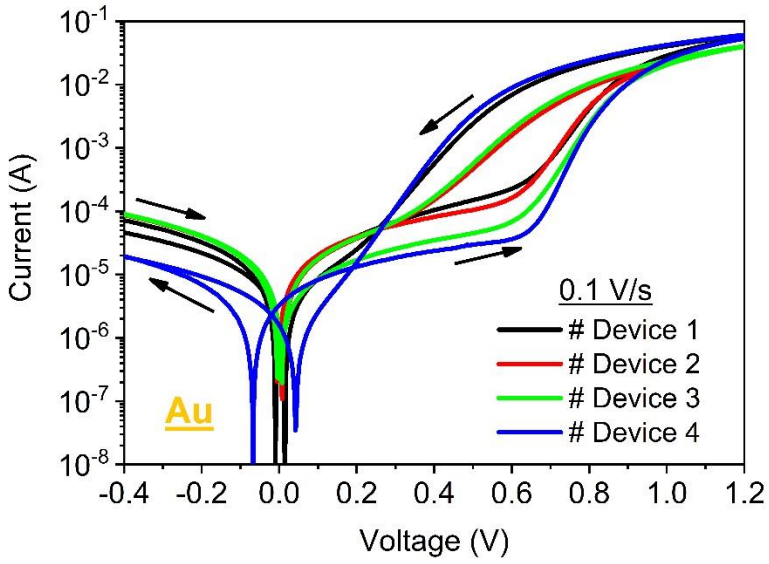

Fig. S1. Initial *I-V* curves for different devices fabricated in the same batch as those shown in Fig. 2 using Au electrodes (FTO/PEDOT:PSS/MAPI/Au).

I-V Characteristics of $MAPbI_3$/Al/Au Device

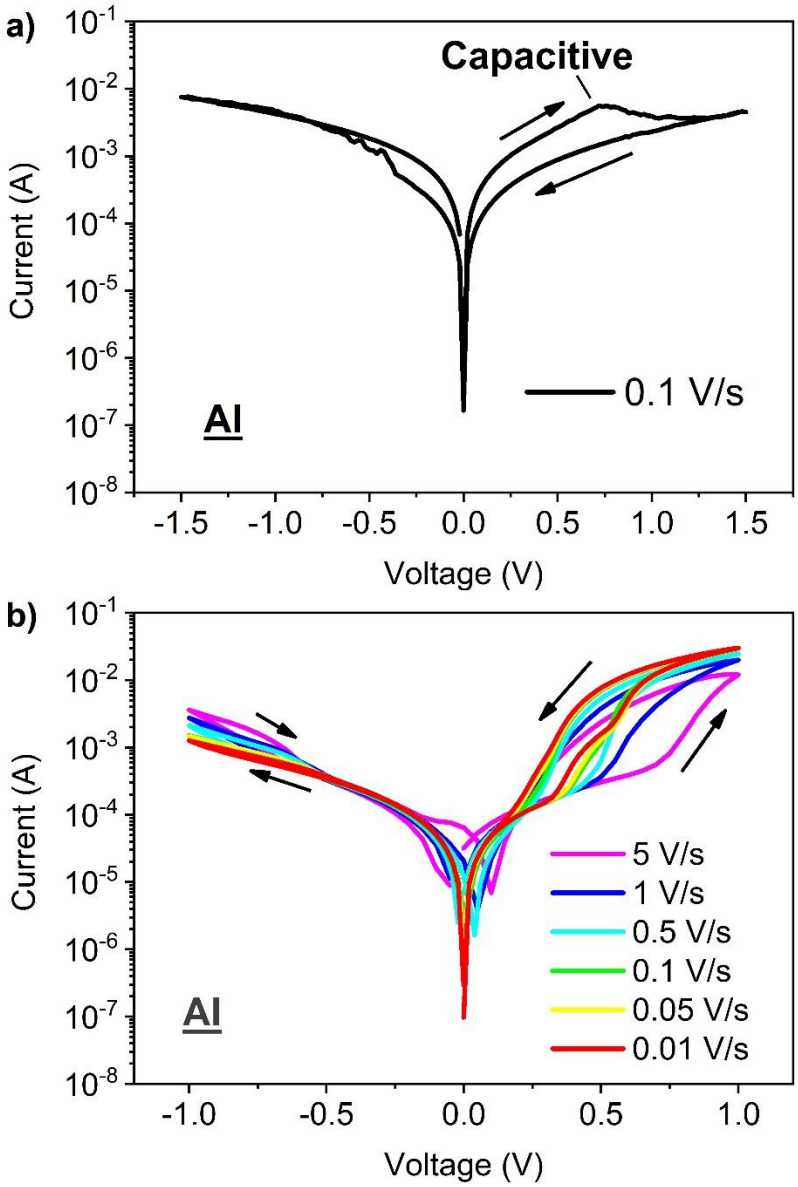

Fig. S2. a) Initial *I-V* curve for FTO/PEDOT:PSS/MAPI/Al/Au devices. b) Dependence of *I-V* curve with the scan rate for devices after the initial scans.

