Open-circuit voltage limit caused by recombination through tail states in bulk heterojunction polymer-fullerene solar cells

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The output open-circuit voltage of bulk heterojuntion polymer-fullerene solar cells exhibts an offset of $\Delta \approx 0.3$ V with the difference between the donor highest-occupied molecular orbital (HOMO) and the acceptor lowest-unoccupied molecular orbital (LUMO), as discussed by Scharber *et al.* [Adv. Mater. (Weinheim, Ger.) **18**, 789 (2006)]. We show that the energetic disorder of the electronic density-of-states (DOS) of acceptor and donor materials reduces the splitting of the electron and hole Fermi levels in bulk heterojunction solar cells, by restricting the accumulation of carriers into the tails of the DOS. A simple model based on the kinetic balance between photogeneration and recombination fluxes provides a lower limit to the energy offset $\Delta > (\sigma_n^2 + \sigma_p^2)/k_B T$ in terms of the disorder parameters. © *2010 American Institute of Physics*. [doi:10.1063/1.3358121]

Well known thermodynamic arguments show that radiative recombination puts a fundamental upper limit on the energy conversion efficiency of every solar cell. The Shockley–Queisser (SQ) (Ref. 1) limit relies upon regarding radiative recombination as the only loss process. For crystalline Si solar cells the difference between achieved and SQ-predicted efficiencies is attributed to the additional Auger recombination mechanism.[2,3] In case of amorphous Si photovoltaic devices, nonradiative recombination through band tail states, which are induced by the intrinsic energetic disorder, was identified as the determining loss mechanism.[4] The highest reported efficiency for bulk heterojunction organic solar cells is still far below the thermodynamic limit, being the origin of the energy loss attributed to several reasons.[5–7] Because high internal quantum efficiency is usually encountered in these organic photovoltaic systems, approaching even 100% values,[8] it is derived that energy conversion efficiency must be mainly limited by the achieved photovoltage.[9] In organic solar cells nonradiative recombination between electrons in the acceptor lowest-unoccupied molecular orbital (LUMO) and holes in the donor acceptor highest-occupied molecular orbital (HOMO) has been stated as one of the more detrimental factors.[10] Furthermore, the open-circuit voltage V_{oc} is found to scale with the difference between the HOMO of the donor and the LUMO of the acceptor materials,[11–13] then suggesting that recombination losses mainly take place at the donor/acceptor interface.[14–18]

Disorder was recognized as a unique factor producing a distinctive loss mechanism in amorphous Si solar cells in comparison with their crystalline counterparts.[4] However, the role of energetic disorder, which is also inherent to organic layers, in the recombination processes and the reachable open-circuit photovoltage of bulk heterojunction organic solar cells has not deserved much attention up to now. In this letter, we explore the effect of energetic disorder and propose a simple model which takes into account the occupancy statistics of the electronic states and the recombination process at the donor/acceptor interface for deriving the output V_{oc}. The model readily explains the experimentally observed energy offset ($\Delta = 0.2–0.3$ eV) between the donor HOMO and acceptor LUMO difference, and the reached V_{oc} value.

It is known that the opne-circuit photovoltage which can be achieved equals the difference between the electron and hole chemical potentials (quasi-Fermi levels) under steady-state illumination,[19] $-qV_{oc} = E_{Fn} - E_{Fp}$, being q the elementary charge. Hence the output voltage measured in open-circuit conditions monitors the splitting of the Fermi levels, which in turn are stated by the charge-carrier concentrations. It is also known that the carrier concentration is determined by the kinetic balance between photogeneration and recombination rates. In order to include the energetic disorder into a useful model which predicts achievable open-circuit voltage values we will assume density of states (DOS) distributions of both donor HOMO and acceptor LUMO manifolds. The energy disorder common for organic conductors is usually modeled by means of Gaussian DOS with mean energy E_{LUMO} and width σ_n for the acceptor fullerene (and E_{HOMO} and width σ_p for the donor polymer).[20] A broad distribution of the Gaussian DOS is considered because $\sigma \approx 2k_B T - 4k_B T$ (being $k_B T$ the thermal energy),

$$g_n(E_n) = \frac{N_n}{\sqrt{2\pi}\sigma_n} \exp\left[-\frac{(E_n - E_{LUMO})^2}{2\sigma_n^2} \right], \quad (1)$$

$$g_p(E_p) = \frac{N_p}{\sqrt{2\pi}\sigma_p} \exp\left[-\frac{(E_p - E_{HOMO})^2}{2\sigma_p^2} \right], \quad (2)$$

N_n (and N_p) represent the total density of electron (hole) states. The carrier density can be calculated by considering the Fermi–Dirac function

$$f(E_F, E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T} \right)}, \quad (3)$$

as photogenerated electrons n in the fullerene (and holes p in the polymer) depending on the position of the respective Fermi level E_{Fn} (E_{Fp})

