Nanoscale Imaging of Photocurrent in Perovskite Solar Cells using Near-field Scanning Photocurrent Microscopy

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ABSTRACT

We study photocurrent generation and collection of methylammonium lead iodide perovskite solar cells with nanoscale resolution using a near-field scanning photocurrent microscopy (NSPM) technique. For NSPM measurements, we employ a non-contact mode atomic force microscopy probe with an attached optical fiber coated with Cr/Au metal. We observe an increased photocurrent at grain boundaries in samples annealed at moderate temperature (100 °C); however, the opposite spatial pattern is observed in samples annealed at higher temperature (130 °C). Combining the NSPM results with other characterization techniques such as electron microscopy, X-ray diffraction, and quantum efficiency measurements, we show that the cause of the photocurrent contrast is the material inhomogeneity and the dynamics of lead iodide. The NSPM technique is further used to establish the mechanism of the cell degradation under extended light illumination.

I. INTRODUCTION

Due to their easy fabrication, low-cost, and surprisingly fast improvement in the power conversion efficiency, perovskite solar cells have attracted significant interest in the photovoltaic (PV) research community [1], [2]. Recent developments offer a pathway for high efficiency solar cells without costly tandem structures [3], [4] and/or nanophotonic engineering [5]–[11]. However, various instability issues caused by environmental factors (*e.g.*, extended light illumination, humidity, temperature, etc.) have impeded their deployment as commercial solar cells. The as of yet unknown factors causing degradation should be firmly established.

Multiple measurement techniques have been applied for the characterization of material composition and structural properties of perovskite solar cells [12]–[15] at the micro- or nanoscale. However, the detailed studies connecting the degradation with the nanoscale photo-excited carrier generation and collection are still lacking.

In this study, we image nanoscale photocurrent collection of perovskite solar cells by a near-field scanning photocurrent microscopy (NSPM) technique. Correlating the nanoscale photocurrent images with other characterization techniques (X-ray diffraction, electron microscopy, quantum efficiency measurements, etc.), we relate the cell preparation temperature with its operation at the macro-/nanoscale. We also determine how the light-

induced degradation affects the cell microstructure and the local carrier collection by monitoring the changes in the NSPM photocurrent images which occur during the experiment (on the timescale of hours).

II. RESULTS AND DISCUSSION

For the NSPM measurements, we employ a tuning forkbased non-contact mode atomic force microscopy (AFM) probe with an attached multimode optical fiber to locally inject light [9], [11], [16]. The end of the optical probe is coated with Cr (20 nm) and Au (200 nm) metal, and the probe has an output hole with a diameter of ≈ 200 nm (see



Fig. 1. (a) An SEM image showing an AFM probe used for NSPM measurements. Metal-coated optical fiber used for near-field light injection is attached to a tuning fork. Insets: enlarged side-view of the probe (left), enlarged view of the probe at the bottom (right). (b) A schematic (not to scale) describing NSPM measurements on perovskite solar cells. Photocurrent amplified by a variable gain amplifier is detected with a lock-in technique.

Fig. 1a). The perovskite solar cell is placed onto a piezo stage of an AFM system, and topography and photocurrent signals are simultaneously obtained (see Fig. 1b). The NSPM probe has a force constant of 15 N/m and a resonance frequency of \approx 35 kHz. A diode laser with a wavelength of 635 nm is connected to the optical fiber of the NSPM probe via a FC/PC connector. A variable-gain low-noise current amplifier is used for signal amplification, and the amplified photocurrent is detected with a lock-in amplifier. During the raster scanning, the distance between the NSPM probe and the top surface of the perovskite solar cell is kept \approx 10 nm. In some measurements, we used different output hole sizes of the NSPM probe (between 50 nm and 300 nm) or changed the laser power to generate a measurable photocurrent or to avoid the degradation during the measurements.

Our perovskite solar cell has methylammonium lead iodide $(CH_3NH_3PbI_3, MAPbI_3$ hereafter) as its active layer. It is enclosed by [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and nickel oxide (NiO_x) as electron and hole transport layers, respectively. The full device structure is shown in Fig. 2a, and the device consists of silver (Ag) contact/PCBM/400 nm thick perovskite layer (MAPbI₃)/NiO_x/indium tin oxide (ITO), from top to bottom.

First, we determine macroscopic electrical properties of perovskite solar cells annealed at two different temperatures: 100 °C and 130 °C (see Fig. 2b). The sample annealed at moderate temperature (100 °C) exhibits superior photovoltaic properties (*i.e.*, short circuit current density, J_{SC} , open circuit voltage, V_{OC} , and fill factor, *FF*) compared to the sample annealed at higher temperature (130 °C). The power conversion efficiency is $\eta = 16.98$ % for the sample annealed at 100 °C vs. $\eta = 14.81$ % for the sample annealed at 130 °C. Repeated measurements under identical conditions yield maximum variation of less than 1 % [11], [16].

The difference between the cells is clearly seen in NSPM photocurrent images (see Fig. 2c). The nanoscale photocurrent patterns are exactly opposite for the two samples annealed at different temperatures: the photocurrent is higher at grain boundaries for the sample annealed at 100 °C while it is higher at grain interiors for the sample annealed at 130 °C. The beneficial role of grain boundaries in carrier generation and collection is attributed to the dynamics of lead iodide (PbI₂) segregation [16], [17]. In the sample annealed at 100 °C, a moderate amount of PbI₂ segregates at grain boundaries leading to the defect passivation. However, more structural and compositional transformation from MAPbI₃ to PbI₂ takes place with further annealing, resulting in distinguishable crystalline phases of PbI₂ at grain boundaries in the sample annealed at 130 °C. This leads to an increased grain boundary recombination, and grain interiors become more efficient carrier collectors. Note that the measured photocurrent is not caused by surface morphology or thickness variation of the perovskite solar cells, as confirmed by the significant contrast in the measured photocurrents (up to ≈ 20 % and ≈ 36 % in the sample annealed at 100 °C, respectively).

