Origin of the enhanced performance in poly(3-hexylthiophene)

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Solar cells based on a blend of conjugated polymers and functionalized fullerenes are an attractive option for cost effective, large area, and light-weight applications. Initially, the attention has mainly been focused on blends of poly(2-methoxy-5-(3′, 7′-dimethoxynaphthyl)-1,4-phenylene vinylene) (MDMO-PPV) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM). By optimizing the morphology of the MDMO-PPV:PCBM BHJ, certified AM1.5 power efficiencies of 2.5% (with [60]PCBM) and 3% (with [70]PCBM) have been achieved. Recently, we have developed a device model that quantitatively describes the operation characteristics of PPV:PCBM BHJ solar cells. An important process that limits the photocurrent is the dissociation of bound electron-hole pairs, formed after the ultrafast electron transfer at the donor/acceptor interface. Another remarkable feature of MDMO-PPV:PCBM solar cells is that the optimum performance is reached adding up to 80 wt % of PCBM, a hardly absorbing material in the solar spectral region. The necessity of such a large amount of PCBM arises from a strong enhancement of the hole transport due to crystallization of the active layer. Slowing down the drying process of the wet films leads to an enhanced self-organization, which is expected to enhance the hole transport in the P3HT. In another study even efficiencies approaching 5% have been demonstrated, although the devices were not measured under standard AM1.5 test condition. The charge transport in the slowly dried P3HT:PCBM blends has been investigated using time-of-flight (TOF) measurements. Electron and hole mobilities of $\mu_e = 7.7 \times 10^{-9}$ m$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 5.1 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ were reported, respectively. It should be noted that these values were not measured in highly efficient solar cell devices but in films with a thickness of $\sim 1 \mu$m, since for TOF experiments the sample should be significantly thicker than the light-absorption region. It is, however, remarkable that the reported mobility values for these slowly dried films with superior photovoltaic performance are much lower than the values reported for MDMO-PPV:PCBM and annealed P3HT:PCBM devices: For MDMO-PPV:PCBM (1:4 wt %) values of $\mu_e = 2.0 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 1.4 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ have been found, and for P3HT:PCBM (1:1 wt %) using fast drying and annealing similar values of $\mu_e = 3.0 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 1.5 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$ have been measured. Therefore, from the reported values it is not clear whether an enhanced hole transport is responsible for the improved performance after slow drying. In the present study we perform mobility measurements in solar cells using space-charge limited (SCL) currents. It is observed that after slow drying the hole mobility of the P3HT improves to a record value of $\mu_h = 5.0 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$, which is 33 times higher than in blends that are annealed after spin coating and two orders of magnitude higher than earlier reported values. Device simulations show that because of this increased hole transport the active P3HT:PCBM layer can be made much thicker, up to

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The origin of the enhanced performance of bulk heterojunction solar cells based on slowly dried films of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) is investigated, combining charge transport measurements with numerical device simulations. Slow drying leads to a 33-fold enhancement of the hole mobility up to $5.0 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ in the P3HT phase of the blend, thereby balancing the transport of electrons and holes in the blend. The resulting reduction of space-charge accumulation enables the use of thick films ($\sim 300$ nm), absorbing most of the incoming photons, without losses in the fill factor and short-circuit current of the device.

300 nm, without a large reduction of the fill factor. The increased layer thickness then leads to an enhancement of the optical absorption, that subsequently increases the short-circuit current. Combined with the preservation of fill factor and open-circuit voltage, this leads to the observed enhancement of the power efficiency.

All devices during the course of this study were fabricated using indium tin oxide (ITO) coated glass substrates. Subsequently, an aqueous suspension of poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) (Bayer AG) was spin coated on top of the ITO surface, under ambient conditions, before drying the substrates at 140 °C in an oven. For fast drying films the active layer was fabricated by spin coating a solution of regioregular P3HT and PCBM (1:1 w/w) in chloroform on top of the PEDOT:PSS coated substrate. The devices were subsequently annealed in the nitrogen glove box on a hot plate at a temperature of 110 °C for 4 min. For slow drying films the active layer was spun from a chloroform solution, followed by drying of the films at room temperature in a closed Petri dish overnight.15 Subsequently, a LiF/Al top electrode was thermally evaporated on the ITO/PEDOT:PSS coated substrate. The devices were subsequently annealed in the nitrogen glove box on a hot plate at a temperature of 110 °C for 4 min. For slow drying films the active layer was then annealed by thermal annealing of the completed device at 110 °C for 4 min; (□) the active layer was spun from an ODCB solution and subsequently dried in a covered Petri dish overnight before the actual top electrode was thermally deposited. The film thicknesses are also indicated.

FIG. 1. Experimental photocurrent \( (J_L) \) vs applied voltage \( (V) \) of the ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al devices fabricated by two different recipes: (☆) the active layer was spun from a chloroform solution, followed by thermal annealing of the completed device at 110 °C for 4 min; (□) the active layer was spun from an ODCB solution and subsequently dried in a covered Petri dish overnight before the actual top electrode was thermally deposited. The film thicknesses are also indicated.

