The interplay between space charge and recombination in conjugated polymer/molecule photocells

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We present an analytic description for the loss of photocurrent efficiency at moderate light intensities and demonstrate a simple technique for extracting the mobility of electrons in semiconducting polymer layers. The underlying theoretical analysis, which is based on a simple drift-recombination scheme, shows good agreement with the measured intensity-dependent photocurrent quantum efficiency over five orders of magnitude in intensity. The electron mobility extraction is demonstrated for pristine MEH-PPV. We use the combination of theoretical and experimental studies to discuss the role of recombination and space-charge effects in reducing photocurrent efficiency. We apply the analytical results to device design criteria and deduce that the minimum, low-field, mobility value of the slow carrier required to achieve close to ideal fill factor is $\sim 10^{-2}$ cm^2 V^{-1} s^{-1} at AM1.5. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2005374]

INTRODUCTION

Organic photocells have been developed for over a decade[1–17] and are nowadays approaching the commercial performance level. It is therefore important to understand the factors limiting the performance of photocells or more importantly point at methods for improving their performance. For example, it is known that in amorphous organic semiconductors electron and hole mobilities are typically an order (or more) of magnitude apart.[18] This phenomenon has led to the suggestion that space-charge effects play an important role.[1,3,12,15,16] In Ref. 1 the authors used a regional approximation to achieve an intuitive explanation for the formation of space charge and its effect on the photocurrent extraction. In our Ref. 12 we have employed a more detailed numerical analysis which extends over a wider intensity range and hence yields results that are somewhat more general. For example, it was found that space-charge-like effects take place even for equal electron and hole mobilities.[12] Also, it was shown that the power dependence of the quantum efficiency scales with the value of the space-charge-limited current of the slowest charge carrier. A most relevant finding, to the present paper, was that the onset of space-charge limit for the extracted current is (inevitably) accompanied by an onset of charge-recombination limit (otherwise the specimen would accumulate charge indefinitely). It is worth noting that the interplay between space charge and charge recombination was found not only in single-layer but also for double-layer photocells.[15] In this paper we show analytically that for semiconductors where the recombination is of the Langevin type[19] the onsets of space-charge limit and of recombination limit are very similar and are practically inseparable. These expressions are compared to experimental results spanning five orders of magnitude in excitation intensity. As a by-product we are also able to extract the slow carrier (electron) mobility.[12]

The physical picture we are concerned with is as follows. At sufficiently low light intensities one would expect a linear relation between the photocurrent and the light intensity, as the Langevin recombination is insignificant at low carrier concentrations. As the light intensity is increased, for a fixed applied voltage, so do the carrier concentrations and two inter-related mechanisms come into play—space-charge limit (SCL) and recombination. At this point the photocurrent quantum efficiency (QE) starts to decline. In the context of photodetector the above means that at steady state there cannot be any charging process and hence any loss of carriers can take place either as bimolecular recombination or as charge transfer across the electrode interface (we do not invoke any other loss/lifetime mechanism). Our goal here is to link the intensity at which the efficiency starts to decline to the term describing the space-charge-limited current for the low mobility carrier (typically electrons). The validity of such analytical expressions must be tested against carefully measured photocell properties spanning a wide range.

EXPERIMENT

Devices were fabricated by spin coating a solution of MEH-PPV in toluene on a substrate of indium tin oxide (ITO) covered with a previously spin-coated PEDOT layer. The layers were annealed in a vacuum oven followed by evaporation of an aluminum back contact. The layer thickness was approximately 300 nm. A representative *I-V* measurement of the device is shown in Fig. 1 exhibiting the expected diodelike behavior. For the photocurrent measurements the device was placed in front of an opening in an integrating sphere (Labsphere IS-040-SL) that was fed by a light-emitting diode (LED) with peak intensity at 505 nm (Lumileds LXHL-ME1D). The integrating sphere was equipped with a calibrated Si detector for monitoring the light intensity. The device was sourced and the photocurrent was measured using an Agilent 4155B Semiconductor Parameter Analyzer. The built-in potential of the device was

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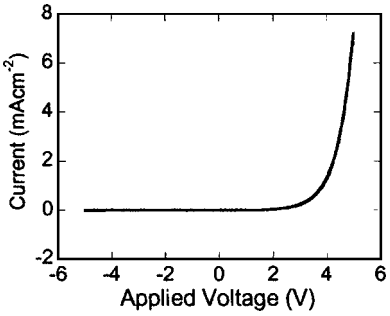

FIG. 1. (Color online) *I-V* measurement of the device showing the diodelike behavior.

measured as the saturation value for the open circuit voltage of the device at high illumination intensity and was found to be approximately −1 V.

