Trap states limited nanosecond response of organic solar cells

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***Index Terms*—Organic solar cell, organic photodetector, numerical simulation, optical modeling, P3HT:PCBM blend, trap distribution, nanosecond photoresponse**

***Abstract*—Measured transient current voltage characteristics of organic solar cells exhibit a tail in the decline characteristic which is proportional to $t^{-\alpha}$. Common numerical drift-diffusion simulations neglecting dispersive charge carrier transport fail to describe the observed long tail of the current density decline up to micro seconds. Our approach is to account for the observed dispersive charge carrier transport by introducing an exponential distribution of trap states into our simulation. These trap states represent the tail of a bimodal distribution of energy states, which is commonly used to describe the distribution of transport sites of the highest occupied / lowest unoccupied molecular orbital (HOMO/LUMO) in organic materials. By doing so, we can reproduce the measured characteristics over four decades in time. Results are qualitatively and quantitatively in excellent accordance for different laser intensities, different applied biases and different device diameters at the same time.**

I. Introduction

Most of the previous simulation work of organic solar cells (OSCs) concentrated on modeling the steady state of the current density [2], [7], [8]. Our approach is to investigate the transient photoresponse on an impinging laser pulse [11], whereby the influence of electrons and holes on the current density can be distinguished, as the respective part becomes dominant at different time regimes. This is done in the framework of a one-dimensional numerical drift-diffusion model by incorporating a distribution of sites which act as trap states for the free charge carriers. Therewith we account for the energetic disorder in organic materials. Due to the mention disorder, the transport-levels (HOMO and LUMO) are broader and can be well described by a bimodal distribution of sites, consisting of a narrow Gaussian distribution and an exponential tail of sites [9], [5], [4], [1], [3]. Within our model the transport via sites lying in the Gaussian distribution is described by a constant mobility, which is enhanced in comparison to the commonly measured average mobility, while sites in the tail of the distribution are modeled as trap states. Moving photogenerated charge carriers are getting trapped with an trapping rate given by

$$R_{\mathrm{t_{e,h}}} = \mu_{\mathrm{e,h}} \cdot \sigma \cdot \left(\frac{k_{\mathrm{B}} T}{e_0 d} + |F| \right) \cdot \left(n_{e,h} \cdot (N_{\mathrm{trap_{e,h}}} - n_{\mathrm{t_{e,h}}}) \right), \quad (1)$$

before getting released with the detrapping rate

$$R_{\mathrm{d_{e,h}}} = -v_{e,h} \cdot \sigma \cdot \left(n_{\mathrm{t_{e,h}}} (N - n_{\mathrm{e,h}}) \cdot e^{\left(\frac{-E_{\mathrm{t_{e,h}}}}{k_{\mathrm{B}} T} \right)} \right) \quad (2)$$

$N_{\mathrm{trap_{e,h}}}$ is the density of acceptor/donor traps, N the density of free states at the center of the Gaussian distribution of the LUMO/HOMO, F the electric field, $n_{\mathrm{e,h}}$ the electron/hole density, $n_{\mathrm{t_{e,h}}}$the density of trapped charge carriers, $\sigma_{\mathrm{e,h}}$ the cross section dimension, $v_{\mathrm{e,h}}$ the thermal velocity and the trap depth E_{t}.

Regarding transient measurements and high laser intensities, it is of particular relevance to account for the external resistance R. High current densities are leading to a voltage drop V_{ext} at the external resistance, changing the effective applied voltage at the OSCs. As there is a time derivative of the effective applied voltage V_{eff} in the calculation of the total current density

$$j_{\mathrm{total}} = \frac{1}{L} \left(\int_0^L \left(j_{\mathrm{cond}}(x,t)\, dx \right) - \epsilon_0 \epsilon_{\mathrm{r}} \frac{\partial V_{\mathrm{eff}}}{\partial t} \right), \quad (3)$$

the calculation of Eq. 3 is done iteratively via Newton's method for each time-step. Therewith we can account for the impact of the device diameter (2D effect) in our one-dimensional simulation, as the total current is proportional to the device size.

Simulation results are compared to experimental measurements based on the absorber blend P3HT:PCBM. As we focus in this letter on the simulation part of our work, we refer for detailed description of the device architecture, its fabrication as well as the experimental setup to [11] and [6]. In the last mentioned reference one can find also further information of the implemented optoelectronic model, as well as in [10].