ON State and OFF State Retention and Endurance Measurements

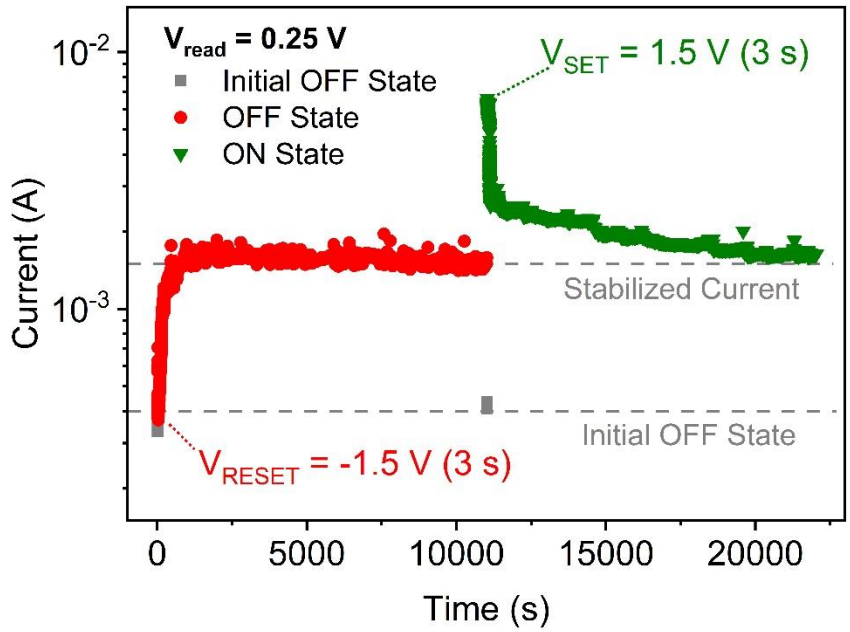

Fig. S3. The OFF State and ON State retention times by a RESET voltage pulse of -1.5V for 3 s and a SET voltage pulse of 1.5V for 3 s measured at 0.25V for FTO/PEDOT:PSS/MAPI/AgI/Au devices.

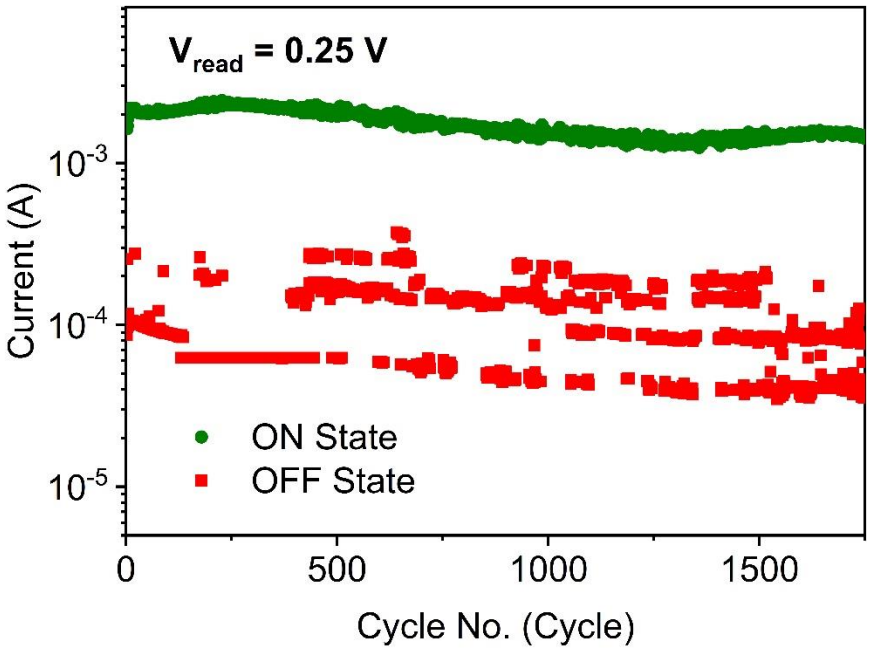

Fig. S4. Endurance measurements of the OFF State and ON State results during cyclic voltammetry consecutive cycling measured at 0.25V for FTO/PEDOT:PSS/MAPI/AgI/Au devices.

