ESCAPING THE LIMITATIONS OF OPEN CIRCUIT BASED MEASUREMENT TECHNIQUES WHEN CHARACTERIZING ORGANIC SOLAR CELLS

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Introduction

In recent years, organic solar cells have shown great promise as a low-cost, low-carbon way to generate electricity. The ability to manufacture them in high volume using roll-to-roll printing techniques has attracted considerable attention from both academia and industry. Recently efficiencies of over 9.5% have been reported. Despite this success there is still considerable debate surrounding key physical mechanisms within the devices. The mechanisms controlling charge recombination and transport are still hotly debated. Recent analysis of the recombination mechanisms within organic solar cells have been based on combining the transient photovoltage technique (TPV) to measure carrier lifetimes with charge extraction measurements of electron and hole densities. [1] Based on these studies, a formulation of the charge carrier dynamics in terms of macroscopic charge density was presented, and was used to show that it is possible to obtain excellent reproductions of the light and dark J-V curves. [2] However, techniques such as TPV are limited as they are confined to the study of charge carrier decay dynamics for open-circuit conditions alone.

In this work we escape the limitations of TPV by using detailed device modeling in combination with experimental photocurrent transients across the light and dark J-V curves. This combination of transient measurements and modeling provides a direct approach to study the competition between charge transport and recombination in organic solar cells under all incident light and voltage conditions.

The Model

To describe carrier transport our 1D device model solves Poisson's equation and the bi-polar drift-diffusion equations. In energy space the model describes the interaction of free carriers with a distribution of trap states using Shockley-Read-Hall (SRH) theory. A 0D section of the model is depicted in figure 1, the free electron and hole carrier distributions are labeled as n_{free} and p_{free} respectively. The trapped carrier populations are denoted with n_{trap} and p_{trap}, they are depicted with filled red and blue boxes. SRH theory describes the rates at which electrons and holes become captured and escape from the carrier traps. If one considers a single electron trap, the change in population of this trap can be described by four carrier capture and escape rates as depicted in figure 1. The rate r_{ec} describes the rate at which electrons become captured into the electron trap, r_{ee} is the rate which electrons can escape from the trap back to the free electron population, r_{hc} is the rate at which free holes get trapped and r_{he} is the rate at which holes escape back to the free hole population. Recombination is described by holes becoming captured into electron traps. Analogous processes are also defined for the hole traps.

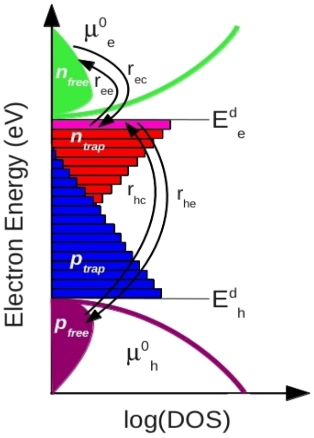

Figure 1: A 0D in energy space slice through our 1D device model.

Results

The numerical device model was calibrated against the dark JV curve, light JV curve, dark charge extraction data, light charge extraction data, a transient photocurrent (TPC) transient in the dark at 0 mV, a TPC transient in the dark at 400 mV, a TPC transient in the light at 50 mV and a TPC transient in the light at 400 mV. Thus the model is able to reproduce eight sets of experimental data from three different experiments. Using the same set of model parameters obtained by this calibration we are able to reproduce TPC transients over a range of voltages across the JV curve. Figure 2 shows both simulated and experimental TPC transients and figure 3 shows the simulated and the experimental JV curves. If figure 2 is examined, it can be seen that the model can predict the shape of the -1000 mV transient, this is notable because this transient is over 1V away from any calibration data. Furthermore after calibration, the model is able to predict TPV transients over a rang of light intensitiesalthough the model was not calibrated against TPV data. This suggests that carrier trapping and recombination are being modeled correctly. Consequently, we are able to directly calculate the recombination rate at any point on the light/dark JV curve and escape the limitations of previous open circuit based measurement techniques.

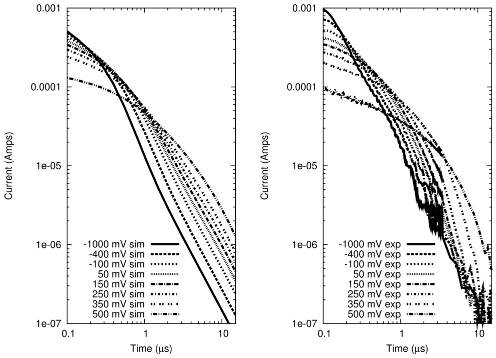

Figure 2: Experimental and predicted transient photocurrent measurements in the light over a range of voltages.[3]

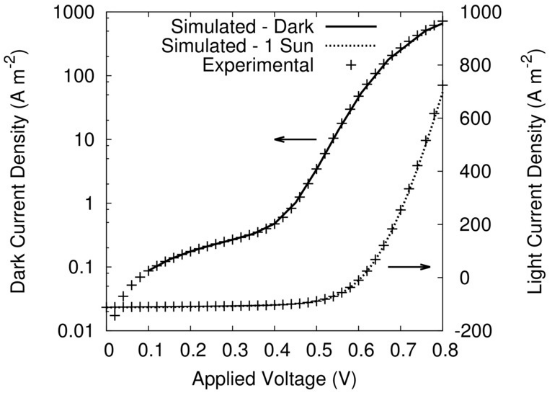

Figure 3: Simulated and experimental light and dark JV curves.[3]

Conclusion

We have demonstrated that SRH recombination can be successfully used to describe both the steady state and transient behavior of an organic solar cell. This provides further evidence for trap limited recombination being the dominant recombination mechanism in organic solar cells. Using transient photocurrent measurements to calibrate the numerical device model we have been able to predict TPC transients at voltages where the model was not calibrated and TPV transients when no calibration against TPV data was performed. This suggests that the model can correctly describe recombination, trapping and de-trapping away from open circuit.

[1] C. G. Shuttle,R. Hamilton, B. C. O'Regan, J. Nelson, and J. R. Durrant, “Charge-density-based analysis of the current-voltage response of polythiophene/fullerene photovoltaic devices”, Proceedings of the National Academy of Sciences of the United States Vol. 107 no. 38, pp. 16448-16452,
[2] R. MacKenzie, T. Kirchartz, G. Dibb and J. Nelson, “Modeling non-geminate recombination in P3HT:PCBM solar cells.”, submitted to Journal of Physical Chemistry C
[3] R. C. I. MacKenzie, C. G. Shuttle, M. L. Chabinyc and J. Nelson, accepted for publication 1st February 2012, Advanced Energy Materials