II. Results

While simulation results neglecting any trap effects show a good agreement with experimental results up to 140ns[6], there are huge discrepancies regarding the long-term behaviour. The current density drops nearly vertical at a characteristic time ($t_{\mathrm{c}} \approx 120$ ns), which is the time given by the transit time of the charge carriers being generated furthest off the electrodes. Furthermore, the strong rise of the measured photoresponses cannot be modeled with average mobilities for the electrons

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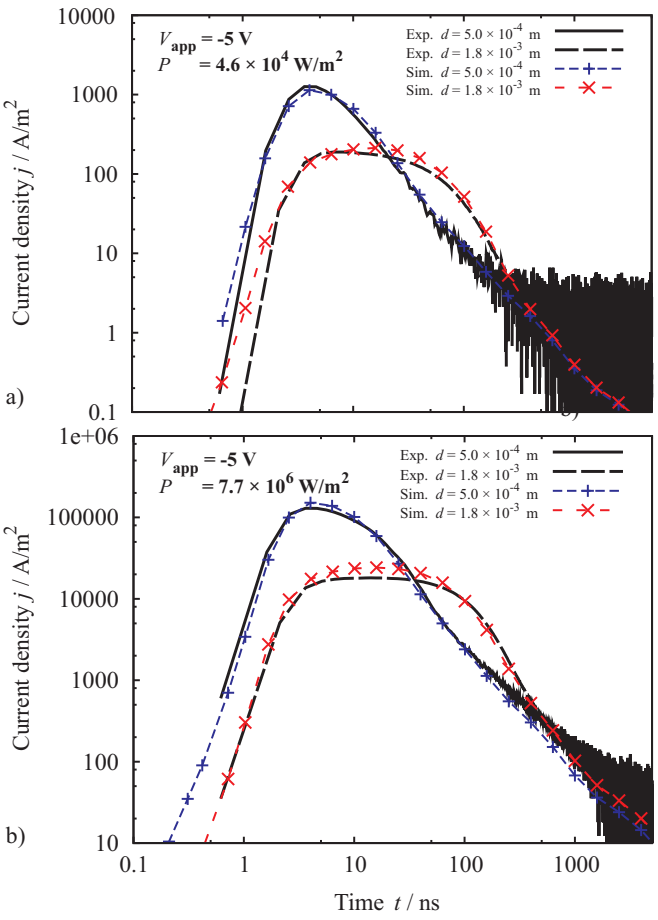

Figure 1. Transient photoresponses modeled with exponential distribution of trap states in comparison with measurements for two different device diameters, respectively, and a laser intensity of a) $P = 4.61 \times 10^4$ W/m^2 and b) $P = 7.73 \times 10^6$ W/m^2. The applied voltage is $V_{\mathrm{app}} = -5$ V.

and holes fitting the rest of the current density at the same time, as can be seen in Fig. 9 in [6].

By extending the classical drift-diffusion model trough consideration of five traps states representing the bimodal distribution of sites, excellent agreement of the simulated results and measurements is achieved over four decades in time, as pictured in Fig. 1. In both subfigures of Fig. 1 the curves represent the comparison for a device diameter of $d = 5{\times}10^{-4}m$ and $d = 1.8{\times}10^{-3}m$, whereas subfigure a) are photoresponses for a laser intensity of $P = 4.6 \times 10^4$ W/m^2 and subfigure b) for a hundred times higher laser intensity of $P = 7.7 \times 10^6$ W/m^2.

Taking a closer look at the results in Fig. 1, one can see that the characteristic $t^{-\alpha}$ decline is reproduced very well with our new model. The tail of the photoresponse decline is governed by the addition of the release of trapped charge carriers out of trap states with different trap depth. Due to the considerably higher electron than hole mobility in P3HT:PCBM, the photoresponse up to approximately 100 ns is dominated by the electrons, while the tail of the decline is dominated by the release of holes. This is why we can extract the magnitudes of the various parameters for the electrons and holes independently.

Besides the explanation of the origin of the measured photoresponse decline, there is a second striking effect we can deduce from our results. The determined mobilities of $\mu_{\mathrm{e}} = 7.5 \times 10^{-7}$ m^2/Vs and $\mu_h = 5.2 \times 10^{-8}$ m^2/Vs are three two four times higher than usually measured values [8]. We believe to see the trap-free and therefore unperturbed charge carrier mobility in the very first nanosecond, before charge carriers are getting trapped leading to an decrease of the average mobility. This is why we can extract the trap-free mobilities from the steep rise of the current density.

To conclude, by incorporating a bimodal distribution including an exponential trap distribution into our numerical drift-diffusion model, we achieve excellent accordance of measured and simulated photoresponses after an impinging laser pulse. The results demonstrate that considering the voltage drop at an external resistance is of crucial importance as with it we are able to account for RC-effects in a our one-dimensional simulation.

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