RESULTS AND DISCUSSION

Since in Ref. 12 it was shown that the power dependence of the photocurrent quantum-efficiency saturation should scale as V^2, photocurrent versus light intensity was recorded under three different applied biasing conditions: 0, −0.5, and −1.5 V. The normalized photocurrent QE graphs of the measurements are shown in Fig. 2 (filled shapes) along with fittings to those measurements with the analytical model that will be discussed below (solid lines). As can be clearly seen, increase in the backward bias causes the bend in the curve to move to higher excitation intensities in good agreement with Ref. 12.

This saturation phenomenon, of the quantum efficiency, can be explained by realizing that the difference between electron and hole mobilities (μ_e and μ_h) results, under the lack of reinjection, in charging of the device and thus in reduction of the photocurrent that can be extracted at a given potential difference.[12] The regional approximation used in Ref. 1 predicts that the extracted photocurrent should scale as the incident light to the power of $\frac{3}{4}(P^{0.75})$. To this end we calculated the power law (L) that is exhibited by our data that is taken over five orders of magnitudes [$L=(dJ_{\mathrm{PC}}/dP)\cdot(P/J_{\mathrm{PC}})$]. The result of this derivation is shown in the inset of Fig. 2. At low incident powers the dependence is linear ($L=1$) and as the power is increased the power law gradually decreases to values well below the 0.75 predicted by Ref. 1. In Ref. 1 it was assumed that the current cannot exceed the value of the space-charge-limited current as derived for current injection scheme. It is true that the same set of equations governs the operation of a LED and a photocell, however, the boundary conditions are very different between a voltage source and optical source giving rise to a somewhat different solution. This shows that while the model in Ref. 1 is highly useful for understanding the essence of the picture it is probably not quantitative or general enough to predict or design devices.

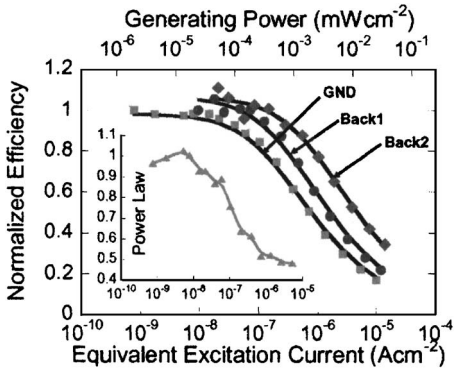

FIG. 2. (Color online) QE vs excitation—measurements and fittings for 300-nm-thick MEH-PPV device. Ground (GND) (squares) refers to no applied bias (i.e., built-in voltage only of about −1 V), Back1 (circles) refers to a total voltage of −1.5 V, and Back2 (diamonds) refers to a total voltage of −2.5 V. The inset shows the power-law dependence of the photocurrent on the photoexcitation power for the GND measurement.

The space-charge-limiting picture discussed above does not make explicit the internal recombination mechanism by which the QE begins to drop. Detailed numerical results, as in Ref. 12, show that the two phenomena of space-charge limit and recombination are strongly entangled. Therefore, we shall attempt to explain the above results by starting rather from the recombination scheme and then relate the results to the SCL current. By doing so we arrive at an analytical expression that is general enough to allow analysis and design of devices.