As mentioned above, the instability and the performance degradation under operational environment is the major issue for perovskite solar cell technology. We study how perovskite solar cells change their operation under extended light illumination. First, we identify the microscopic material and compositional changes of perovskite solar cells using X-ray diffraction measurement and electron microscopy (Fig. 3a). Measurements are performed when samples are aged under the Air Mass 1.5 Global (AM1.5G) spectrum with an intensity of 10 mW/cm² (0.1 sun illumination). The moderate light dose is selected to avoid any possible degradation due to overheating. A relative humidity is kept ≈ 25 % at room temperature during the whole measurements.

The diffraction peak corresponding to PbI_2 is observed at a diffraction angle of 12.75° (marked with #) for both samples annealed at different temperatures. The intensity of this peak increases as the cell ages, indicating continuous material decomposition from MAPbI₃ to PbI₂. PbI₂ crystallites are clearly distinguishable in cross-



Fig. 2. (a) Device structure of perovskite solar cells. Scale bar is 200 nm. (b) Current-Voltage characteristics of perovskite solar cells annealed at two different temperatures. The sample annealed at moderate temperature (100 °C, blue line) exhibits higher power conversion efficiency than the sample annealed at higher temperature (130 °C, red line). (c) Nanoscale photocurrent imaging of perovskite solar cells using the NSPM technique. Opposite photocurrent collection patterns are observed between the two samples. Scale bars are 500 nm.

sectional scanning electron microscopy (SEM) image of the sample annealed at 130 °C. Distinct spots with bright contrasts are observed at grain boundaries due to their low conductivity and increased accumulation of charges (see yellow dotted lines in Fig. 3a). However, as seen in SEM images, the distribution of PbI₂ is quite different in two samples annealed at different temperatures: PbI₂ is evenly distributed in the active area for the sample annealed at moderate temperature (100 °C), and it is concentrated at grain boundaries for the sample annealed at higher temperature (130 °C). However, as the aging time increases, the distribution of PbI₂ in the sample annealed at 100 °C is no longer uniform over the sample, showing distinguishable phases of PbI₂ in SEM images.

The external quantum efficiency (EQE) of the samples is determined as a function of illumination time (see Fig. 3b). Minor changes are observed for 200 min of light degradation, however, both samples show significant deterioration as aging time increases. The sample annealed at higher temperature (130 °C) collects more photo-generated carriers than the sample annealed at 100 °C for the same aging time. Repeated measurements under identical conditions yield maximum variation of less than 1 % [11], [16], [18].

We investigate how the extended light illumination affects nanoscale carrier generation and collection by monitoring the changes in the NSPM photocurrent images during the aging process (see Fig. 4). As shown in Fig. 2c, photocurrent patterns are opposite for two samples annealed at two different temperatures: grain boundaries are more efficient carrier collectors for the sample annealed at moderate temperature (100 °C), while they are less efficient than grain interiors for the sample annealed at the higher temperature (130 °C). Even though the photo-generated current is reduced under the aging process, this carrier collection pattern persists for the sample annealed at higher temperature (130 °C). However, the sample annealed at moderate temperature (100 °C)

exhibits quite different behavior. At 400 min of aging process, the photocurrent collection at the grain boundary marked with a white dotted-circle is strongly suppressed. The photocurrent was significantly higher at this spot in pristine condition (t = 0). The loss of photocurrent enhancement with aging for this sample is attributed to the dynamics of PbI₂ segregation.

As seen in Fig. 3a, more structural decomposition from MAPbI₃ to PbI₂ occurs under the continuous light illumination, and this leads to a growth of distinguishable PbI₂ crystallites at grain boundaries, somewhat similar to the pristine state of the sample annealed at higher temperature. The enhanced carrier collection at grain boundaries is no longer observed for this sample. The suppression of the enhanced collection at grain boundaries significantly affects the overall device performance. This can explain the faster degradation of this sample during the aging process (see Fig. 3b). For the other sample, the main paths for carrier generation and collection remain the same, resulting in relatively robust photovoltaic properties under aging process, as seen from the macroscopic EQE measurements in Fig. 3b.

IV. CONCLUSIONS

We study nanoscale photocurrent of methylammonium lead iodide perovskite solar cells using a near-field scanning photocurrent microscopy. We show that the spatial pattern of photocurrent is related to the sample preparation temperature: higher photocurrent is observed at grain boundaries in samples annealed at moderate temperature (100 °C), while lower



Fig. 3. (a) X-ray diffraction patterns for perovskite solar cells under light-induced aging process. # and * denote the identified diffraction peaks corresponding to PbI₂ and MAPbI₃, respectively. Yellow dotted lines show distinguishable PbI₂ crystallites at grain boundaries. Inset SEM images show cross-sectional view of samples under the light-induced aging process. Scale bars are 200 nm. (b) EQEs of perovskite solar cells under the light-induced aging process.



Fig. 4. NSPM-based nanoscale photocurrent images of perovskite solar cells at multiple stages of light-induced aging. Scale bars are 500 nm.

photocurrent is observed at grain boundaries and higher photocurrent is observed at grain interiors in samples annealed at higher temperature (130 °C). Correlating nanoscale photocurrent images with other characterization techniques, we show that the particular spatial patterns of photocurrent are due to the material inhomogeneity and the dynamics of segregation of lead iodide. We also determine how the light-induced aging process affects the nanoscale carrier collection in perovskite solar cells. The structural and compositional changes of materials through the aging process suppress the beneficial role of grain boundaries in samples annealed at moderate temperature.

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