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## Dark carrier recombination in organic solar cell

Ying-Xuan Wang,<sup>1</sup> Shin-Rong Tseng,<sup>1</sup> Hsin-Fei Meng,<sup>1,a)</sup> Kuan-Chen Lee,<sup>2</sup> Chiou-Hua Liu,<sup>3</sup> and Sheng-Fu Horng<sup>3</sup>

<sup>1</sup>*Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*

<sup>2</sup>*Institute of Electronic Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China*

<sup>3</sup>*Institute of Electronics Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China*

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The carrier recombination in organic solar cells is investigated by numerical modeling to understand the weak dependence of the open-circuit voltage on the workfunction of the electrodes. In Ohmic contact structures, photocarriers recombine predominantly with dark carriers diffused from the electrode into the semiconductor. Such dark carrier recombination becomes the main limit of power conversion efficiency and open-circuit voltage. For a given semiconductor decreasing the workfunction difference of the electrodes reduces simultaneously the dark carrier recombination and the flat band voltage. The balance between these two opposite factors gives a nearly constant open-circuit voltage. In an ideal bilayer structure there is no dark carrier recombination and the efficiency is demonstrated to be 60% higher than single layer blend. © 2008 American Institute of Physics. [DOI: 10.1063/1.2972115]

Organic solar cells have attracted great interest recently due to their unique properties such as easy solution process, light weight, and mechanical flexibility. Currently power conversion efficiencies (PCEs) approaching 5% have been reported for solar cells based on single layer of polymer bulk heterojunction (BHJ).<sup>1,2</sup> However, the efficiency is not enough for practical applications. One of the key factors to determine the solar cell efficiency is the open-circuit voltage ( $V_{oc}$ ). In the simplest approximation,  $V_{oc}$  is given by the flat band voltage which is equal to the difference between the workfunctions of the two metal electrodes. Therefore, in the ideal cell, metal Fermi levels are aligned with the valence band of the donor and the conduction band of the acceptor in the BHJ blend. For the commonly studied polymer cell with poly(3-hexylthiophene-2,5-diyl) (P3HT) donor and [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) acceptor the energy difference is 1 eV. However,  $V_{oc}$  of such solar cell is only about 0.6 V experimentally. Furthermore, many works show that  $V_{oc}$  is rather insensitive to the type of the metal electrodes,<sup>3,4</sup> contrary to the simplest approximation based on the flat band condition. Despite the extensive experimental<sup>3,5-8</sup> and theoretical studies,<sup>4,9-12</sup> so far the limit of the  $V_{oc}$  remains unclear and the way to raise it to nearly 1 V is unknown. In this work we employ a numerical model to understand the microscopic origin of the weak dependence of the  $V_{oc}$  on metal workfunctions and the main limit of the efficiency.

The theoretical model follows the previous works on organic light-emitting diodes,<sup>13,14</sup> and some assumptions have been made for simplicity. The mobility is assumed to be field independent and same for electrons and holes. The photocarrier generation rate is assumed to be constant in space and there is no trap inside the device. The boundary conditions are given by matching the thermionic-emission current plus backflow current at the metal-semiconductor interface with the drift-diffusion current in the bulk.<sup>13,14</sup>

We first apply the model to the case of low barrier height between the metal Fermi level and the semiconductor energy bands. The energies of the semiconductor bands are chosen to describe the blend of P3HT and PCBM. So the electron affinity (EA) is 3.7 eV and the ionization potential (IP) is 5.1 eV. The barrier height (0.2 eV) in an Ohmic contact is chosen to be symmetrical between electron and hole as shown in the inset of Fig. 1(b). Such Ohmic contacts exist in most experiments where poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and a low workfunction metal such as Ca are used for the electrodes. The total current density  $J_{tot}$  versus applied voltage is shown in Fig. 1(a) for various mobilities. The recombination current density  $J_r$  is the integration of the recombination rate  $R$  over space also shown in the inset. It is clear that the total current is a constant negative total photogeneration current plus the positive recombination current  $J_r$ . In other words the recombination is the main limit of efficiency for the solar cell with Ohmic contact. The dependence on the mobility indicates the same. When the carrier mobility increases from  $10^{-3}$  to  $10^{-1}$  cm<sup>2</sup>/V s,  $V_{oc}$  is reduced due to the enhanced recombination between the photocarriers and the dark carriers. With higher mobility, there is an easier supply of the dark carriers diffused from the electrodes. The efficiency would monotonically increase with the mobility if the recombination was mainly between the photocarriers themselves, since such recombination always decreases with the increasing mobility due to shorter transit time.

