Numerical simulation of HTM-free and WO_X based perovskite cells: Effects of interface conditions

Y. Huang[1], S. Aharon[2] A. Gheno[3], S. Vedraine[3], L. Pedesseau[1], J. P. Burin[1], O. Durand[1], J. Bouclé[3], L. Etgar[2], J. Even[1], A. Rolland[1]

[1]FOTON, UMR 6082, CNRS, INSA Rennes, Université de Rennes 1, 35708 Rennes, France
[2]Institute of Chemistry, Casali Center for Applied Chemistry, The Hebrew University of Jerusalem, Edmond J. Safra Campus,Givat Ram, 91904 Jerusalem, Israel
[3]XLIM, UMR 7252, CNRS, Université de Limoges, 87069 Limoges, France

yong.huang@insa-rennes.fr

***Abstract*-Hole transport material (HTM) free and WO_x based perovskite solar cells are theoretically investigated by using drift-diffusion and small signal models. The influence of interface states and leakage current is studied, and the current-voltage (J-V) and capacitance-voltage (C-V) characteristics are reproduced in reasonable agreement with experimental data, including build in potential (V_{bi}) variation, open circuit voltage (V_{OC}) loss and hysteresis effects.**

I. INTRODUCTION

The last highest certified record for a single-junction halide perovskite solar cell (PSC) with 22.1% has been reported by KRICT and UNIST's researchers in February 2016. Theoretical Photon-to-electron Conversion Efficiency (PCE) and open circuit voltage (V_{OC}) limits have not yet been achieved experimentally, e.g. PCE of 37% [1] and V_{OC} of 1.33 V [2] for $MAPbI_3$ based PSCs. Although the interface conditions of halide perovskite absorbers [3] are carefully refined with the aim of high performance and hysteresis-free device operation, only few theoretical analyses were dedicated to interface conditions, especially on HTM-free or WO_x based PSCs. In our study, the current-voltage (J-V) and capacitance-voltage (C-V) characteristics of PSCs are simultaneously modeled to investigate the influence of interface (IF) conditions, including interface ions which could act as deep traps (IFDTs) [3] , dopants (IFDs) [4] or interface leakage current paths (LCP) [5].

II. NUMERICAL MODELING

The physical model is numerically simulated using Silvaco Atlas, which solves a set of coupled equations including Poisson's equation, continuity and transport equations for electrons and holes densities under steady state and small signal conditions. The photo-induced carrier generation processes are introduced through complex refractive index of the materials in addition to the bimolecular recombination (BR) and the trap-assisted recombination (TR). The shallow traps (STs) are directly considered as dopants, while the energy levels of deep traps (DTs) are 0.5 eV away from the band edges. More details could be found in our previous contribution [6].

III. HTM-FREE PSCS

PSCs without HTM layer are proposed as a solution for easy process and high efficiency solar cells. After Etgar and coworkers early attempts to deposit gold on $MAPbI_3$ surface, leading to PCE of 8% [7], PSCs with single-walled carbon nanotubes as hole collector achieved efficiency of 15% [8]. Based on Etgar's work, the modeled architecture of HTM-free PSCs in our work is illustrated in fig.1. N and p type $MAPbI_3$ (nHOIP and pHOIP) PSCs with and without IFDs are studied and the relevant J-V and C-V characteristics are shown in fig.2 and fig.3, respectively. To match the experimental data, a heavily n-doped interfacial layer is assumed at the nHOIP/Au interface, whose existence has been indirectly observed by ultraviolet photoemission spectroscopy [9]. Fig.2. and 3. show that the elimination of such IFDs is expected to result in an increase of the V_{OC} and the build in potential (V_{bi}), which is extracted from Mott-Schottky capacitance analysis.

IV. WO_X BASED PSCS

Recently, printable WO_x based PSCs show up as the candidates for the future flexible photovoltaic applications, due to their stability and high efficiency. In 2014, nano-structured WO_x was firstly employed as electron transport material (ETM) in PSCs, while state of the art PCEs of 15.65% was achieved by Wang et al [10]. Furthermore, drastic improvement of device stability in the dark under ambient conditions of WO_x-based PSCs was reported recently by A. Gheno et al [11], in comparison with TiO_2-based PSCs. Two simulation architectures based on Gheno's work are illustrated in fig.4: a (top) basic 1D structure and a (bottom) 2D simplified structure with LCP, designed to mimic the porosity of the WO_x layer with a direct connection between the perovskite and the conductive ITO where the WO_x material is absent. The BR and TR recombination models are taken into

account in all models except one presented with dash dot line, which accounts only for BR process. As shown in fig.5 b and c, a V_{OC} loss could be caused by IFDTs and LCP in addition to TR. And IFDs could result in J-V curve shift, namely hysteresis effect. In order to fit experimental data, the IFDTs are donor-like (acceptor-like) at IF1 (IF2), while the IFDs are n-type (p-type) at IF1 (IF2); the density of IFDTs and IFDs are $6x10^{18}$ and 10^{19} cm^{-3}, respectively. Other extensions of the simulation will be also reported.

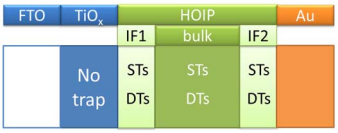

Fig.1. Schematic of HTM-free PSCs.

