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Origin of the light intensity dependence of the short-circuit current of polymer/fullerene solar cells

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A typical feature of polymer/fullerene based solar cells is that the current density under short-circuit conditions (J_{sc}) does not scale exactly linearly with light intensity (I). Instead, a power law relationship is found given by $J_{sc} \propto I^{\alpha}$, where α ranges from 0.85 to 1. In a number of reports this deviation from unity is speculated to arise from the occurrence of bimolecular recombination. We demonstrate that the dependence of the photocurrent in bulk heterojunction solar cells is governed by the build-up of space-charge in the device as a consequence of a difference in electron- and hole mobility. We have verified this for an experimental model system in which the mobility difference can be tuned from one to three orders of magnitude by changing the annealing treatment. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2130396]

Organic photovoltaic devices are a potential alternative to conventional inorganic solar cells with several unique benefits; ease of processing and the possibility of making devices on flexible substrates being their most important merits. Power conversion efficiencies of 3.5% have been obtained by using poly(3-hexylthiophene) (P3HT) as electron donor and 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM) as electron acceptor in a bulk heterojunction.[1] One of the key parameters is the current density under short-circuit conditions, J_{sc}, and its optimization is of great importance for the further improvement of organic solar cells. An important issue, in this respect, is the incident light intensity dependence of J_{sc}. Several authors have reported a power law dependence of J_{sc} upon light intensity I, i.e., $J_{sc} \propto I^{\alpha}$, where α ranges typically from 0.85 to 1 for polymer/fullerene based solar cells.[2–8] Thus far, the deviation from $\alpha = 1$ has been conjectured to arise from a small loss of carriers via bimolecular recombination.[3,5,8]

Recently, we have demonstrated that a large difference in electron- and hole mobility leads to space-charge limited photocurrents at high intensity due to unbalanced transport of electrons and holes.[9] When the photocurrent (J_{ph}) is space-charge limited, the following relation holds:[9,10]

$$J_{ph} \propto G^{0.75}\sqrt{V_0 - V_a}, \tag{1}$$

where G is the generation rate of free charge carriers and $V_0 - V_a$ reflects the effective voltage across the active layer. Thus, fully space-charge limited photocurrents are characterized by a square-root dependence on voltage and are proportional to $I^{0.75}$, irrespective of the amount of bimolecular recombination. On the other hand, non space-charge limited devices have a linear dependence of J_{ph} on I. Therefore, it is expected that the three-quarter power intensity dependence gradually increases to a linear dependence if the difference between the mobility of electrons and holes is reduced. Since the occurrence of space-charge is sensitive to the mobility difference, it is easy to understand that various material combinations will give different exponents α.

The solar cells addressed in this study are bulk heterojunctions consisting of a 97 nm thick blend of P3HT as electron donor and PCBM as electron acceptor in a 1:1 weight ratio. This blend is sandwiched between a hole-conducting layer of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS), and an evaporated lithium fluoride (LiF) (1 nm)/aluminum (100 nm) top electrode. Depending on postproduction thermal annealing treatment, the ratio of electron- and hole mobility ranges from three orders of magnitude to a factor of 20,[11] see Fig. 1, making this an ideal model system for our purpose of tuning the mobility difference. After fabrication the current-voltage characteristics of these devices were measured in a nitrogen atmosphere both in dark and under illumination. A white light halogen lamp set at approximately 1.15 kW/m^2 was used to illuminate the devices. To obtain light intensity dependent measurements, a set of neutral density filters was used, yielding an intensity variation of slightly more than one order of magnitude. It is important to note that the shape of the transmission spectrum is very nearly constant for the filters used, since this ensures that the intensity is proportional to the number of absorbed photons. Therefore, the generation rate of electrons and holes is expected to be proportional to the intensity. Figure 2
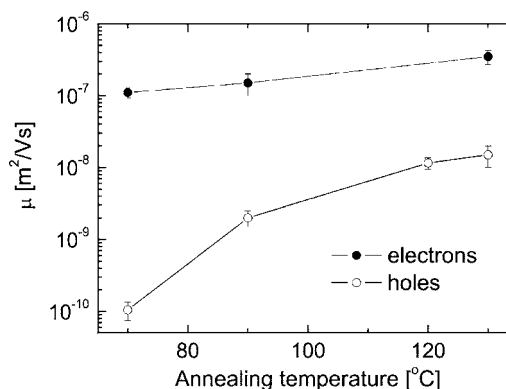