FIG. 2. Experimental dark current densities \( (J_D) \) of the 50:50 wt% P3HT:PCBM blend devices, measured at room temperature in the hole-only device configuration. The symbols correspond to different drying conditions of the photoactive layer (see text). The solid lines represent the fit using a model of single carrier SCL current with a field-dependent mobility.

The solid line is the calculated current employing a hole mobility \( \mu_h = 1.1 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1} \), similar to the value reported before.14 For the slowly dried films a mobility of \( \mu_h = 5.0 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1} \) is obtained, accompanied by a negative field dependence. Such a negative field dependence has been observed for pristine P3HT (Ref. 17) as well as P3HT:PCBM blends,18 and it is attributed to large spatial disorder of the charge transport sites. Applying slow drying we observe that the hole mobility in the P3HT phase increases by a factor of 45 with respect to the annealed films of Fig. 2, and compared to a previously reported value for annealed films it is 33 times higher.14 Furthermore, the measured mobility is almost two orders of magnitude larger than the earlier reported values for slowly dried films.15

In order to study the effect of such a mobility increase on the efficiency we apply a recently developed numerical device model17 to analyze the photocurrent \( J_L \) of the solar cells, as represented in Fig. 1. In this model the photocurrent in conjugated polymer/fullerene blends is dominated by the dissociation probability \( P(E,T) \) of electron-hole pairs at the donor/acceptor (D/A) interface, which is a field- and temperature-dependent process.6,19 The input parameters required to calculate the photocurrent in the model are \( \mu_c \) and \( \mu_h \), the spatially averaged dielectric constant \( \varepsilon_r \) of P3HT and PCBM, the dissociation parameters \( a \) and \( k_F^{-1} \), and maximum generation rate \( G_{\text{max}} \). \( G_{\text{max}} \) was determined from the full saturation of the photocurrent, and \( a \) and \( k_F^{-1} \) were determined from the field-dependent dissociation probability \( P(E,T) \) by fitting the temperature dependence of the photocurrent. Using \( \mu_c = 1.1 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1} \) and \( \mu_h = 3.0 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1} \), the photocurrent of the annealed device is consistently described, as shown in Fig. 3. For comparison, we also calculated the photocurrent for a device with a thickness \( L = 304 \text{nm} \), keeping all other parameters fixed. It
is evident from the curve that the fill factor strongly reduces to a value of only 42%, which is detrimental for the performance. Such a low fill factor is indicative for the formation of space charge in such a thick active layer device. In this case, an increase of the active layer thickness \( L \) will lead to an increase of the photocurrent until it reaches the thickness independent space-charge limit. Then, a transition will occur from a non-SCL to a SCL device, leading to a strong decrease of the fill factor. As a result, for a thick 304 nm device already a mobility difference of one order of magnitude is sufficient to induce significant space-charge effects.

In Fig. 4 the photocurrent of the slowly dried device is modeled using the enhanced mobility of \( \mu_e = 5.0 \times 10^{-7} \) m\(^2\) V\(^{-1}\) s\(^{-1}\) as input, while the other parameters were kept the same, except for \( G_{\text{max}} \) that was fitted from the photocurrent under reverse bias. Taking the enhanced mobility into account, the calculated photocurrent is in excellent agreement with the measurements. As a reference the dashed line of Fig. 3, using the lower mobility, is also included in the plot. As expected, the increase of the mobility leads to a strong enhancement of the FF, going from 42% to 61%. The small loss compared to the thin device shown in Fig. 3 is overruled by a significant increase of the \( J_{\text{sc}} \) due to the increased absorption, enhancing the power efficiency from 3.1% to 3.7%. The role of the increased mobility is that the transition from non-SCL towards the SCL regime is extended to higher thickness. With a mobility of \( \mu_e = 5.0 \times 10^{-7} \) m\(^2\) V\(^{-1}\) s\(^{-1}\), the 304 nm device is still in the regime where space-charge effects do not play a role. This is also confirmed by the linear intensity dependence of \( J_{\text{sc}} \). We also note that with the low mobilities reported before it is not possible to obtain a good fit of the experimental data. With these low mobilities, the calculated recombination losses in the device strongly increase, thereby lowering the FF far below the experimental values.

In conclusion, the origin of the enhanced performance in P3HT:PCBM bulk heterojunction solar cells, made with slowly dried active layer films, was investigated. Using hole transport measurements, we demonstrate that slow drying leads to a 33-fold enhancement of the hole mobility, reaching a value as large as \( 5.0 \times 10^{-7} \) m\(^2\) V\(^{-1}\) s\(^{-1}\) in the P3HT phase of the blend. This mobility increase reduces the accumulation of space charges in films with the necessary thickness to absorb most of the incoming photons. The resulting increase in short-circuit current together with the preserved fill factor increases the power conversion efficiency of these cells to a value of 3.7%.

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