Understanding lead iodide perovskite hysteresis and degradation causes by extensive electrical characterization

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ABSTRACT

We studied the hysteresis and electric field effects on planar $CH_3NH_3PbI_3$ perovskite devices, synthetized from laser-ablated precursors, by means of electrical characterizations at different scan rates and optical measurements. The aim of our investigation is to characterize the phenomena behind perovskite degradation under prolonged applied electric field. Using a perovskite more resistant to electric field induced degradation, we run long time characterizations that were not accomplishable before. Thus, we distinguished all the degradation-involved phenomena. The results point to the presence of ions migrating in the perovskite when the device is biased. Our data showed that ion migration degrades the interfaces with the consequent creation of degradation layers that limit the current injected in the device and the extracted photocurrent. These layers where detected also by means of optical Raman characterization. In order to explain the details of the mechanisms concurring to the observed behaviors, we presented a qualitative model.

The observed phenomena exacerbated by the planar structure are even more destructive on standard solution processed perovskites to which the results of this work can be extended. Since, the same degradation dynamics occur on vertical devices, typical on perovskite solar cells, this work provides a useful in-depth analysis of the ionic migration effects.

1. Introduction

Organometal hybrid perovskite materials have gained huge visibility since the first application of halide perovskite as dye-sensitizer material in hybrid Dye-Sensitized Solar Cells (DSSCs) [1]. Encouraged by the promising optical and electrical properties of these materials, many researchers focused their efforts on improving the performances of solar cells based on organometal hybrid perovskites, called perovskite solar cells (PSCs). Their performance quickly raised from the initial 3.8% efficiency to the highest so far record of 22.1% [2] and efforts are continuously being invested to bring the efficiency close to its theoretical ∼ 31% limit [3]. Furthermore, due to the tunable properties of perovskites [4–6], these materials have gathered increasing interest on several fields. Besides photovoltaic devices, perovskites have been investigated also for other applications such as photo-detectors

[7], thin film transistors (TFTs) [8], LASER [9–11] and LEDs [12,13].

Perovskite precursors are inexpensive and require low processing temperatures compared to traditional inorganic semiconductors making them suitable for low-cost roll-to-roll industrial processes [14–18]. Despite the promising performances, stability and reliability are still the bottleneck for an extensive industrial application of perovskites, which exhibit several weaknesses mostly related to their hybrid organic nature [19–27].

Several issues require further research and solutions in order to make perovskite-based devices ready to enter into the market. Among them, moisture represents one of the major weaknesses of perovskite materials [28–30]. Another issue is the temperature susceptibility. In fact, even if an initial annealing generally improves the device performances by increasing the film quality, the prolonged exposure of the perovskite to high temperatures usually damages the device [19,21].

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Furthermore, perovskites exhibit a hysteretic behavior, emphasized by the adoption of planar configurations [31]. While in some applications long persistence phenomena are desirable [32], in the majority of the cases hysteresis is detrimental such as in photovoltaic devices. Several works [33–37] agreed on explaining such hysteretic phenomena by means of ions moving within the perovskite layer. However, other studies [38–42] concluded that the perovskite behaves as a ferroelectric material to some extent.

In order to stabilize and make the perovskite more resistant and less hysteretic, a lot of effort has been invested. Several works tried to prevent hysteresis by adding polymers at the perovskite/transport layer interfaces [43–47].

A promising alternative to the usage of polymers is the perovskite processed from solution-ablated precursors developed by Lamberti et al., which proved outstanding resistance and low hysteresis [48,49]. Indeed, while standard solution processed perovskite could not survive extensive electrical characterization and showed irreversible degradation in a few hours, laser-ablated derived perovskite proved higher tolerance and resistance both to electric field and environmental exposure.

In this work, we exploit the endurance of methylammonium lead iodide (MAPI) derived from laser-ablated precursors to investigate the hysteretic phenomena of MAPI perovskite, i.e. one of the most commonly used material in high performance PSCs. Since MAPI from laser-ablated precursors endures prolonged electric field application, it allows for extensive electrical characterizations, permitting measurements that were impossible on standard solution processed MAPI. Thus, we could investigate whether the hysteresis is mostly due to ions and/or ferroelectric properties of the perovskite material (PVK) by using extremely low scan rates. Besides, having MAPI derived from laser-ablated precursors a slower degradation dynamic, we could detect the effects of the hysteresis on the material. We proved that different mechanisms contribute to the hysteresis observed in PSCs and that ion migration is responsible for both long term transitory effects and permanent structural changes in the PVK layer, altering the electrical properties of the studied devices. Since the studied material is similar to the standard MAPI, we believe that our results can be extended to solution-processed perovskite both on planar and vertical structures, despite being more challenging to study the phenomena on those devices.

Finally, we modeled the perovskite bands bending explaining the mechanisms behind current injection/extraction into/from the hybrid-organic semiconductor, which is of the utmost importance in the understanding of the band alignment for photovoltaics applications.