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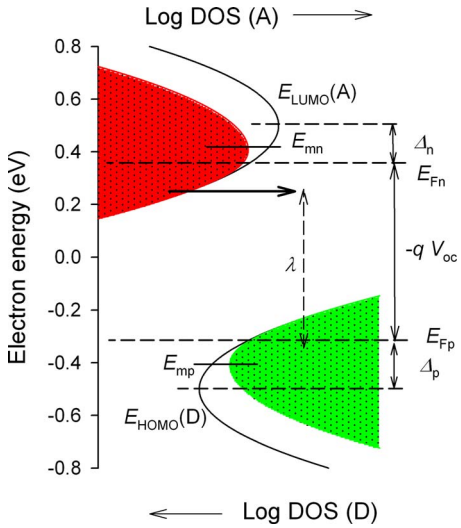

FIG. 1. (Color online) Diagram showing the acceptor HOMO (donor LUMO) Gaussian DOS (line), and LUMO occupied (HOMO unoccupied) states (filled area) by thermalized carriers resulting from the kinetic balance between photogeneration and recombination fluxes. The recombination event (horizontal solid arrow) is indicated for a given value of the reorganization energy λ. The origin of the photovoltage is marked as $-qV_{oc}=E_{Fn}-E_{Fp}$, and the offset energy $\Delta=\Delta_n+\Delta_p$. Photogenerated carriers accumulate around E_{mn} and E_{mp}.

$$n(E_{Fn}) = \int_{-\infty}^{+\infty} g_n(E_n) f(E_{Fn}, E_n) \mathrm{d}E_n, \tag{4}$$

$$p(E_{Fp}) = \int_{-\infty}^{+\infty} g_p(E_p)[1 - f(E_{Fp}, E_p)] \mathrm{d}E_p. \tag{5}$$

In case of low occupancy ($n/N_n < 10^{-2}$),[21] the mean energy of the carriers turns out to be independent of the Fermi level. In steady-state conditions the photogenerated carriers, which are initially distributed along DOS shape, thermalize in the Gaussian tail following a Boltzmann statistics with an average, equilibration energy $E_{mn}=\sigma_n^2/k_BT$ below the LUMO mean. Such energy signals the mean energy level of the charge carriers and is located above the Fermi level, i.e., $E_{Fn}<E_{mn}$.[20] Similarly for holes one can define $E_{mp}=\sigma_p^2/k_BT$ above the HOMO mean. Since usual irradiation levels are able to create low concentration of photogenerated charges ($n,p<10^{18}$ cm^{-3}, whereas total available states $N_n,N_p\approx 10^{20}$ cm^{-3}), it is derived that the DOS occupancy will be limited to the tail of the Gaussian distribution. We have displayed in Fig. 1 the expected steady-state situation under continuous irradiation in which photogenerated electrons and holes accumulate at the Gaussian tail of the DOS. By examining Fig. 1 one can observe that electron Fermi level which position depends on the light intensity, is located below the constant thermalization mean energy E_{nm} (hole Fermi level above E_{nm}).

Recombination is described by a charge-transfer between an occupied electron state of the LUMO manifold and an unoccupied hole state of the HOMO distribution. We adopt here the Marcus model (or polaron hopping) approach,[22] which involves a reorganization energy λ. The charge-transfer rate is given by

$$v_{rec}(E_n - E_p) = k_0 \exp\left[-\frac{(E_n - E_p - \lambda)^2}{4k_B T\lambda}\right], \tag{6}$$

where k_0 is a parameter with dimension (cm^3 s^{-1}). The total recombination rate is calculated by integration of all charge-transfer events following a bimolecular-like process as[23]

$$R(E_{Fn},E_{Fp}) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} g_n(E_n) f(E_{Fn},E_n) g_p(E_p) \times [1 - f(E_{Fp},E_p)] v_{rec}(E_n - E_p) \mathrm{d}E_n \mathrm{d}E_p. \tag{7}$$

This is a general expression of the recombination rate which substitutes the simplified version $R=knp$ by considering energy distributions and occupancy.

The outlined model might be completed by considering transport and outer contact effects. However we adopt a simple formulation because it captures essential features of the electrical response in open-circuit conditions with a high degree of prediction. In the steady state under continuous irradiation, the photogeneration rate G equals the recombination rate because no direct current is allowed $R(E_{Fn},E_{Fp})=G$. We are assuming here that bulk recombination is dominant over outer interface recombination. Several recent studies suggest that this is indeed the case,[23,24] although the outlined model could readily regard more than one recombination route by including additional terms in Eq. (7) related to outer surface recombination velocities. Assuming that photogenerated carries exceed intrinsic carrier densities $n>n_0$ ($p>p_0$), one should consider electroneutrality, $n(E_{Fn})=p(E_{Fp})$. The Fermi level positions can be evaluated by requiring the equation system to satisfy the previously mentioned conditions: first photogeneration rate must be balanced by the recombination rate, and that the absorber layer should be space-charge neutral. The latter condition holds at open circuit for uniformly absorbed light. The actual Fermi level position is finally governed by the kinetic balance, which in turn depends on the statistics of occupancy. The equation system should be solved numerically with the help of Eqs. (1)–(7).