The recombination distribution is plotted in Fig. 1(b) for various bias voltages. At low voltage there is a strong built-in field to prevent the dark carriers from diffusing deeply into the semiconductor bulk. The recombination, dominated by those between photocarriers and dark carriers, is consequently confined near the electrode. Note that the distribution would be uniform through the bulk even at low voltage if it was dominated by the recombination between photocarriers, which are generated uniformly. As the voltage approaches the flat band condition and the built-in field diminishes, the

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: meng@mail.nctu.edu.tw.

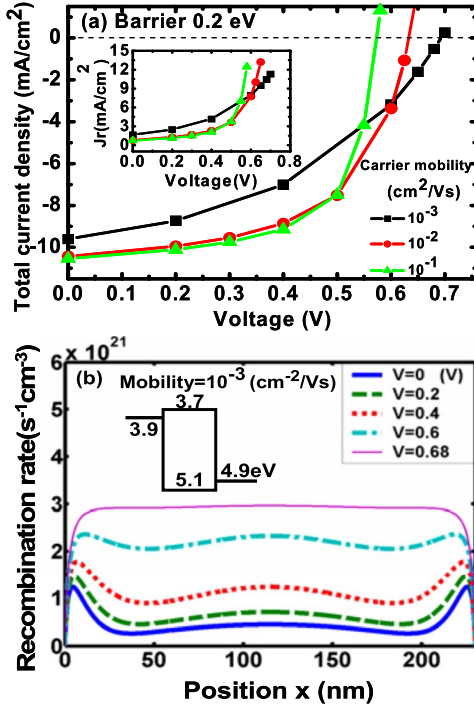


FIG. 1. (Color online) (a) The total current density of a single-layer cell with thickness of 230 nm, generation rate  $G$  of  $3.145 \times 10^{21} \text{ s}^{-1} \text{ cm}^{-3}$ , relative dielectric constant  $\epsilon_r$  of 3, temperature of 300 K, and barrier height of 0.2 eV for various mobilities. The inset shows recombination current density. (b) Recombination rate in the bulk at different applied biases. The mobility is  $10^{-3} \text{ cm}^2/\text{V s}$ . The position of 0 nm is defined as the interface between the cathode of workfunction (3.9 eV) and the blend.

dark carriers then diffuse easily into the bulk so the recombination distribution becomes more uniform. Combining the results above, we conclude that dark carrier recombination is the dominating factor to limit the solar cell efficiency.

In order to further verify the origin of the recombination current, we consider the case of a high injection barrier, i.e., Schottky contact, for comparison with the case of Ohmic contact discussed above. The energy band diagram is shown in Fig. 2. All model parameters are the same as in Fig. 1 except that the band gap is enlarged to have an injection barrier of 1 eV. In particular the photogeneration rate  $G$  is artificially chosen to be the same as the low band gap case in order to isolate the effects of the dark carriers. Figure 2(a) shows that  $V_{oc}$  now increases from 0.6 V for the Ohmic contact to 1 V for Schottky contact, simply the difference between metal workfunctions, and becomes independent of the mobility because of inhibition of dark carriers by the large barrier. This is in sharp contrast to the case of Ohmic contact where  $V_{oc}$  depends strongly on mobility due to various levels of dark carrier recombination. The fill factor is higher for high mobility because there is less diffusion current which leads the carriers to the wrong electrode. The recombination current  $J_r$  as a function of voltage is shown in the inset of Fig. 2(a). The total current is now not just a negative constant plus a positive  $J_r$  as in the case of Ohmic contact, implying that the recombination is no longer the main limit of efficiency. Instead, the total current is now limited by the diffusion current. With lower mobility the diffusion current is larger because the photocarriers are more likely to accumulate inside the bulk. The recombination rate distribution for the high barrier case is shown in Fig. 2(b). The recombination is away from the metal contact for all