Assuming for simplicity a uniform illumination of the active layer and a low excitation power such that recombination is negligible the photocurrent and its dependence on intensity can be expressed as

$$J_{\mathrm{PC}} \simeq q\mu_e \frac{V}{d} n + q\mu_h \frac{V}{d} p = A \cdot P, \tag{1}$$

where q is the electron charge, V is the voltage drop across the active layer, d is the thickness of the layer, n and p are the electron and hole concentrations, respectively, A is a field-dependent constant that relates to the generation efficiency of free charges, and P is the excitation intensity. Since the contacts are blocking for reinjection, under steady state, the electron current that is extracted at the cathode is equal to the hole current that is extracted at the anode and the following relation between the concentrations of the carriers can be derived:

$$\mu_e \frac{V}{d} n = \mu_h \frac{V}{d} p. \tag{2}$$

Under these low excitations the charge density can be written as

$$n = \frac{A \cdot P}{2q\mu_e} \frac{d}{V}. \tag{3}$$

At higher powers the charge density will rise and at some stage the bimolecular recombination sets in and reduces the extracted current. Using the Langevin recombination and Eq. (2) we can write the recombination rate as a current loss mechanism:

$$J_L = \frac{q}{\varepsilon\varepsilon_0}(\mu_h + \mu_e)n \cdot p \cdot d \cdot q = \frac{q^2}{\varepsilon\varepsilon_0}\mu_e \frac{(\mu_h + \mu_e)}{\mu_h} n^2 \cdot d, \tag{4}$$

where ε_0 is the permittivity of free space and ε is the relative permittivity of the material. The effect of the recombination on the total photocurrent can then be written as

$$J_{PC} = A \cdot P - J_L = A \cdot P - \frac{q^2}{\varepsilon\varepsilon_0}\mu_e \frac{(\mu_h + \mu_e)}{\mu_h} n^2 \cdot d, \tag{5}$$

where we recall that AP is the generation current. Inserting Eq. (2)–(4) into (5) we get

$$2q\mu_e \frac{V}{d} n = A \cdot P - \frac{q^2}{\varepsilon\varepsilon_0}\mu_e \frac{(\mu_h + \mu_e)}{\mu_h} n^2 \cdot d, \tag{6}$$

and solving for the charge density n we find

$$n = \frac{-\frac{V}{d} + \frac{V}{d}\sqrt{1 + AP - \frac{d^3}{V^2\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_e\mu_h}}}{\frac{dq}{\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_h}}. \tag{7}$$

Reinserting n into the J_{PC} expression (5) results in the power dependence of the photocurrent,

$$J_{PC} = AP - \frac{q^2\mu_e d}{\varepsilon\varepsilon_0}\left(\frac{-\frac{V}{d} + \frac{V}{d}\sqrt{1 + AP\frac{d^3}{V^2\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_e\mu_h}}}{\frac{dq}{\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_h}}\right)^2 \times \frac{(\mu_h + \mu_e)}{\mu_h}. \tag{8}$$

This expression can be simplified by introducing the expression for the electron SCL current $[J_{SCL} = (9/8)\varepsilon\varepsilon_0\mu_e(V^2/d^3)]$ and assuming that $\mu_h \gg \mu_e$. Having done that, the expression for the photocurrent can be simply written as

$$J_{PC} = AP - \frac{\left(-1 + \sqrt{1 + AP\frac{d^3}{V^2\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_e\mu_h}}\right)^2}{\frac{d^3}{V^2\mu_e\varepsilon\varepsilon_0}\frac{(\mu_h + \mu_e)}{\mu_h}}$$

$$@AP - \frac{\left(-1 + \sqrt{1 + \frac{AP}{J_{SCL}}\frac{9}{8}}\right)^2}{\frac{1}{J_{SCL}}\frac{9}{8}},$$

and normalizing by the generation current value we finally arrive at

$$QE \cong 1 - \frac{\left(-1 + \sqrt{1 + \frac{AP}{J_{SCL}}\frac{9}{8}}\right)^2}{\frac{AP}{J_{SCL}}\frac{9}{8}}. \tag{9}$$

The linear term $A \cdot P$ can be deduced for the entire intensity span by extrapolating from the low-intensity measurements (as A is a constant). Note that the QE as defined by Eq. (9) is normalized by the charge generation efficiency at low powers (or by the absolute quantum efficiency obtained in the low power limit). Examination of Eq. (9) reveals that the QE should begin to drop at a charge generation rate that is close to the value of the low mobility carrier SCL current for the given voltage.