FIG. 1. Electron and hole mobility in P3HT/PCBM blends as a function of annealing temperature.
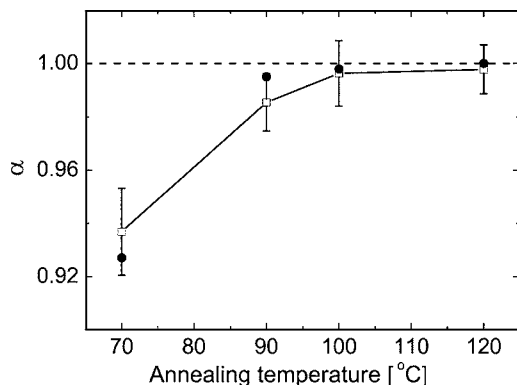
FIG. 2. The experimentally determined exponent α as a function of annealing temperature (open symbols) and the prediction by the numerical model (filled symbols), the solid lines are drawn as a guide to the eye, while the dashed line corresponds to $\alpha=1$.

shows the experimentally obtained exponents α, ranging from 0.94 (70 °C) to 1.00 (120 °C). Apparently, α is close or equal to unity for a small difference between the electron- and hole mobility (corresponding to high annealing temperatures), while α deviates significantly from unity for large differences in mobility (low annealing temperatures).

The photocurrent density J_{ph} is defined as $J_{\mathrm{ph}}=J_L-J_D$, where J_L is the current density under illumination and J_D is the current density in dark. The compensation voltage V_0 is defined as $J_{\mathrm{ph}}(V_0)=0$, consequently V_0 is very close, but some what larger, than the open-circuit voltage where $J_L=0$. The effective applied voltage across the device is given by V_0-V_a, where V_a is the applied bias voltage.[9,12] Figure 3(a) shows J_{ph} as a function of effective applied voltage V_0-V_a of a device annealed at 70 °C under 1.15 kW/m^2 illumination. Such a plot typically shows three regimes: a linear dependence of J_{ph} on V_0-V_a for small fields, a square-root part (the space-charge limited regime due to the large mobility difference), and a gradual transition to saturation of J_{ph} at high fields corresponding to high reverse-bias (where $J_{\mathrm{ph}}=qGL$).[9] Figure 3(b) shows the intensity dependences of the photocurrent at three different V_0-V_a corresponding to the various regimes, clearly, the intensity dependence changes when going from low to high V_0-V_a. The extent of the space-charge limited regime depends on the thickness of the active layer and on light intensity: when light intensity is increased, the space-charge limited regime grows and extends to higher V_0-V_a. In the present case the photocurrent is space-charge limited for the effective applied voltage range 0.1–0.35 V (the square-root regime with $J_{\mathrm{ph}}\propto I^{0.8}$), as evidenced by Fig. 3. Furthermore, Fig. 3 shows that J_{ph} indeed saturates at high enough (reverse bias) voltages as indicated by the linear dependence on intensity at $V_0-V_a=1.5$ V. It should be noted that V_0 is typically 0.03 V larger than the open-circuit voltage, consequently short-circuit conditions correspond to $V_0-V_a=0.64$ V. Therefore, the short-circuit current, at $V_0-V_a=0.64$ V, corresponds to a regime where the transition from the space-charge limited regime to the saturation regime occurs and, as a consequence, $0.8<\alpha<1$.

In order to describe the full current-voltage characteristics of organic bulk heterojunction solar cells we have developed a numerical model,[13] including both drift and diffusion of charge carriers, the effect of space-charge on the electric field, bimolecular recombination and a field- and temperature
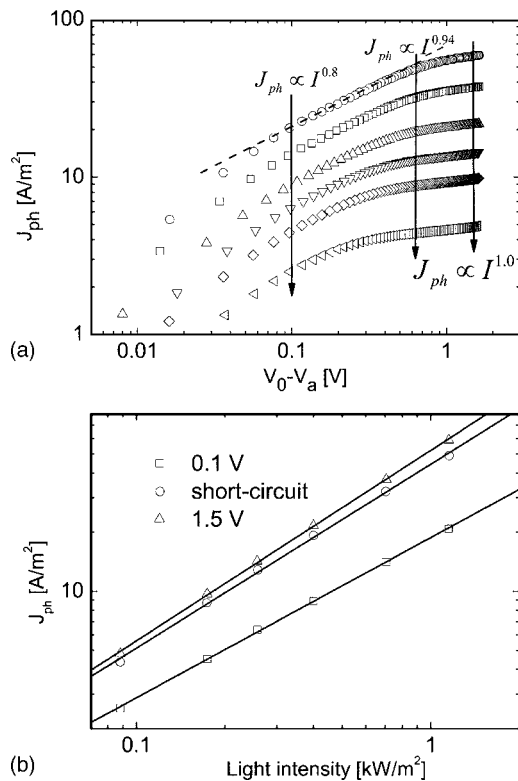

