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Current status and challenges of the modeling of organic photodiodes and solar cells

Invited paper

R. Clerc¹, B. Bouthinon², M. Mohankumar³, P. Rannou³, J. Vaillant⁴, T. Maindron⁴, B. Racine⁴,
Y-F Chen⁵, L. Hirsch⁵, J. M. Verilhac⁶, A. Pereira⁶, A. Revaux⁶.

¹ Univ. de Lyon, UJM-Saint-Etienne, Institut d'Optique Graduate School, CNRS, UMR5516, Lab. Hubert Curien, Saint-Etienne France, email: raphael.clerc@institutoptique.fr, ² ISORG, Grenoble, France, ³ UMR5819-SPRAM (CEA/CNRS/UGA), INAC, CEA-Grenoble, France ⁴ CEA LETI Grenoble France, ⁵ Univ. Bordeaux, IMS, UMR CNRS 5218, Talence, France ⁶ CEA, LITEN, Grenoble, France

Abstract— Progress in the modeling of charge transport in solution processed solar cells and photodiodes is reviewed. Through several examples involving modeling and original experiments, the role of intentional doping, structural defects, and oxygen contamination are discussed.

I. INTRODUCTION

Organic electronics is an emerging technology using π -conjugated molecules or polymers (i.e. organic semiconductors) [1] to produce electronic devices. Batteries, photovoltaic, (bio) sensors, displays, lighting are among the most relevant fields of applications of this technology [2-4]. One particular challenge of this domain consists in taking advantage of solution-processed organic materials to produce low-cost and large area devices by either roll-to-roll, sheet-to-sheet or printing technologies [3]. In this context, solution processed photodiodes are of particular interest, either for outdoor [5-6] and indoor [7] photovoltaic or imaging applications [8-10]. In the field of solar energy, External Power Conversion Energy (EPCE) exceeding 10 % have been reported using Bulk HeteroJunction (BHJ) polymer based devices [6] (approaching its fundamental limits [11]) and more than 20 % using solution processed hybrid inorganic/organic perovskite semiconductors [12]. Organic imagers are also attractive, either to improve silicon CMOS imagers [13], or to realize large-area, flexible, low-weight full organic imagers. Dark current level comparable with silicon photodiodes have already been reported [14][15]. In particular, large-area organic imagers, either deposited on the top of a thin-film transistor (TFT) or organic transistor backplane are attractive alternatives to amorphous silicon imagers in X-ray detectors for medical applications [9][16]. In all cases, despite the instability of most organic material in presence of UV, water and/or oxygen, the reliability of polymer-based devices has greatly improved and is no longer considered as a major obstacle, provided that suitable materials, processes, and encapsulations are used [17][18].

With the emergence of this technology, device modeling is more and more needed, either to support device processing or to predict system performances. The aim of this paper is to review the existing physical models, to discuss the main ingredients needed for device simulations, and to give example of application of modeling, in close comparison with experiments.

II. CHARGE TRANSPORT IN DISORDERED ORGANIC SEMICONDUCTORS.

It is generally admitted that π -conjugated small molecules and polymers behave as disordered semiconductors [19], even if the exact origins of such disorder are still under debate, and are material/process dependent. Structural heterogeneities in amorphous or polycrystalline semiconductors, induced by processes and interfaces, are of course a major sources of disorder, and many studies have reported significant mobility improvements by optimization of the material morphology [20]. However, it seems that disorder may have also intrinsic origins, induced either by chemical impurities, by changes in the surrounding polarization during charge transport [19], or as recently proposed, induced by large thermal molecular motions (transient localization), a direct consequence of the weak strength of van der Waals intermolecular interactions [21]. This later theory is supposed to explain the low temperature mobility improvement reported in some high mobility ($> 1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) organic single crystals, and sometimes referred as “band like” transport [22].