TABLE I. Fitting results for the QE measurements. J_{SCL} is the SCL current density as calculated by fitting the recombination model and the electron mobility was calculated from the SCL expression assuming a relative permittivity value of 2.5.

Applied voltage (V)	Voltage drop (V)	J_{SCL} (A/cm^2)	Calculated μ_e [cm^2/(V s)]
0	−1	1.18×10^{-7}	1.28×10^{-8}
−0.5	−1.5	1.96×10^{-7}	9.45×10^{-9}
−1.5	−2.5	5.49×10^{-7}	9.53×10^{-9}

We have compared the prediction of Eq. (9) with the results obtained by the full drift-diffusion-Poisson-recombination model described in Ref. 12 and found the curves to overlap when the same mobility value is used in the two models (not shown here). In Fig. 2 the measured data points are shown as markers while the solid lines are fits using Eq. (9), with J_{SCL} as the fitting parameter (note the good agreement over the wide range). The results of the fitting procedure are shown in Table I. The fitting parameter J_{SCL} is indeed found to scale as $\sim V^2$ thus strengthening the validity of the model. As a by-product, the resulting values for the electron SC current enable the calculation of the electron mobility (see Table I). As can be seen in Table I, the SCL current scales quite well with the square of the voltage, and hence the extracted mobility is almost constant in this range ($\mu_e \sim 10^{-8}$ cm^2 V^{-1} s^{-1}). We have also conducted independent time-of-flight measurements under the same conditions (to be published elsewhere) and found similar values for the electron mobility.

To further prove the validity and generality of the model we applied the same fitting procedure to the results obtained for a nanocrystal-polymer (CdSe nanorods-P3HT) blend photocell.[3] The symbols in Fig. 3 represent the values extracted from the experimental data in Ref. 3 and the solid line is the fit using Eq. (9). The deduced mobility using this

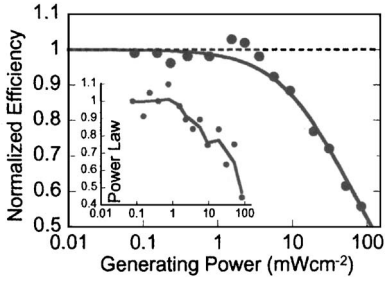

FIG. 3. (Color online) Round symbols are the normalized data extracted from Fig. 7 in Ref. 3 (CdSe nanorods-P3HT blend). According to Ref. 3 the device used had a built-in voltage of $V_{bi}=0.7$ V, excitation was at ~500 nm, and its length (Ref. 20) $d=220\pm10$ nm. The solid line is a fit. The inset shows the power-law dependence of the photocurrent on Eq. (9) using photoexcitation power derived from the data reported in Ref. 3.

TABLE II. The minimum mobility value that is required to avoid photocurrent loss due to recombination calculated for different applied bias using Eq. (11).

V_{appl}	$V_{bi}-V_{appl}$	μ_{min} ($cm^2\ V^{-1}\ s^{-1}$)
0	−1	8.3×10^{-5}
0.5	−0.5	3.3×10^{-4}
0.8	−0.2	2.1×10^{-3}
0.9	−0.1	8.3×10^{-3}
0.95	−0.05	3.3×10^{-2}

procedure is $\sim10^{-4}$ $cm^2\ V^{-1}\ s^{-1}$ in good agreement with the empirical procedure employed in Ref. 12. The inset shows, like in Fig. 2, that the power law as derived from the experimental data of Ref. 3 decreases as a function of excitation intensity and, again, that the 0.75 power law is found over a very short range only.

