Transient simulation of halide perovskite-based solar cells with mobile ions and carriers

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***Abstract*—Halide Perovskites are considered as solid semiconductors since the beginning of their solar cell development. However, on their film or devices, direct and indirect observations of mobile ions are currently reported. Mobile ions are included in the present study within the drift-diffusion approximations, in addition to general carriers. Ion migration inside the perovskite layer and the abnormal hysteresis effect in the current-voltage measurements are simulated in comparison with the experiments of classic perovskite solar cells. The work is promising for the advancements of halide-perovskite-based devices, such as solar cells, light emitting diodes, lasers, photodetectors, transistors, or memoirists.**

Keywords—halide perovskite, ion migration, hysteresis

I. INTRODUCTION

More comprehensions of the halide perovskites accompany the robust improvement of their solar cells, whose record of the single junction [1] and 2-terminal tandem [2] are 22.7% and 25.2%, respectively. Halide perovskite materials (ABX_3) share a similar cell structure with the classic mineral oxide perovskite (ABO_3). The cation A site is typically composed of organic methylammonium (MA), formamidinium (FA), or inorganic Cs or Rb cations. Generally, lead (Pb) sits in the B site, and the X site is filled with halide atoms I, Br, or Cl. Based on linear combinations of orbitals including spin-orbit coupling (SOC) [3], the atomistic computations explained that the appropriate absorption and transport properties are afforded by the multi-bandgap and multivalley nature of their band structure. This hypothesis is further confirmed by the study of the structural and optical properties [4]. The low effective mass of excitons in $MAPbI_3$ was accurately determined using magneto-reflectivity at very high magnetic fields model [5]. As a result, halide perovskites are considered as solid semiconductors [6] with an efficient photo-conversion. Nevertheless, many groups recently reported the direct and indirect measurements [7][8] of mobile ions inside halide perovskites under different operation conditions, which is quite different from the traditional silicon or III-V materials. The ion migration is assumed to contribute to one of the major instabilities of perovskite solar cells (PSCs), the abnormal hysteresis effect [9], which means the current-voltage (J-V) characteristics depends on the scan rate, the scan direction or the precondition. With such effect, the effective photon-to-electron conversion eficiency could be questioned.

In the study, the drift-diffusion approximations and the continuity equations of electrons and holes are extended in the simulator atlas to consider ions moving inside the perovskite layer. One of the most widely studied compounds, $MAPbI_3$ perovskite is chosen to investigate the ion migration within the $TiO_x/MAPbI_3$/Spiro-OMeTAD architecture. The simulated ion migration and the corresponding hysteresis effect are presented and discussed.

II. MODELING AND DISCUSSION

The architecture is experimentally studied as mentioned in the previous report [10]. The anatase TiO_x (165 nm-thick) is the electron transport layer, and the Spiro-OMeTAD (50 nm-thick) is the hole transport layer, sandwiching the absorber $MAPbI_3$ (total 335 nm-thick). The 135 nm-thick $MAPbI_3$ is related to the part inside the porosity of mesoporous TiO_x layer. The electrodes are Ohmic. The photo-induced carrier generation processes are introduced by the complex refractive index of the materials, in addition to the bimolecular recombination, and the trap-assisted recombination in the bulk and at the $TiO_x/MAPbI_3$ interface.

The schematic architecture of PSC is drawn (Fig. 1), along with the simulated band alignment and the electric field (E_{fd}). Two E_{fd} spikes in a logarithm scale are related to two hetero-junctions, while the E_{fd} is uniform in the middle. In the dark and short circuit (Fig. 2 a-c), carriers are depleted under built-in potential, and the negative ions accumulate near the TiO_x layer, where the ionized dopants are positive. Under illumination of one sun and 1.5 V bias (Fig. 2 d-f), the perovskite layer is filled with photo-generated carriers, and the negative ions shift towards to the positively biased anode. After preconditioned under one sun and 1.5 V bias for 20 seconds, the J-V characterization is performed from 0 to 1.5 V then back to 0 V. The hysteresis effect is observed in the experiments and simulations (Fig. 3). The variation of the open circuit voltage is well reproduced, while the difference of the short-circuit current might come from the thickness of

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the $MAPbI_3$ layer or the device surface area. The simulated J-V characteristic above 1 V shows a similar trend to the experiments, indicating a saturation of the ion migration. According to the simulation in the study, the interface recombination at $TiO_x/MAPbI_3$ is mandatory to reproduce the hysteresis effect, besides the ion migration. This might interpret the observation of ion migration in the inverted PSCs, however, who are almost free of the hysteresis effect. The interface condition between perovskite and PCBM is assumed to be better than that at $TiOx/MAPbI_3$ interface.