(a)

(b)

FIG. 3. (a) Experimental photocurrent density J_{ph} as a function of effective applied voltage V_0-V_a for a device annealed at 70 °C under 1.15 kW/m^2 illumination (symbols). The dashed line corresponds to a square-root dependence of J_{ph} on V_0-V_a, while the arrows indicate the intensity dependence at 0.1 V, short-circuit, and 1.5 V, respectively. The corresponding current densities as a function of light intensity are shown in (b) (symbols), together with linear fits to the data (lines).

dependent generation rate of free charge carriers. This model enables us to investigate theoretically the intensity dependence of J_{sc}. Figure 4 shows fits to the current-voltage characteristics of devices annealed at different temperatures illuminated at 1.15 kW/m^2 (no filter). In Ref. 11 the modeling of P3HT/PCBM devices is discussed in greater detail. By decreasing the generation rate G proportionally to the intensity, the value of α predicted by the model can be determined. The full symbols in Fig. 2 denote the simulation results, clearly these results are in good agreement with the experimental data, showing that our model describes the intensity dependence of J_{sc} correctly.
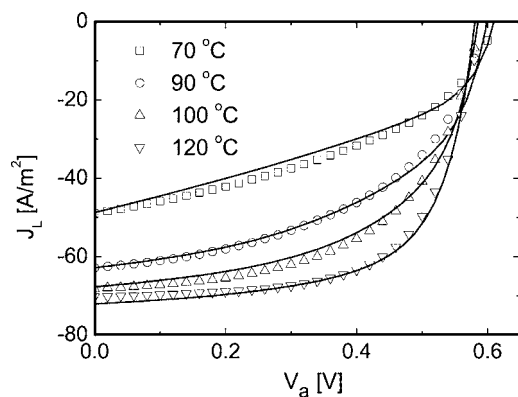

FIG. 4. Current density under illumination J_L as a function of applied bias V_a of devices annealed at various temperatures (symbols). The lines denotes the fits made with the numerical model.
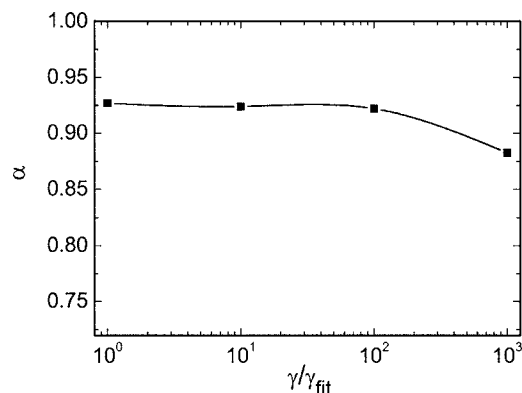
FIG. 5. The exponent α as a function of recombination strength γ normalized to the value used in the fit to the experimental data (symbols), showing that α is only weakly dependent on γ. The line is drawn as a guide to the eye.

Our numerical device model allows us to address the influence of bimolecular recombination on α, by increasing the recombination strength in our numerical calculations for the device annealed at 70 °C. Figure 5 shows the resulting α when the recombination strength γ is increased up to three orders of magnitude. It appears that α is only weakly dependent on γ; even increasing the bimolecular recombination strength by a factor of 100 does not change α, only an increase of more than two orders of magnitude influences α. This confirms that bimolecular recombination does not account for the observed sublinear dependence of J_{sc} on intensity. Note, however, that this does not imply that bimolecular recombination is not an important loss mechanism with respect to the device performance;[13] our simulations indicate

that the efficiency would increase by 24% if bimolecular recombination would not be present at all.

To conclude, we have shown that the sublinear dependence of J_{sc} on light intensity stems from the occurrence of space-charge caused by a large difference between electron- and hole mobility. Additionally, it is demonstrated that bimolecular recombination does not contribute to the experimentally observed light intensity dependence.

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