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Origin of the dark-current ideality factor in polymer:fullerene bulk heterojunction solar cells

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In organic bulk heterojunction solar cells, a deviation of the ideality factor of the dark current from unity is commonly put forward as evidence for the presence of trap-assisted recombination. We demonstrate that the non-ideality of the dark characteristics is determined by deeply trapped carriers in the transport-dominating constituent of the donor:acceptor blend, rather than a trap-assisted recombination mechanism. The light-intensity dependence of the open-circuit voltage confirms the absence of trap-assisted recombination and demonstrates that the dominant recombination mechanism in the investigated polymer:fullerene solar cells is bimolecular. © 2011 *American Institute of Physics.* [doi:10.1063/1.3651752]

Since the discovery of organic semiconductor solar cells comprising a phase-separated blend of a conjugated donor and acceptor material,[1] great effort has been put in understanding the physics behind their operation.[2] Particularly, the mechanisms governing charge transport and recombination have received considerable attention. For a conventional (Si) *p-n* junction solar cell, the dark current density is given by

$$J_D = J_s \left[\exp\left(\frac{qV}{nkT} \right) - 1 \right], \qquad (1)$$

where J_s is the (reverse bias) saturation current density, V the applied voltage, q the elementary charge, k Boltzmann's constant, T temperature, and n the ideality factor. The ideality factor determines the slope of the exponential regime of the dark J–V characteristics on a semi-logarithmic plot and can be expressed as

$$n = \left(\frac{kT}{q} \frac{\partial \ln J}{\partial V} \right)^{-1}. \qquad (2)$$

The current density under illumination is given by $J_L = J_D - J_{ph}$, where J_{ph} is the photogenerated current density. Subsequently, the open-circuit voltage is given by ($J_L = 0$)

$$V_{oc} = (nkT/q) \ln (J_{ph}/J_s + 1). \qquad (3)$$

The ideality factor contains important information on the transport and recombination processes in organic solar cells. It is evident from Eqs. (1) and (3) that the ideality factor can be independently determined from the slope of the exponential regime of dark J–V characteristics on a semi-logarithmic plot [Eq. (1)] or by measuring the slope of the dependence of V_{oc} on the logarithm of the light intensity, that scales linearly with J_{ph} [Eq. (3)]. For an ideal p-n junction diode without trapping of charge carriers and where recombination is

absent or governed by bimolecular recombination, the ideality factor is expected to be equal to unity. However, already in 1957, Sah *et al.*[3] showed that the ideality factor of a classical p-n junction is calculated to increase due to trap-assisted recombination in the space-charge region. In their calculations, electrons immobilized in trapping sites recombine with free holes as described by the Shockley-Read-Hall (SRH) formalism.[4,5] Their predicted enhancement of the ideality factor, reaching a value of 2 for fully trap-assisted recombination, has also recently been found in organic light-emitting diodes.[6,7] From dark current measurements on polymer: fullerene organic solar cells, ideality factors of typically 1.3-2.0 have been reported.[8–11] Furthermore, it was first demonstrated by Mandoc *et al.*[12,13] that the presence of trap-assisted recombination in organic solar cells can, as implied by Eq. (3), be visualized by measuring the open-circuit voltage (V_{oc}) of an organic solar cell as a function of the incident light intensity. In these experiments on all-polymer solar cells,[13] also a deviation of n from unity was observed due to trap-assisted recombination. This result seems to be consistent with the observation of n larger than unity in dark-current measurements. As a consequence, an ideality factor greater than unity is often used as evidence for a dominant trap-assisted recombination process in organic solar cells.[8–10]

However, it appears that an unresolved discrepancy exists between the dark ideality factor and the light-intensity dependence of V_{oc}, which should have equal values according to Eqs. (1) and (3). A dark ideality factor larger than unity is often measured in organic solar cells of which both electron and hole transport are demonstrated to be trap free, which is in contradiction with the appearance of trap-assisted recombination to explain the ideality factor. Furthermore, V_{oc} vs light intensity measurements also showing a deviation from unity[13] were carried out on all-polymer solar cells of which the electron transport was observed to be clearly trap limited. On the other hand, solar cells with trap-free transport indeed show an ideality factor of unity when V_{oc} vs light intensity is measured, whereas in the dark current still a deviation from unity is found.[11] Attributing the occurrence of a

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dark ideality factor larger than unity to trap-assisted recombination is therefore highly questionable. Cowan et al.[10] recently argued that the higher density of charge carriers under illumination could impose a crossover from trap-assisted to bimolecular recombination, due to a difference in density dependence of these recombination mechanisms.[6,7] This would lead to a lower ideality factor under illumination as compared to the dark ideality factor. In this letter, we demonstrate that in organic solar cells with trap-free transport, the dark ideality factor is determined by the transport-dominating carrier in the blend, whereas the ideality factor under illumination is solely governed by bimolecular recombination.

