Simulations of 3-dimensional ferroelectric domains in perovskite solar cells based on $MAPbI_3$

D. Rossi[†,*], M. Auf der Maur[†], A. Pecchia[‡], A. Di Carlo[†]
[†]Dept. of Electronic Engineering, Università degli Studi di Roma "Tor Vergata", Via del Politecnico 1, 00133 Rome, Italy
[‡]CNR-ISMN, Via Salaria km 29.300, 00017 Monterotondo, Rome, Italy
[*]Email: daniele.rossi@uniroma2.it

***Abstract*—In this work we present how 3-dimensional ferroelectric domains observed in $MAPbI_3$ affect the performance of perovskite solar cells. We simulated a 3D system with dimensions of 500 nm x 500 nm x 300 nm, considering domains with 100 nm side length which have been assigned random orientations of the polarization field. Calculations are performed with the simulator TiberCAD using a 3D drift-diffusion model, that simulates the light absorption and charge carrier transport, including the local polarization. We show that the presence of polarization domains have a strong impact on the charge carrier separation, leading to a reduction of electron-hole recombination and current pathways formation at interfaces.**

I. Introduction

Since they have been introduced for the first time in 2009 by Kojima et al. [1], organic-inorganic hybrid lead halide perovskites ($MAPbI_3$) became soon a viable alternative to dye-sensitized solar cells (DSC). Record efficiencies of solar cells completly based on perovskite have been quickly increasing up to the current certified value of 21.02%, achieved in 2016 at EPFL [2].

Besides being a cheap solution which leads to high efficiencies, the most intriguing point is the material itself. Similar to other perovskites like $BaTiO_3$ and metal-oxide perovskites like BiFe O_3, also hybrid perovskites show ferroelectric properties, hence spontaneous polarization due to the deformation of its crystalline structure like in all ABO_3 crystals. The local polarization field in the crystal is due to the non centro-symmetric position of the charge center. Furthermore the Methylammonium molecule (MA) is relatively free to rotate within the inorganic cage at room temperature. In support of these studies, PFM measuraments recently performed by Rohm et al. [4] proved the existence of ferroelectric domains with typical sizes of dozens of nanometers.

As a follow up of the recent work done on the microscopic scale [5], in order to test the role of ferroelectric domains on trasport properties in perovksites solar cells on mesoscopic scale we have performed 3D drift-diffusion simulations for a bulk perovskite layer in presence of a polarization field with different orientations in different domains within the volume. We demonstrate that ferroelectric domains act on the transport properties of the material, leading to a reduction of electron-hole recombination due to the effective charge space separation that occurs within bulk. Furthermore, we show how distinct electron and hole current pathways locally arise at domain interfaces.

II. The Model

A. Model for ferroelectric domains

The quantitative estimation of the spontaneous polarization P in $MAPbI_3$, was performed by different authors using Berry phase calculations and suggests a value in the range between 0.13 C/m^2 [5] and 0.03 C/m^2 [6]. Taking into account that these results are referred to the unit cell of the lattice, we considered a different scenario on mesoscopic scale, where the crystal is not perfectly ordered. For these reasons we choose an effective polarization field with magnitude of 0.001 C/m^2.

A 3-dimensional structure of 5x5x3 (500 nm x 500 nm x 300 nm) cubic domains is considered, associating a local polarization to each cube. The maps of domains, as shown in Figure 1, were built using an ad hoc algorithm that randomly assigns to each domain one among the 6 configurations ($\pm P_x$, 0, 0), (0, $\pm P_y$, 0) and (0, 0, $\pm P_z$).

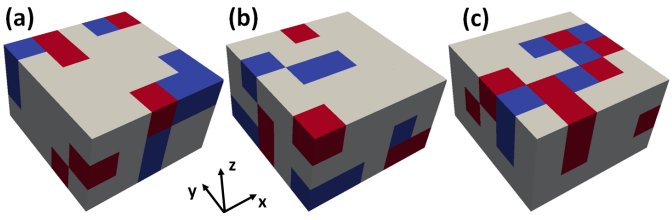

Fig. 1. Polarization map of the sample 1 for P_x (a) , P_y (b) and P_z (c), where red (blue) sites indicate a polarization component of $+P$ ($-P$).

In order to consider different scenerios we performed simulations on three different 3-dimensional polarization patterns.

B. The Drift-diffusion Model

To compute the solar cell characteristics, we consider a simple structure consisting of an intrinsic 300 nm thick perovskite layer with band edges $E_V = -5.4$ eV and $E_C = -3.85$ eV ($E_g = 1.55$ eV). Light incidence is assumed from the anode (bottom contact). The transport layers and electrodes are modeled using two selective Schottky contacts with work functions of, respectively, $E_f = -3.9$ eV at the anode and $E_f = -5.35$ eV at the cathode. Charge trasport is computed by solving the drift-diffusion model, based on the coupled system of Poisson and continuity equations. The equation system is discretized using the finite element method (FEM) and solved by the Newton method, as implemented in the TiberCAD simulation

978-1-5090-5323-0/17/$31.00 ©2017 IEEE

tool. The equations have been discretized using a cubic mesh of approximately 300,000 elements.