Electrochemical Impedance Spectroscopy and C-F Measurements

Impedance measurements have been carried out in order to corroborate the inductive behavior shown in *I-V* curves for different devices. The inductive phenomenon appears at higher voltages (~0.4 V) in devices with an inert metal (Au) (Fig. S5a) and at lower voltages (~0.2V) with pre-oxidized metal (AgI) (Fig. S5b) according to shown in Fig. 5a. Capacitance spectra have been measured and shows different peaks (at different voltages), where there is a transition from positive to negative capacitance at different frequencies. Devices with inert metal (Au) show this peak at 0.4 V (Fig. S5c) On the other hand, in devices with pre-oxidized metal (AgI) this peak appears at 0.2V (Fig. S5d). These results correlate with data from impedance and I-V curves measurements.

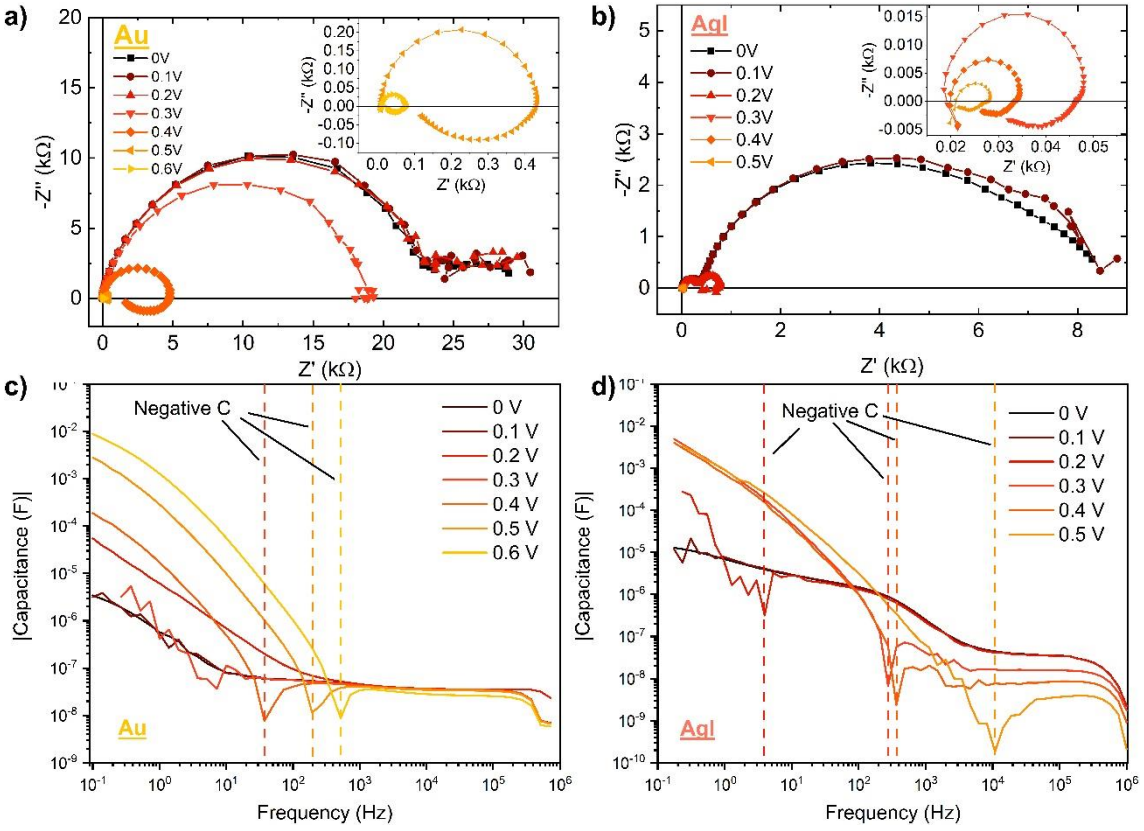

Fig. S5. (a-b) Electrochemical impedance spectroscopy (EIS) spectra and (c-d) capacitance spectra measured between 100 mHz and 1MHz of nearly inert metal (Au) and pre-oxidized metal (AgI) at different voltage.

References

[1] elements, E. w. f. o. t., CRC Handbook of Chemistry and Physics 84 ed.; CRC Press: 2003; p 12–124.