In this study, organic bulk heterojunction solar cells were fabricated using the well-studied donor materials poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV), and poly[9,9-didecanefluorene-alt-(bis-thienylene) benzothiadiazole] (PF10TBT), blended with the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor material in a 1:4 weight ratio. Photoactive layers were prepared by spin-casting the chlorobenzene solutions under nitrogen atmosphere on clean glass substrates, pre-patterned with indium tin oxide and a 60 nm thick film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (VP AI4083, H.C. Starck). The devices were finished by thermal evaporation of a LiF(1 nm)/Al(100 nm) cathode. Electrical measurements were conducted in an N_2 controlled atmosphere in dark and under illumination of a Steuernagel SolarConstant 1200 metal halide lamp, which was set to 1 sun intensity using a silicon reference cell and correcting for spectral mismatch.

In Fig. 1, dark J–V characteristics for the investigated solar cells are depicted. The characteristics show typical diode behavior, with a leakage contribution at low voltages and an exponential regime at intermediate voltages, with a transition to the space-charge-limited regime at the built-in voltage (V_{bi}). The built-in voltage is determined by the work fun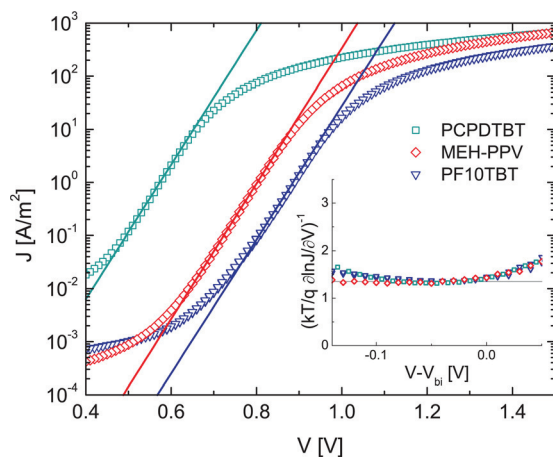ction difference between the electron- and hole-extracting electrodes. As can be observed from the inset in Fig. 1, where the differentiated characteristics according to Eq. (2) are plotted as a function of voltage, the ideality factors for all these solar cells amount to an identical value of ~1.3. In contrast, the slope S of the V_{oc} vs light intensity characteristics equals kT/q, as depicted in Fig. 2. This can be interpreted as an ideality factor of 1 under illumination, clearly indicating the dominance of bimolecular recombination.[11]

Recently, we demonstrated that the ideality factor often deviates from unity even in single-carrier diodes of a single material, where recombination is completely absent.[14] This deviation from unity was ascribed to a violation of the Einstein relation, caused by a small number of deeply trapped carriers that are not in thermal equilibrium with free carriers in the transport sites. It was shown that by releasing these trapped carriers by means of recombination, quasi-equilibrium is recovered so that the Einstein relation is valid again. Since the occurrence of a small number of deeply trapped carriers can be material dependent, each component of the blend of a bulk heterojunction solar cell might have a different dark ideality factor. To investigate if the dark ideality factor of the solar cell is affected by the ideality factors of its components, we compared the n–V characteristics of a MEH-PPV:PCBM solar cell and single-carrier diodes of its two constituents. As can be seen from Fig. 3, the ideality factor of the dark current of the solar cells matches the ideality factor of a PCBM electron-only diode. This is consistent with the fact that the electron mobility in PCBM is an order of magnitude higher than the hole mobility in MEH-PPV, so the dark current of the solar cell is dominated by the electron transport through the PCBM phase.[2] For an MEH-PPV hole-only diode, an ideality factor of 1.6 was measured, in agreement with the hole-only diode of the MEH-PPV:PCBM blend. It should be noted that, in these single-carrier diodes, recombination is completely absent. It can therefore be concluded that the dark ideality factor of the blend is determined by the dominant type of charge carrier, resulting in a PCBM ideality factor of 1.3. An important prerequisite for dominant electron transport is that there exist percolative pathways in the fullerene network, so that charge transport is not limited
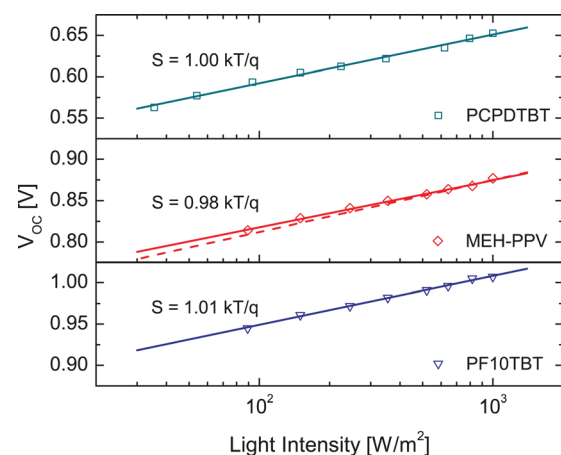

FIG. 1. (Color online) Dark J–V characteristics of PCPDTBT:PCBM, MEH-PPV:PCBM, and PF10TBT:PCBM solar cells. The solid lines are fit to the exponential regime of the characteristics. The inset shows the differential plot of the data according to Eq. (2).