In the literature, two main approaches have been used to model transport in disordered semiconductor. The first one consists in solving the hopping master equation, either by Monte Carlo [23] or by direct solving [24]. Quantum chemistry can be used to calculate hopping site energy distributions [25]. In many cases however, the disordered energy positions of hopping sites is assumed to follow a Gaussian law, and hopping probabilities are modeled by Miller-Abrahams expressions, leading to the so-called Gaussian Disorder Model (GDM) [19]. This model predicts an increasing mobility with temperature, electric field and carrier concentrations, in agreement with several experiments [26]. There are exceptions, such as P3HT [27] or the high mobility “band like” single crystal for instance [22]. Numerically expensive, this approach is typically used to get insight on transport [26], recombinations [29] noise properties [24] or blend morphology [28] of organic materials (rather than to simulate complete device).

An illustration of the capability of GDM models to reproduce a large set of experimental data is shown in Fig. 1-5. In these experiments, several asymmetrical α -NPB p-only devices have been realized by evaporation, featuring different thicknesses in the 20-110 nm range. α -NPB is a hole transport material (HTM), classically used in OLED [30]. Interestingly,

the conductivity of α -NPB has been tuned by molecular doping of MoO_3 , as in [31]. In agreement with GDM theory, the conductivity shows a clear exponential dependency with doping concentration (Fig.2), despite significant process induced variability. Moreover, using low-field conductivity extracted on each device, I-V experiments can be satisfactory reproduced with the same set of GDM parameters, provided that the mobility electric-field dependence is included [30].

III. DRIFT DIFFUSION (DD) MODELS FOR ORGANIC SEMICONDUCTOR DEVICES.

The second commonly used approach to model organic device is the well-known Drift Diffusion model, numerically efficient and versatile. Disorder is included via Gaussian Bands (or exponential bandtails), shallow and deep traps and GDM inspired mobility models, as it was done in the past for amorphous silicon solar cells [32]. It can account for electron and holes transport in heterostructures [33] and interface charges and dipoles [30], which both play an important role in organic devices. Light propagation is performed by solving Maxwell equations [34]. DD requires detailed calibration with experiments, and especially band structure parameters (using UPS), mobility (using Time of Flight TOF), optical index and recombination (deep and shallow traps, bandtails). Even if the applicability of DD to model organic semiconductors is questionable [35], the efficiency of this approach to tackle many sophisticated phenomena such as transient low-light intensity in organic photodiodes [36], impact of blend morphology in BHJ solar cell [37][38], role of electron/hole transport layer (sometimes causing S shape [39]), analysis of impedance spectroscopy experiments [40] (and many others) is remarkable.

In that respect, let us give a recent example illustrating the strengths and weaknesses of the drift diffusion model (Fig. 6-8). The p-only polycrystalline perovskite MAPbI_3 has been processed and characterized at low temperature. Accounting for volume and interface shallow traps, I-V curves at 10 K have been nicely fitted by a simple DD model (Fig.7), extracting data from electroluminescence, I-V, TOF and C-V experiments (not shown here). Interestingly, with no additional fitting parameters, the model also correctly predicts the higher temperature I-V curves, however with a lower accuracy (Fig.8). A closer look to experiments has indeed revealed that the experimental temperature activated conductivity was in better agreement with hopping models, suggesting the occurrence of transport from traps to traps, not included in the DD model.

IV. AN EXAMPLE OF DEVICE SIMULATION: FRONT AND BACK SIDE QUANTUM EFFICIENCY DIFFERENCES IN SEMI-TRANSPARENT ORGANIC PHOTODIODES CAUSED BY OXYGEN CONTAMINATION

To conclude, let us give another example of the capability of device simulation to support device processing. Semi-transparent organic photodiodes may feature significantly different external quantum efficiency (EQE) when measured from front and back sides (see Fig. 9-13). It was initially suspected that this difference was caused by the different optical properties of top and bottom layers. However

simulations has shown that optics can hardly explain of fraction of this discrepancy, and not its thickness and voltage dependency. On the other hand, the introduction of deep acceptor traps, inducing a negative charge within the active layer in presence of light generated carriers was able to explain this effect (Fig. 11&12). In fact, the introduction of a single level acceptor deep traps, inducing both recombination and space charge effects, was able to reproduce a large set of experimental data (Fig.12). As oxygen is known to potentially induce negative charges and trapping [41], new experiments have been performed in absence of oxygen. In this later case, in agreement with simulations (Fig. 13), the difference of EQE has almost disappeared. The comparison between experiments and DD simulations has thus been of great help, indicating oxygen contamination as the potential origin of this effect.