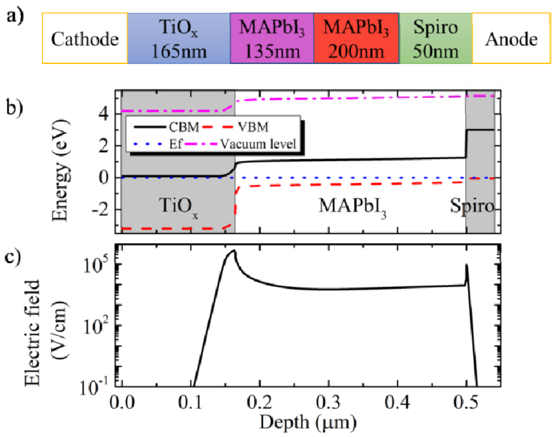

Fig. 1. a) Schematic architecture of PSCs, b) the simulated band alignment and c) the electric field profile. The band alignment and the electric field share the same x-axis. Spiro is short for Spiro-OMeTAD.

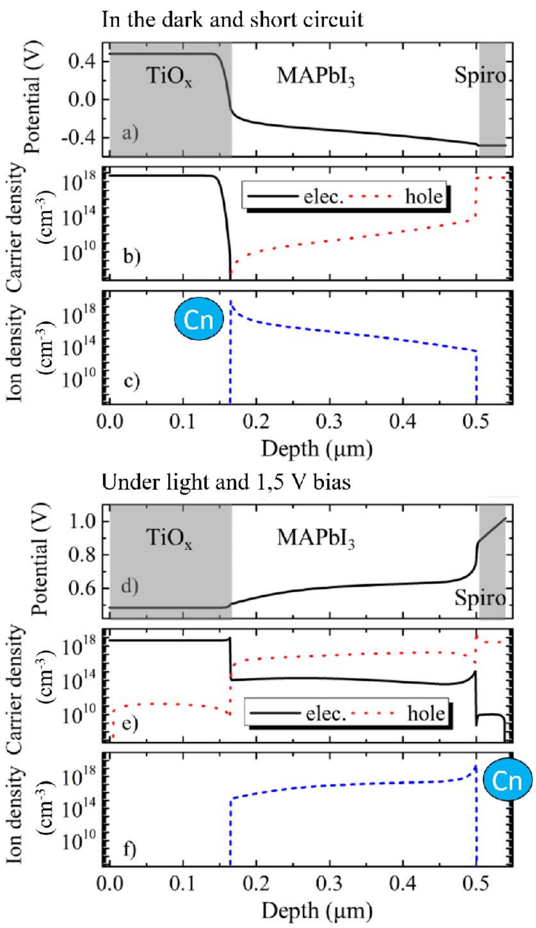

Fig. 2. Potential, carrier and ion density a-c) in the dark and short circuit, d-f) under light and 1.5 V bias. Cn indicates major part of the negative ions.

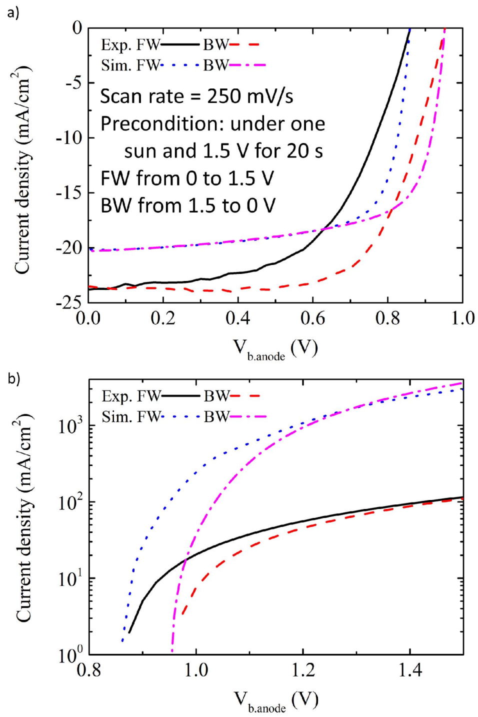

Fig. 3. Experimental and simulated hysteresis J-V characteristics. FW is the forward scan and BW is the backward scan. Before any scan, the devices are preconditioned under one sun and 1.5 V bias for 20 seconds. The y-axis in b) uses a logarithm scale.

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