FIG. 2. (Color online) V_{oc} vs incident light intensity for PCPDTBT:PCBM, MEH-PPV:PCBM, and PF10TBT:PCBM solar cells. The solid lines represent the best fits to the data, for which the slope S is indicated. The dashed line represents the slope (S = 1.07 kT/q) of an MEH-PPV:PCBM cell in a 1:2 weight ratio.
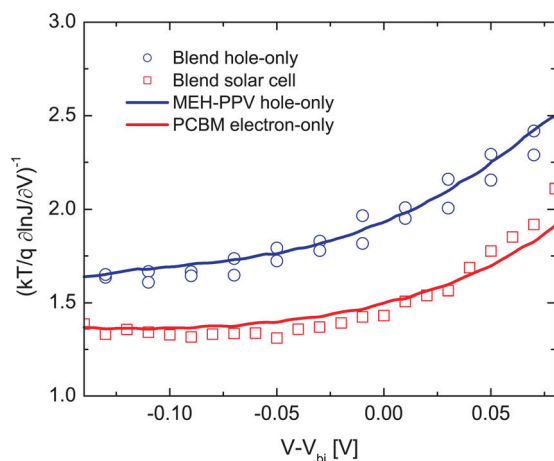
FIG. 3. (Color online) n–V characteristics of the dark current of an MEH-PPV:PCBM blend solar cell and hole-only. The lines represent experimental n–V characteristics for an MEH-PPV hole-only device and a PCBM electron-only device.

FIG. 4. (Color online) Temperature resolved n–V characteristics of the dark current of an MEH-PPV:PCBM solar cell.

by the microstructure of the blend. We therefore validated that an ideality factor of 1.3 was also measured in solar cells with a lower fullerene content, such as MEH-PPV:PCBM in a 1:2 ratio and poly(3-hexylthiophene):PCBM in a 1:1 ratio. It is also important to note that the occurrence of the fullerene ideality factor in a solar cell is expected for other fullerene derivatives that exhibit virtually trap-free electron transport, such that the dominant recombination mechanism is bimolecular. Indeed, also for the C_{70} analogue of PCBM, we found similar differences between the ideality factor in dark and under illumination.

In general, V_{oc} is determined by a competition between recombination and generation of charges.[15] As a result, recombination mechanisms can be excellently extracted by studying the open-circuit voltage as a function of generation rate, which can be tuned linearly by variation of the incident light intensity. For the solar cells investigated here, the dominant recombination mechanism is bimolecular, as evidenced by the slope of kT/q in the V_{oc}–intensity measurements in Fig. 2. Apparently, the light-intensity dependence of V_{oc} is not affected by the individual ideality factors of the donor and acceptor material in the blend. The reason is that the deeply trapped carriers that give rise to greater-than-unity ideality factors in the dark current of the separate materials are released from the trap by recombination with photogenerated charges, so that their effect on the ideality factor is neutralized. As a result, the light-intensity dependence of V_{oc} can be used as a reliable tool to evaluate the presence of trap-assisted recombination.

A remaining issue is the large apparent temperature dependence of the ideality factor in organic solar cells, as observed in previous publications.[11,16] In our recent work,[14] we showed a temperature independent ideality factor for single-carrier devices. If the dark current of the blend has an ideality factor equal to that of PCBM, the blend ideality factor should also be temperature independent. This temperature independence can be directly observed for the MEH-PPV:PCBM cell in Fig. 4. Therefore, these measurements confirm once again that the solar cell dark current and its ideality factor are dominated by the electron current
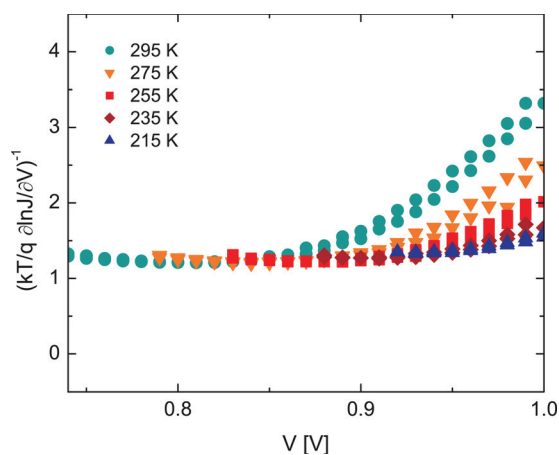
through PCBM. Previous observations of a temperature dependent ideality are likely caused by a too large leakage current.[6,14]

In conclusion, we have demonstrated that the ideality factor of the dark current of organic bulk heterojunction solar cells is dominated by the fastest transporting material in the blend. The non-ideality is caused by deeply trapped carriers, of which the effect is neutralized under illumination, so that the ideality factor under illumination is a reliable indication of the recombination mechanism taking place. Consequently, a dark ideality factor deviating from unity cannot be used as an indication for the presence of trap-assisted recombination in an organic solar cell.

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