2. Materials and methods

2.1. Setup and devices structure

Performing the characterization in inert atmosphere and at controlled temperature is mandatory in order to limit degradation to electric field induced effects. Fig. 1 describes the developed setup (Fig. 1a) and the devices structure (Fig. 1b). We run all the electrical characterizations in nitrogen at 25 °C, if not otherwise stated, by using custom developed hardware and instrumentation. An additional external black box encloses the nitrogen box in order to prevent external light and EMI radiation interferences; both boxes are grounded. The temperature controller is peltier-based and allows setting the sample temperature from 80 °C to − 20 °C.

We fabricated planar interdigitated devices (IDs), using $10 \times 10 \, mm^2$ crystalline silicon substrates (FBK, Fondazione Bruno Kessler) covered by silicon oxide and patterned with interdigitated golden electrodes (work-function $\Phi_{Au} = -5.1 \, eV$). IDs have a 20 μm PVK active layer between golden electrodes; Fig. 1b gives more details on the geometries of the substrate. Furthermore, we coated a $10 \times 10 \, mm^2$ FTO/glass substrate (TEC 7, 2 mm thickness, Sigma-Aldrich) for optical characterizations.

2.2. Devices preparation

The IDs and FTO/glass devices were obtained depositing the precursor ink into the respective substrates by spray coating. Spray coating was performed by using a home-made system based on Professional Dual Action Airbrush Set / Kit with gravity feed (ExquizonEU) operating with nitrogen flow of 3 bar (20 °C). The substrate was positioned vertically, 2 cm far from the nozzle tip and kept at 50 °C during the deposition. 1 ml of precursor ink was sprayed in air under extractor hood (20% humidity). The spray-coating process was controlled by means of stepper motors with horizontal and vertical steps equal to 10 mm and 200 μm respectively, for 3 cycles. The width of the spray-coated layer was about 1/3 of the substrate dimension. After PbI_2 film deposition, the sample was converted to PVK dipping the substrate in 10 mg/ml methylammonium iodide (MAI) anhydrous isopropyl alcohol (IPA) solution for 3 min, then rinsed in fresh anhydrous IPA and finally in anhydrous dichloromethane. Converted perovskite films thickness is about 1 μm as measured by scanning electron microscopy (SEM) cross section. More details on the processing of laser ablated (LASiS) materials are available in Ref. [49].

2.3. Optical characterizations

We run ultraviolet photoelectron spectroscopy (UPS) analysis on MAPI PVK sample to estimate the work function of the materials under investigation. We used a Kratos Axis UltraDLD spectrometer. The UPS measurements were taken using a He I (21.22 eV) discharge lamp, on an area of 55 μm in diameter, at pass energy of 10 eV and with a dwell time of 100 ms. The work function (i.e. the position of the Fermi level with respect to vacuum level) was measured from the threshold energy for the emission of secondary electrons during He I excitation. A − 9.0 V bias is applied to the sample in order to precisely determine the low kinetic energy cut-off, as discussed in ref [50].

We collected Raman measurements by means of a custom setup equipped with an Ar + / Kr + gas laser (Coherent, Innova 70) tuned for emission at 514.5 nm. The laser is focused on the sample through an Olympus BX 41 microscope with a 20× objective (Olympus, LMPlan FLN 20×, NA = 0.40). The Raman scattering diffused by the sample is coupled into the slit of a three-stage subtractive spectrograph (Jobin Yvon S3000) and detected by a liquid nitrogen-cooled CCD (Jobin Yvon, Symphony, 1024 × 256 pixels, front illuminated). The laser spot diameter is about 2 μm. The laser power used during the measurements is 250 μW for PbI_2 powder, MAI powder and PVK on SiO_2, 25 μW for PVK on Au. The integration time is 10 s (and 30 averaged acquisitions) for PbI_2 and 20 s (and 100 averages) for MAI powders, 20 s (and 30 averaged acquisitions) for PVK on SiO_2 and 20 s (and 60 averaged acquisitions) for PVK on Au. All measurements were carried out in standard conditions.

We recorded X-ray diffraction spectra (XDR) with a BRUKER D8 ADVANCE diffractometer with Bragg–Brentano geometry and equipped with a Cu Kα1 (λ = 1.544060 Å) anode at operating voltage of 40 kV and operating current of 40 mA. All the diffraction patterns were measured at room temperature over an angular range (2θ) between 6° and 60°, at step size of 0.020°, and an acquisition time of 1 s. Step size was used as error source for experimental data.

2.4. Electrical characterization

An Agilent B1500 parameters analyzer is used for the electrical characterization of the samples and control of the white led lamp used as light source. High-resolution source measurement units (SMU) are used to measure electrodes current, while a high-power SMU unit drives the light source. We run light measurements under a white LED biased to give a light power density of approximately 50 mW/cm^2.

Current voltage scans (I-V) are with a scan rate of 5 V/s and 300 μV/s for fast scan and steady-state scan, respectively. Using two scan rates