For device design purposes it may be useful to formulate an expression for the power at which recombination starts to affect the performance (P_R). Examining Eq. (9) it seems logical to define it as

$$A \cdot P_R = J_{SCL}, \tag{10}$$

which effectively means that for excitation intensity of P_R the efficiency drops by $\sim$20% or that the recombination current becomes significant once the charge generation current value is close to the value of the expression for the slow carrier (electron) SCL current. Using this expression one can deduce the minimum mobility value (for the slow carrier) that is required, for operating under AM1.5 conditions, to achieve a constant current at different voltages. The minimum mobility value that is required for a bias close to the open circuit voltage will ensure an almost ideal fill factor. The calculation is done assuming a device thickness of 100 nm, excitation density of 100 mW/cm^2 that is taken to be concentrated at a wavelength of 550 nm, and assuming a charge generation efficiency of 0.5:

$$\mu_{min} = \left[0.5 \cdot \frac{0.1}{h\nu} q\right] d^3 \Big/ \left[\frac{9}{8}\varepsilon\varepsilon_0 V^2\right]. \tag{11}$$

The representative results displayed in Table II show that, under AM1.5 illumination, if the slow charge-carrier mobility has a value of 10^{-2} $cm^2\ V^{-1}\ s^{-1}$ (at low electric field) one should expect close to ideal photocell characteristics. We note that the minimum value required scales linearly with the excitation intensity and thus in a given device and beyond a certain intensity the fill factor should decrease as a function of intensity, as was indeed reported in Ref. 3.

CONCLUSIONS

In a previous publication[12] we explained the QE curve by emphasizing the SCL scheme. There seems to be a coincidence in the fact that the two seemingly independent schemes result in the electron SCL current as the limiting factor for the photocurrent. This coincidence is understandable, however, when realizing that both SC effects and Langevin recombination become mutually significant when the charges are dense enough to electrostatically influence each other.

We have derived an analytic expression describing the reduction of photocurrent efficiency due to the onset of charge-recombination and/or space-charge effects. A simple approach for extracting electron mobilities in polymer layers was also presented. The minimum mobility value of the slow carrier required to achieve close to ideal fill factor was found to be $\sim10^{-2}$ $cm^2\ V^{-1}\ s^{-1}$.

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[1] A. M. Goodman and A. Rose, J. Appl. Phys. **42**, 2823 (1971).
[2] C. W. Tang, Appl. Phys. Lett. **48**, 183 (1986).
[3] W. U. Huynh, J. J. Dittmer, N. Teclemariam, D. J. Milliron, A. P. Alivisatos, and K. W. J. Barnham, Phys. Rev. B **67**, 115326 (2003).
[4] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, Nature (London) **376**, 498 (1995).
[5] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[6] P. Peumans, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. **76**, 2650 (2000).
[7] A. Hagfeldt and M. Gratzel, Acc. Chem. Res. **33**, 269 (2000).
[8] C. J. Brabec and S. N. Sariciftci, Monatsch. Chem. **132**, 421 (2001).
[9] A. C. Arias, J. D. Mackenzie, R. Stevenson, J. J. M. Halls, M. Inbasekaran, E. P. Woo, D. Richards, and R. H. Friend, Macromolecules **34**, 6005 (2001).
[10] A. C. Arias, N. Corcoran, M. Banach, R. H. Friend, J. D. MacKenzie, and W. T. S. Huck, Appl. Phys. Lett. **80**, 1695 (2002).
[11] G. Yu, J. Wang, J. McElvain, and A. J. Heeger, Adv. Mater. (Weinheim, Ger.) **10**, 1431 (1998).
[12] N. Tessler and N. Rappaport, J. Appl. Phys. **96**, 1083 (2004).
[13] C. Melzer, E. J. Koop, V. D. Mihailetchi, and P. W. M. Blom, Adv. Funct. Mater. **14**, 865 (2004).
[14] J. Nelson and R. E. Chandler, Coord. Chem. Rev. **248**, 1181 (2004).
[15] J. A. Barker, C. M. Ramsdale, and N. C. Greenham, Phys. Rev. B **67**, 075205 (2003).
[16] E. A. Schiff, Sol. Energy Mater. Sol. Cells **78**, 567 (2003).
[17] V. D. Mihailetchi, J. Wildeman, and P. W. M. Blom, Phys. Rev. Lett. **94**, 126602 (2005).
[18] D. J. Pinner, R. H. Friend, and N. Tessler, J. Appl. Phys. **86**, 5116 (1999).
[19] U. Albrecht and H. Bassler, Phys. Status Solidi B **191**, 455 (1995).
[20] W. U. Huynh (private communication).