A uniform absorption along the layer thickness L is assumed so that the photogeneration rate is given by $G=\phi(1-\beta)/L$ where ϕ is the photon flux and β stands for the ratio of geminate electron-hole pairs which recombine before charge separation. It is adopted the value $\beta=0$ for the sake of simplicity, although we recognize this as an important issue involving the formation of intermediate charge transfer,[18] or Coulombically bound radical pair[25] states at the polymer/fullerene interface before charge dissociation. In order to estimate the generation rate at standard AM1.5G conditions (1000 W m^{-2} of integrated power density) a short circuit current of 12 mA cm^{-2} (reported for practical cells[6]) is adopted which entails $\phi=7.5\times10^{16}$ cm^{-2} s^{-1}.

Results of the simulation are summarized in Fig. 2 in which V_{oc} calculated from the splitting of the Fermi levels is plotted as a function of the effective bandgap $E_g=E_{LUMO}(A)-E_{HOMO}(D)$. As expected V_{oc} monotonically increases as E_g increases. The disorder parameter σ has a dramatic effect on the achievable V_{oc}. Since $E_{Fn}<E_{mn}$ as derived for low-occupancy conditions, the energy distance $E_{LUMO}(A)-E_{Fn}$ increases. Similarly for energy losses related to hole-state occupancy of the donor material. Hence narrow disorder entails reduction of the energy loss Δ. One can

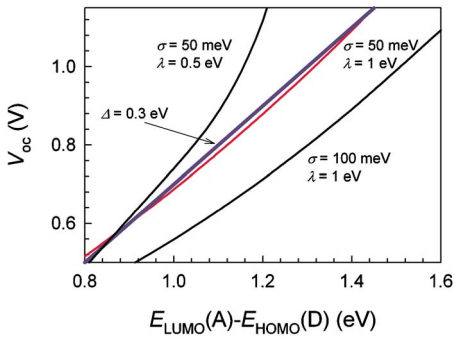

FIG. 2. (Color online) Open-circuit voltage resulting from model simulations for two different values of the disorder parameter $\sigma_n=\sigma_p=50-100$ meV, and recombination rate prefactor $k_0=10^{-14}$ cm^3 s^{-1}. The effect of the reorganization energy λ is also drawn. The experimental correlation $-qV_{oc}=E_{LUMO}(A)-E_{HOMO}(D)-\Delta$ is shown for comparison. Parameters used in the simulation: $N_n=N_p=10^{20}$ cm^{-3}, $k_BT=25$ meV, and $G=7.5\times10^{16}/L$ cm^3 s^{-1} (layer thickness $L=100$ nm). Other parameters marked in each curve.

quantify a lower limit to the energy offset as $\Delta>(\sigma_n^2+\sigma_p^2)k_B/T$ [see Fig. 1]. It is represented for comparison the experimental correlation encountered for different polymer:[6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) combinations between the reached open-circuit voltage and the effective bandgap, i.e., $-qV_{oc}=E_g-\Delta$. An energy shift within the range of $\Delta\approx0.3$ eV has been reported.[12] Simulations in case of relatively low disorder $\sigma=50$ meV, kinetic constant $k_0=10^{-14}$ cm^3 s^{-1}, and relatively high reorganization energy $\lambda=1$ eV are in good agreement with the experimental energy loss Δ. It can be inferred from the simulations that an increment of ~70 mV is to be gained for a factor 10 reduction in k_0. By examining Fig. 2 it is observed that lower λ values implies an increment in V_{oc} because charge transfer occurs through the Marcus inverted region. In this case the reorganization effect blocks the recombination and V_{oc} grows rapidly showing a deviation form the linear relationship $V_{oc}\propto E_g$.

Remarkably, the rate prefactor encountered ($k_0=10^{-14}$ cm^3 s^{-1}), results lower than that predicted by the mobility-related Langevin's theory. Previous studies have observed a retardation effect in the recombination mechanism of several orders of magnitude (10^{-1} to 10^{-4}) in comparison to the Langevin's rate.[23,26,27]

It should be stressed that the electronic DOS of both donor and acceptor materials *in the blend* turns to be a fundamental element for the behavior of the photovoltage. Very few studies are available aiming at determining a detailed view of electronic-state distributions as well as recombination mechanisms. Accurate determinations of the DOS reveal additional characteristics as observed by Hulea *et al.*[28] describing the total DOS for poly(*p*-phenylene vinylene) by means of a more featured structure which includes two Gaussian shapes. Very recently we have reported capacitance and carrier lifetime measurements extracted from impedance spectroscopy to derive recombination kinetics and DOS population.[23] It is observed in that study that higher energy states are not accessible because the recombination kinetics severely limits occupation to the DOS tail. Another important question is the distribution of defect and trap states within the effective band gap.[29] Traps might contribute to the modulation of the Fermi level in conditions of nonequilibrium under continuous irradiation then influencing the output V_{oc}. Therefore, more experimental investigations are needed addressing the origin of nonradiative recombination routes and the electronic states involved.

In summary, we have shown with this simple model that energetic disorder plays a fundamental role in reducing the achievable open-circuit photovoltage in bulk heterojunction organic solar cells. This energy loss appears as a consequence of the carrier thermalization in the tail of the DOS and the consequent entropic limitation to the free energy rise.

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