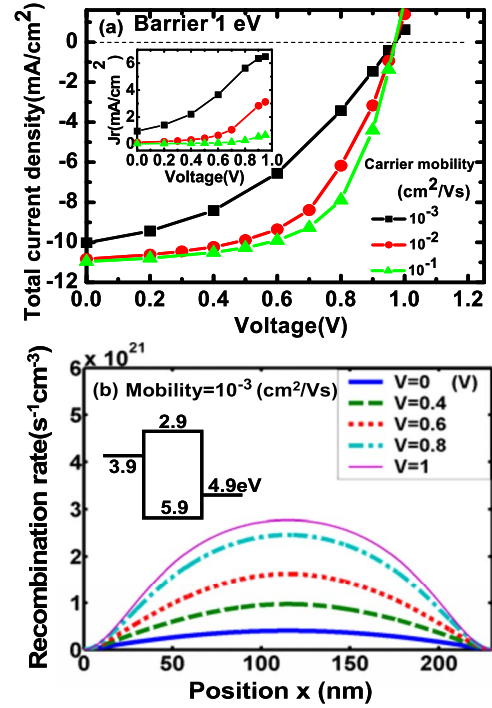


FIG. 2. (Color online) (a) The total current density and recombination current density for a single-layer cell with thickness 230 nm and barrier height 1 eV. (b) Recombination rate at different applied biases for mobility of  $10^{-3} \text{ cm}^2/\text{V s}$ .

bias voltages in sharp contrast to the Ohmic contact case where recombination is confined near the interface. Apparently the rather uniform distribution implies that the recombination is now between the photocarriers themselves instead of between a photocarrier and a dark carrier. The only difference between the model calculation in Fig. 2 and Fig. 1 is that the dark carriers are removed in Fig. 2 by the high barrier. The photocarrier generations and the built-in fields remain the same. The dramatic differences in the current-voltage relations,  $V_{oc}$ , and the recombination distributions strengthen our previous conclusion that the dark carriers play a dominating role in the solar cell.

Once the limit of the solar cell efficiency is understood to be closely related to the dark carriers, one can come to the central question on the dependence of  $V_{oc}$  on the metal workfunction. In Fig. 3 we consider the case of a given semiconductor with various carrier injection barriers  $\phi_B$  shown in the inset. The mobility is  $10^{-3} \text{ cm}^2/\text{V s}$ . The bias for the flat band condition is  $1.4 \text{ V} - (2/q)\phi_B$ . For a small  $\phi_B$ , the flat

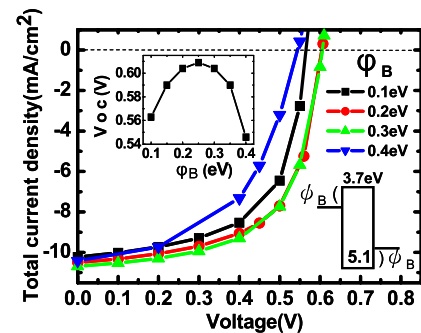


FIG. 3. (Color online) The total current density with different barrier heights  $\phi_B$  for a fixed semiconductor EA of 3.7 eV and IP of 5.1 eV. The inset plots  $V_{oc}$  against the barrier height.

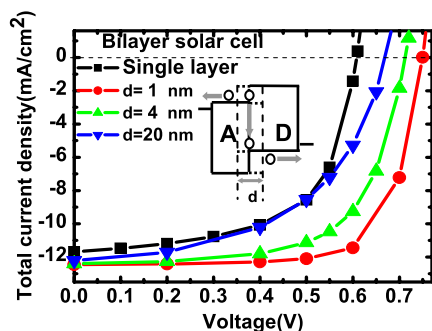


FIG. 4. (Color online) The total current density in bilayer structure with different recombination thicknesses at the donor-acceptor interface. Both the thickness and exciton diffusion length of donor for bilayer structure are 230 nm. The thickness of acceptor is 40 nm. The performance of devices are given in the form of  $V_{oc}$  (V),  $J_{sc}$  ( $\text{mA}/\text{cm}^2$ ), Fill Factor (%), and PCE (%); for single layer: (0.61, 11.68, 60.44, 4.29); for  $d=1$  nm: (0.75, 12.45, 73.57, 6.87); for  $d=4$  nm: (0.71, 12.36, 63.20, 5.56); and for  $d=20$  nm: (0.67, 12.22, 52.15, 4.27). The inset shows energy band diagram of a bilayer structure.

band condition occurs at a higher bias but there is simultaneously a higher dark carrier concentration. In addition to causing the recombination with the photocarriers, the dark carriers also result in space charges that cause a band bending, which further reduces  $V_{oc}$ .<sup>4</sup> As the barrier height  $\phi_B$  changes, there are three competing factors that influence  $V_{oc}$ : the dark carrier recombination, the band bending, and the flat-band condition.  $V_{oc}$  is plotted against  $\phi_B$  in the inset. Initially  $V_{oc}$  increases slightly due to reduced dark carrier concentration; then, it decreases as the effect of the flat-band condition sets in. Remarkably due to the compensation of these three factors,  $V_{oc}$  changes only 0.06 V as the flat-band voltage changes as large as 0.6 eV. Therefore, our model predicts that the variation in  $V_{oc}$  is only about 10% of the workfunction difference. This is consistent with the experiments.<sup>3,4,7</sup>

