Effects of bulk and interfacial charge accumulation on fill factor in organic solar cells

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The effects of charge accumulation on fill factor (FF) are studied by using light intensity-dependent current-voltage and capacitance-voltage measurements based on poly-{bi(dodecyl)thiophene-thieno[3,4-c]pyrrole-4,6-dione}:1(3-methyloxycarbony1)propyl-1-phenyl [6,6] (PBTTPD:PCBM) solar cells. We find that the FF of un-annealed device shows a non-monotonic dependence of light intensity: first an increase and then a decrease with increasing light intensity. This suggests that both bulk charge accumulation and recombination determine the FF before thermal annealing. Furthermore, the morphological enhancement of PBTTPD:PCBM film leads to a monotonic decrease of FF as increasing light intensity. This indicates that only surface charge accumulation plays an important role in the determination of the FF after thermal annealing. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4805053]

Organic photovoltaics (OPVs) have attracted much attention in the recent years due to its simple fabrication process, large-area, and flexible properties.[1–7] It is known that the photo-generating carriers can accumulate in both bulk D:A structures and organic/electrode interfaces in organic solar cells.[8–13] The charge accumulation can then change the charge collection and consequently influences the fill factor (FF).[14,15] From current-voltage characteristics, the FF can be described by the change of photocurrent caused by the decrease of the effective electric field: $E_{eff} = E_{int} - E_{ext}$, where E_{int} and E_{ext} are the built-in and applied electric field, respectively. The early studies have shown that charge recombination can cause a loss on the FF in organic solar cells.[16–24] It has been suggested that the charge recombination can be largely reduced by improving donor and acceptor morphological networks towards the improvement of FF.[4,25–27] In this paper, we investigate the charge accumulation and its effects on the FF in organic solar cells by using light intensity-dependent I-V and C-V measurements.

We use the poly-{bi(dodecyl)thiophene-thieno[3,4-c]pyrrole-4,6-dione} (PBTTPD)[28,29] as the electron donor and 1-(3-methyloxycarbony1)propyl-1-phenyl [6,6] (PCBM) as the acceptor to fabricate organic bulk-heterojunction solar cells with device architecture of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT)/PBTTPD:PCBM/Al. The weight ratio of PBTTPD and PCBM was prepared to be 1:1.5 in chloroform ($CHCl_3$) solution with a total concentration of 15 mg/ml. The photovoltaic PBTTPD:PCBM films were spin cast with the thickness of 150 nm on precleaned ITO substrates coated with 40 nm thin layer of PEDOT:poly(styrenesulfonate) (PSS), (Baytron P AI4083). The photovoltaic films were thermally annealed at 80 °C for 10 min in nitrogen atmosphere. The aluminum (Al) electrodes were vacuum-deposited with the 100 nm thickness onto the photovoltaic PBTTPD:PCBM films under the vacuum of 2×10^{-6} Torr. The I-V characteristics were measured by using the Keithley 2400 source meter and the sunlight simulator (Thermal Oriel 96000 1000 W) at AM1.5 G for the fabricated solar cells. The light intensity-dependent C-V characteristics were recorded by using a dielectric spectrometer (Agilent, 4294A) with alternating voltage of 50 mV at 1 kHz at different light intensities.

We know that the photo-generated charge carriers can be divided into three parts: transported carriers, accountable for photocurrent, recombined carriers, a loss mechanism of charges, and trapped carriers, responsible for charge accumulation. The FF can then be essentially described by the ratio between transported carriers and accumulated carriers during the I-V measurement when applied bias is swiped against the built-in electric field. Because charge accumulation can occur in both bulk structures and surfaces of a photovoltaic D:A film, here we investigate the effects of charge accumulation on the FF in two different regimes: bulk and interface.