The polarization field P is included consistently in the Poisson equation 1.

$$\nabla \cdot (\varepsilon \nabla \varphi - P) = -\rho \tag{1}$$

At domain boundaries, where the normal component of polarization changes, an effective sheet charge density is induced leading to accumulation of free carriers. Non radiative defect-mediated Shockley-Read-Hall (SRH) recombination is considered as the main loss process in the perovskite layer, with minority carrier lifetimes of 10^{-10} s [7].

III. Results and Discussion

From the simulation results emerges that local polarization patterns contribute to the appearance of space charge separation effects at domain boundaries, as shown in Figure 2a at open-circuit voltage conditions (V_{oc}).

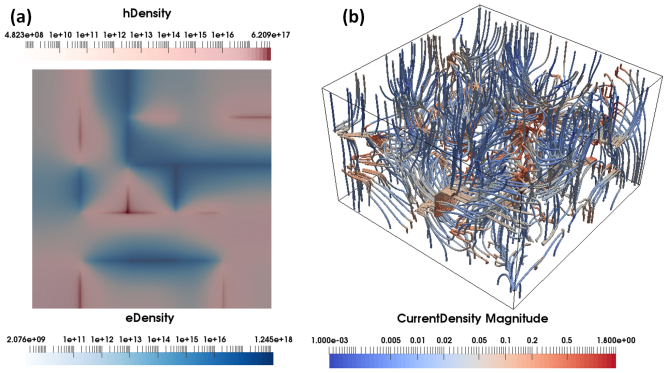

Fig. 2. a) Horizontal slice at z = 150 nm of the device at V_{oc}, where electron (blue) and hole (red) densities are plotted. Color bars are in cm^{-}3. b) Representation of the current patways within the perovskite layer at short circuit conditions J_{sc}. Shown are the total current flow lines. Color scale is in A/cm^2.

The observed carrier separation directly contributes to the reduction of overall SRH recombination losses, leading to an increase of the open circuit voltage V_{oc} of roughly 15-20 mV compared to the homogeneous case, as shown in Figure 3.

The charge carrier accumulation at interfaces also explains the formation of current pathways shown in Figure 2b. Due to the high carrier densities in the accumulation layers, carrier extraction happens preferentially through the path formed by these layers. Photogenerated electrons and holes therefore first drift towards the accumulation layers, from where they are efficiently extracted towards the respective contacts. A simple estimation shows, that the effective conductivity in the perovskite layer with inhomogenous polarization field and resulting accumulation layers is much higher than in the homogeneous case, leading to a more efficient carrier extraction and thus larger short-circuit current density J_{sc} and lower shunt resistance. Similar behavior is observed in all the three different polarization patterns that we have considered, with only small variations.

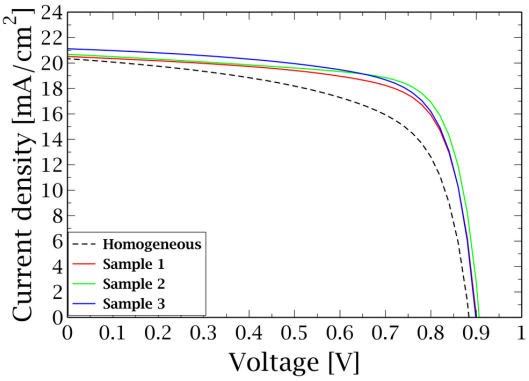

Fig. 3. J-V characteristics of the simulated perovskite solar cells. The homogeneous case with constant polariziation field is shown for comparison.

A comparison of the homogeneous case (dashed line in Figure 3) with the others, shows an overall improvement of the solar cell characteristics, and in particular of the fill factor (FF), which increase up to 73.42% (sample 2) compared to the 62.12% found for the homogeneous device.

This changes can be attributed both to an increase of the carrier extraction efficiency, i.e. an improvement of the transport properties, and a decrease of the effective recombination losses due to carrier separation. An estimation of the ratio between effective volume conductivities ($\sigma_{\mathrm{hom}}/\sigma_{eff}$) gives values around 3-4 orders of magnitude, while the effective recombination losses are also considerably reduced.

References

[1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells", *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050-6051, 2009.

[2] D. Bi, C. Yi, J. Luo, J. Dcoppet, F. Zhang, S. Zakeeruddin, X. Li, A. Hagfeldt and M. Grtzel, "Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21%", *Nature Energy*, vol. 1, no. 10, pp. 16142, 2016.

[3] H. Rohm, T. Leonhard, M. Hoffmann and A. Colsmann, "Ferroelectric domains in methylammonium lead iodide perovskite thin-films", *Energy & Environmental Science*, 2017.

[4] A. Pecchia, D. Gentilini, D. Rossi, M. Auf der Maur and A. Di Carlo, "Role of Ferroelectric Nanodomains in the Transport Properties of Perovskite Solar Cells", *Nature Energy*, vol. 16, no. 2, pp. 988-992, 2016.

[5] J. M. Frost, K. T. Butler, A. Walsh, Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells, *APL Materials,*, vol. 2, no. 8, pp. 081506, 2014.

[6] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, A. Walsh, Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells, *Nano Letters,*, vol. 14, no. 5, pp. 2584-2590, 2014.

[7] C. Wehrenfennig, G. Eperon, M. Johnston, H. Snaith and L. Herz, "High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites", *Advanced Materials*, vol. 26, no. 10, pp. 1584-1589, 2013.