V. CONCLUSIONS

Despite the complexity of disordered organic materials, Drift Diffusion based device simulation remains a powerful tool to analyze organic solar cells and photodiodes, and in particular the role of intentional doping, structural or induced defects states and interfaces. It requires however experimented users, capable on one hand to improve models thanks to the progress of more sophisticated approaches (such as variable range hopping model and quantum chemistry) and on the other hand, to perform detailed calibrations with experiments.

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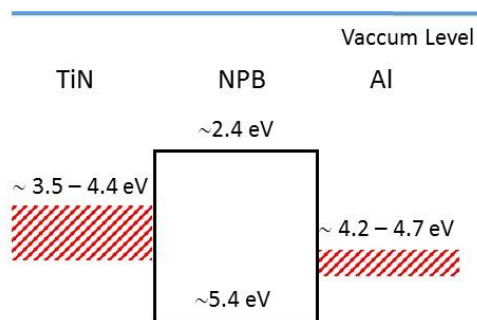


Fig. 1 : Band Diagram of the p-only asymmetrical α -NPB device

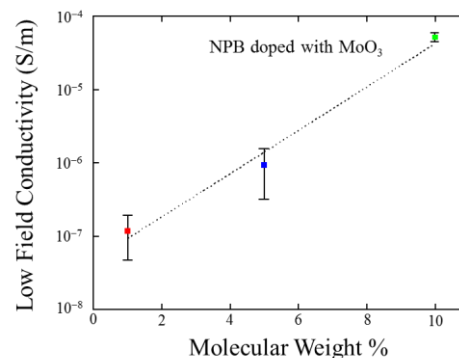


Fig. 2 : Low-field conductivity extracted from I-V experiments on each device versus nominal molecular weight (error bar indicates variability)

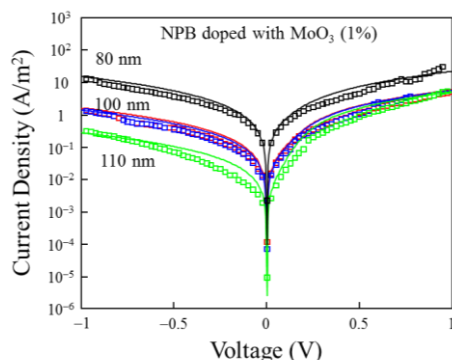


Fig. 3 : I-V curves of doped α -NPB (1%) symbols = experiments, line = simulations.

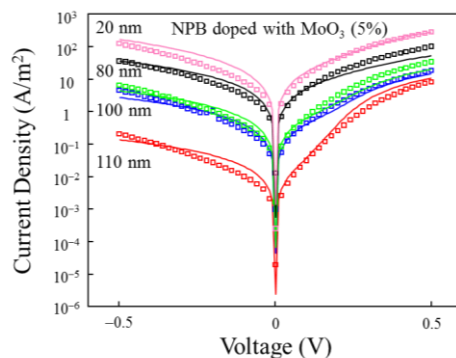


Fig. 4 : I-V curves of doped α -NPB (5%) symbols = experiments, line = simulations.

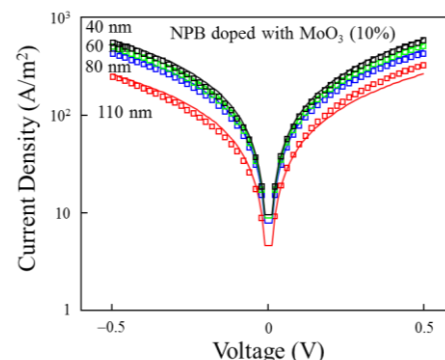


Fig. 5 : I-V curves of doped α -NPB (10%) symbols = experiments, line = simulations.