In bulk D:A structures, the total photo-generated charge carriers can consist of three parts: transported charges (Q_{free}), trapped charges (Q_{trap}), and recombined carriers ($Q_{recombination}$). Therefore, in bulk D:A structures the $(FF)_{Bulk}$ can be described by the ratio between the number of transported charges and the number of total charge carriers when the applied bias increases from zero to V_{oc}

$$FF_{Bulk} \propto \frac{Q_{free}}{Q_{tot}} = \frac{Q_{free}}{Q_{free} + Q_{trap} + Q_{recombination}}. \quad (1)$$

The Q_{free}, Q_{trap}, and $Q_{recombination}$ are three mutual restrictive parameters in the determination of FF in organic solar cells.

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The Q_{trap} and $Q_{recombination}$ can be related to Q_{free}, given by[30–33]

$$Q_{trap} = Q_{free}^{\frac{kT}{U_T}}, \quad (2)$$

$$Q_{recombination} \propto k_0 \cdot Q_{free}^{\lambda+1}, \quad (3)$$

where U_T, k, and T are the Urbach energy of trap distribution, Boltzmann constant, and temperature, respectively; the $\lambda + 1$ is an empirical reaction order; and the k_0 is a constant. Then, the FF_{Bulk} can be expressed as

$$FF_{Bulk} \propto \frac{Q_{free}}{Q_{free} + Q_{trap} + Q_{recombination}}$$
$$= \frac{1}{1 + Q_{free}^{\frac{kT}{U_T}-1} + k_0 Q_{free}^{\lambda}}. \quad (4)$$

For the Urbach energies $U_T > kT$ (25.8 meV) at the room temperature, we can see from Eq. (4) that the FF_{Bulk} would increase first and then decrease through accumulation and recombination, respectively, when the number of transported charges Q_{free} is increased (Fig. 1). Specifically, increasing the number of transported Q_{free} can first occupy the bulk traps with the consequence of forming charge accumulation, leading to an increase on the $(FF)_{Bulk}$ in bulk D:A structures. Further increasing the number of transported carriers can then induce the charge recombination, generating a decrease on the $(FF)_{Bulk}$.

Now, we discuss the surface charge accumulation and its effects on interfacial fill factor $FF_{Interface}$. We know that at the organic/electrode interface the $FF_{Interface}$ can be described by the ratio between collected charges Q_c and accumulated charges Q_a when the applied bias is swiped from zero to V_{oc}

$$FF_{Interface} \propto \frac{Q_c}{Q_c + Q_a}. \quad (5)$$

We should note that the surfaces of a photovoltaic film are often formed with structural defects caused by film formation or high-temperature electrode deposition. These surface defects can function as interfacial traps to accumulate photo-generated charge carriers at organic/electrode interfaces, leading to a decrease on $FF_{Interface}$.
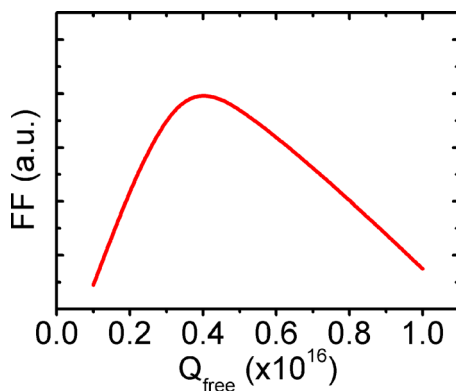
Here, we use un-annealed and annealed PBTTPD:PCBM devices to experimentally study the bulk and surface accumulation and their effects on the FF. It is known that thermal annealing can largely enhance charge transport channels and consequently reduces the density of bulk traps[4,8,16,25] mainly caused by structural defects, structural disorders, and residue solvent molecules.[34–36] The un-annealed and annealed devices can then have high and low densities of bulk traps with weak and strong transport channels, respectively. Therefore, the un-annealed and annealed PBTTPD:PCBM devices can be used to explore the bulk and surface charge accumulation and the relevant FF_{Bulk} and $FF_{Interface}$. Fig. 2 shows the I-V characteristics at different light intensities for un-annealed and annealed devices. At the 1 sun (100 mW/cm^2) condition, the un-annealed and annealed PBTTPD:PCBM devices yield the power efficiencies of 3.73% and 4.66%, respectively. Fig. 2(c) shows the FF as a function of light intensity for both devices. We can see that the FF of un-annealed device shows an increase and then decrease as the light intensity is increased. This non-monotonic dependence of light intensity is in good agreement with the dependence of charge density theoretically developed by Eq. (4). From the experimental results (Fig. 2(c))
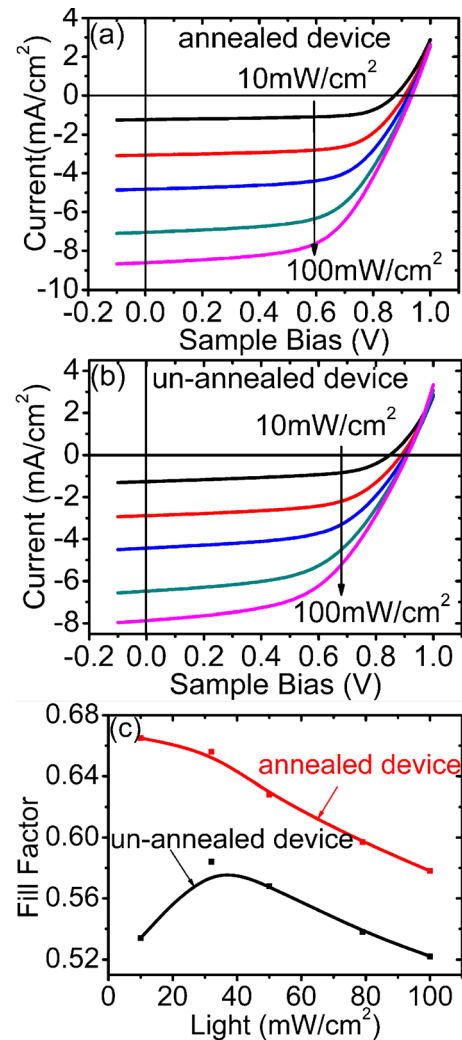