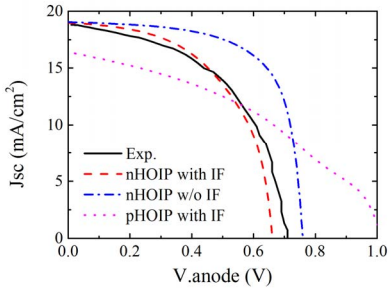

Fig.2. J-V characteristics under 1 sun illumination of the nHOIP HTM-free PSCs with (dash line) and without (dash dot line) IFDs. And a pHOIP with IFDs (dot line) is pictured as comparison.

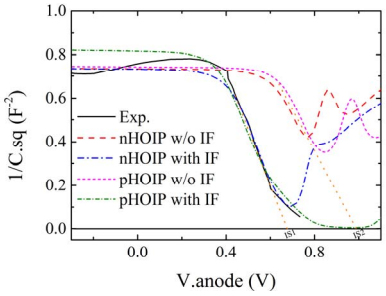

Fig.3. (Colorful online) Simulated and experimental (solid line) C-V characteristics in dark of HTM-free PSCs. nHOIP with (without) n type IFDs at Au/HOIP interface is indicated as dash dot (dash) line. pHOIP with (without) p type IFDs at TiO_x/HOIP interface is indicated as short dash dot (short dash) line. The intersection IS1 and IS2 indicate the V_{bi} of 0.6 and 0.9 V, respectively.

Fig.4. Schematic of WO_x based PSCs without (top) and with (bottom) leakage current path of 10nm width.

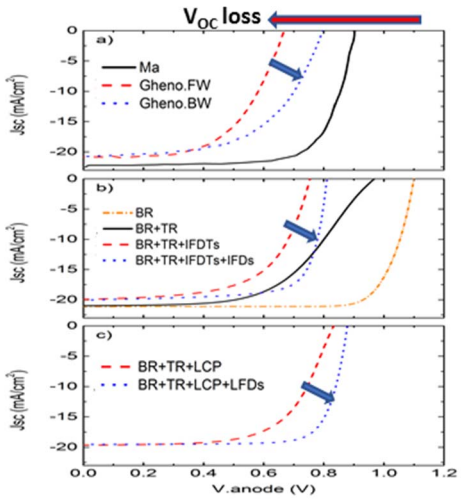

Fig.5. a) Measured and calculated J-V curves of b) 1D and c) 2D WO_x based PSCs. FW (BW) indicates forward (backward) voltage sweep.

The work at FOTON and Xlim was supported by French ANR SupersansPlomb project.

REFERENCES

[1] W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p‐n Junction Solar Cells," *J. Appl. Phys.*, vol. 32, no. 3, pp. 510–519, Mar. 1961.

[2] W. Tress, N. Marinova, O. Inganäs, M. K. Nazeeruddin, S. M. Zakeeruddin, and M. Graetzel, "Predicting the Open-Circuit Voltage of CH3NH3PbI3 Perovskite Solar Cells Using Electroluminescence and Photovoltaic Quantum Efficiency Spectra: the Role of Radiative and Non-Radiative Recombination," *Adv. Energy Mater.*, vol. 5, no. 3, p. 1400812, Feb. 2015.

[3] J. M. Ball and A. Petrozza, "Defects in perovskite-halides and their effects in solar cells," *Nat. Energy*, vol. 1, no. 11, p. 16149, Oct. 2016.

[4] Y. Yuan *et al.*, "Electric-Field-Driven Reversible Conversion Between Methylammonium Lead Triiodide Perovskites and Lead Iodide at Elevated Temperatures," *Adv. Energy Mater.*, vol. 6, no. 2, p. 1501803, Jan. 2016.

[5] A. Burke, S. Ito, H. Snaith, U. Bach, J. Kwiatkowski, and M. Grätzel, "The Function of a TiO2 Compact Layer in Dye-Sensitized Solar Cells Incorporating 'Planar' Organic Dyes," *Nano Lett.*, vol. 8, no. 4, pp. 977–981, Apr. 2008.

[6] Y. Huang *et al.*, "Influence of Schottky contact on the C-V and J-V characteristics of HTM-free perovskite solar cells," *EPJ Photovolt.*, vol. 8, p. 85501, 2017.

[7] L. Etgar *et al.*, "Mesoscopic CH3NH3PbI3/TiO2 Heterojunction Solar Cells," *J. Am. Chem. Soc.*, vol. 134, no. 42, pp. 17396–17399, Oct. 2012.

[8] K. Aitola *et al.*, "Carbon nanotube-based hybrid hole-transporting material and selective contact for high efficiency perovskite solar cells," *Energy Env. Sci*, vol. 9, no. 2, pp. 461–466, 2016.

[9] X. Liu *et al.*, "Electronic structures at the interface between Au and CH3NH3PbI3," *Phys. Chem. Chem. Phys.*, vol. 17, no. 2, pp. 896–902, Dec. 2014.

[10] K. Wang *et al.*, "W(Nb)Ox-based efficient flexible perovskite solar cells: From material optimization to working principle," *Nano Energy*, vol. 31, pp. 424–431, Jan. 2017.

[11] A. Gheno, T. T. Thu Pham, C. Di Bin, J. Bouclé, B. Ratier, and S. Vedraine, "Printable WO3 electron transporting layer for perovskite solar cells: Influence on device performance and stability," *Sol. Energy Mater. Sol. Cells*, vol. 161, pp. 347–354, Mar. 2017.