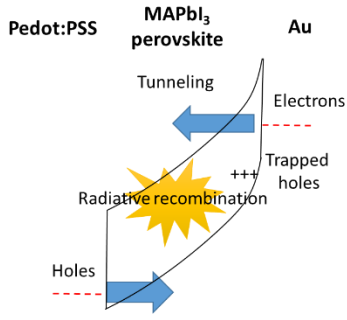


Fig. 6 : Schematic band diagram of the p-only polycrystalline perovskite MAPbI₃

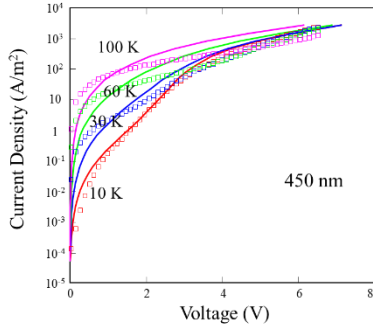


Fig. 8 : I-V curves for several temperature of the device of Fig. 6. Simulations are in good agreement with experiments, but do not perfectly capture the thermally activated low field regime.

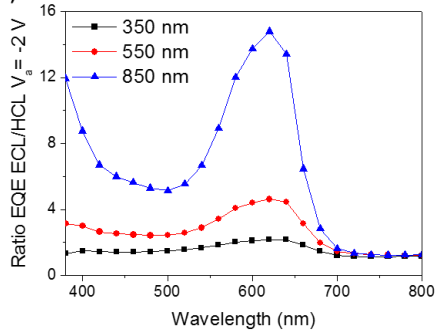


Fig. 10 : Experimental ratio between the back side external quantum efficiency EQE and the front side @ -2V versus wavelength

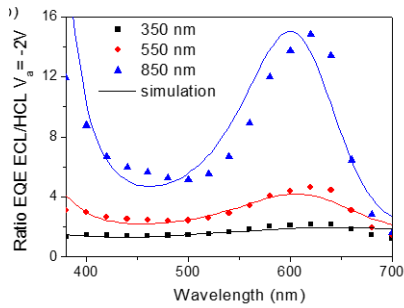


Fig. 12 : Same as Fig. 10, including simulations where an acceptor deep traps has been introduced (same concentration for all curves)

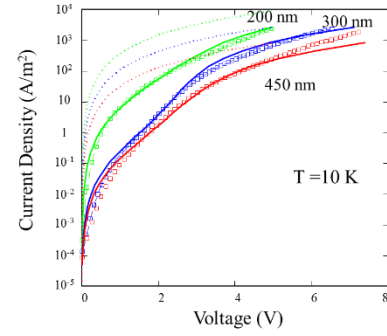


Fig. 7 : I-V curves @ 10 K of the device of Fig. 6. symbols = experiments, line = simulations, dotted line model without trapping.

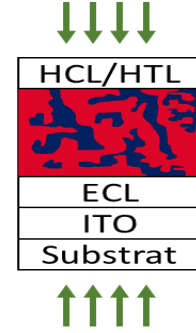


Fig. 9 : Composition of the semitransparent organic photodiode, lighted by either the back side (substrate) or the front side.

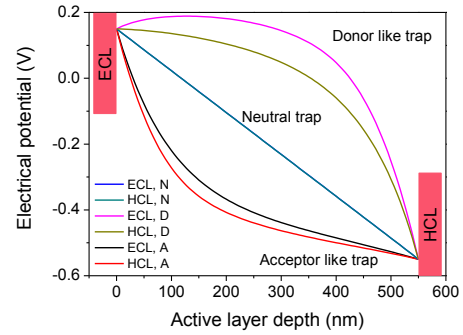


Fig. 11 : Simulation of the impact of negatively charged, positively and neutral volume traps (acceptors) on the electrical potential

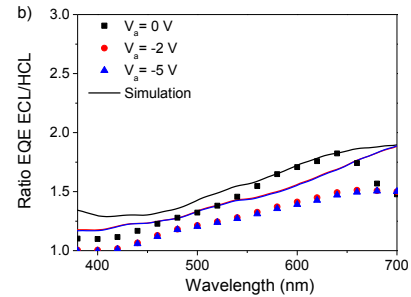


Fig. 13 : Same as Fig. 12, in absence of traps in simulations, where oxygen has been removed from experiments