The key message of Fig. 3 is that it is impossible to raise  $V_{oc}$  to a value close to the band gap whatever metals used for the electrodes. One might expect that an electron blocking layer between the active layer and the cathode or a hole blocking layer between the active layer and the anode will help the efficiency by preventing the dark carriers from diffusing into the active layer. Such approach, in fact, reduces the efficiency because the photocarriers are blocked from collecting at the same time and the short-circuit current will be significantly compromised. In order to raise the  $V_{oc}$  to nearly the band gap value and further improve the efficiency, we propose the approach of a bilayer structure<sup>12</sup> where donor and acceptor are separated in different layers as shown in Fig. 4. The dark carrier recombination problem that prevailed in the BHJ device does not exist here because the dark electrons are confined in the acceptor side while the photogenerated holes are confined in the donor side. The case of holes is similar. It is however well known that the disadvantage of the bilayer structure is that the exciton diffusion length around 10 nm is usually smaller than the film thickness

around 200 nm. By introducing heavy-metal complex dopants, the singlet exciton of the polymer can quickly transform into the triplet exciton of the dopant and be dissociated into free carriers at the junction. Here we assume that a donor material with long exciton diffusion length can be eventually developed and predict the optimal efficiency of the bilayer structure.

The prediction for the bilayer structure with long exciton diffusion length is given in Fig. 4. The thickness of donor layer is 230 nm, the same as that of the single layer above. Such choice makes the comparison between bilayer and single layer devices under the same short-circuit current. Because the interface between the donor and acceptor layers cannot be infinitely sharp, we allow a blend region with thickness  $d$  extending evenly into the donor and acceptor layers. For  $d=1$  nm,  $V_{oc}$  is raised from the single layer value of 0.61 to 0.75 V, and the PCE is raised from 4.29% to 6.87%, which corresponds to a 60% increase. For  $d=20$  nm, the bilayer performance becomes about the same as the single layer one.

In conclusion, through the voltage and mobility dependence of the recombination current and the spatial distribution of the recombination rate in the theoretical model, we find that the recombination between the photocarriers and the dark carriers diffused from the metal into the semiconductor is the main limit for the PCE of the polymer BHJ solar cell. This effect turns out to be the reason for the observed insensitivity of the open-circuit voltage on the metal workfunction. Since it is impossible to increase the open-circuit voltage in single layer blend, we calculate the ideal case of a bilayer structure where the electrons and holes are physically separated to avoid recombination. Up to 60% of efficiency enhancement can be achieved if the donor exciton diffusion length is long enough.

<sup>1</sup>G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nat. Mater.* **4**, 864 (2005).

<sup>2</sup>W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).

<sup>3</sup>C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, *Adv. Funct. Mater.* **11**, 374 (2001).

<sup>4</sup>V. D. Mihailetchi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, *J. Appl. Phys.* **94**, 6849 (2003).

<sup>5</sup>G. Yu and A. J. Heeger, *J. Appl. Phys.* **78**, 4510 (1995).

<sup>6</sup>J. Liu, Y. Shi, and Y. Yang, *Adv. Funct. Mater.* **11**, 420 (2001).

<sup>7</sup>F. B. Kooistra, J. Knol, F. Kastenberger, L. M. Popescu, W. J. H. Verhees, J. M. Kroon, and J. C. Hummelen, *Org. Lett.* **9**, 551 (2007).

<sup>8</sup>P. Peumans, A. Yakimov, and S. R. Forrest, *J. Appl. Phys.* **93**, 3693 (2003).

<sup>9</sup>L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, and P. W. M. Blom, *Appl. Phys. Lett.* **86**, 123509 (2005).

<sup>10</sup>M. M. Mandoc, L. J. A. Koster, and P. W. M. Blom, *Appl. Phys. Lett.* **90**, 133504 (2007).

<sup>11</sup>M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec, *Adv. Mater. (Weinheim, Ger.)* **18**, 789 (2006).

<sup>12</sup>A. Moliton and J. M. Nunzi, *Polym. Int.* **55**, 583 (2006).

<sup>13</sup>M. J. Tsai and H. F. Meng, *J. Appl. Phys.* **97**, 114502 (2005).

<sup>14</sup>C. H. Chen and H. F. Meng, *Appl. Phys. Lett.* **86**, 201102 (2005).