FIG. 1. Theoretical calculation to show effects of bulk charge accumulation and recombination on the FF by using Eq. (4).

FIG. 2. I-V characteristics for annealed and un-annealed ITO/PEDOT/PBTTPD:PCBM/Al devices at different light intensities. (a) Annealed device; (b) un-annealed device; (c) FF dependence of light intensity for un-annealed and annealed devices.

we can see that increasing light intensity can cause an increase and a decrease on the *FF* at low and high light intensity regimes in the un-annealed PBTTPD:PCBM device, respectively. In general, at low light intensities the photo-generated charge carriers can mainly occupy the bulk traps in the un-annealed PBTTPD:PCBM structures. At high light intensities, the photo-generated charge carriers can then experience recombination process. Therefore, we can further suggest that both bulk charge accumulation and recombination are involved in the determination of *FF* in the un-annealed PBTTPD:PCBM solar cell. When the light intensity is increased, the bulk accumulation and recombination generate positive and negative components, respectively, as predicted by the theoretical analysis from Eq. (4). In the annealed PBTTPD:PCBM device, we can see from Fig. 2(c) that the *FF* continuously decreases with increasing the light intensity. It should be noted that the annealed device exhibits a larger short-circuit current (J_{sc}) than that of the un-annealed device (Figs. 2(a) and 2(b)). The enhancement of J_{sc} suggests that thermal annealing can decrease the density of bulk traps and consequently improves the charge transport channels in the annealed PBTTPD:PCBM device. With low density of bulk traps and high charge transport, the negative dependence of *FF* on light intensity can be attributed to two possibilities: bulk recombination or surface accumulation. This means that the charge transport in the annealed device experiences either bulk recombination or surface accumulation in the development of *FF*. Here, we propose that surface accumulation is a major factor which determines the *FF* loss in the annealed PBTTPD:PCBM device.

Now, we investigate the surface charge accumulation in the annealed and un-annealed devices by using the C-V characteristics at different light intensities. We can see in Figure 3 that the maximal voltage (namely V_{peak}) shifts to a lower value as the light intensity increases, generating a ΔV_{peak} in both un-annealed and annealed devices. It should be particularly noted that the un-annealed and annealed devices exhibit smaller and larger ΔV_{peak} values: 15 mV and 60 mV, respectively, when the light intensity increases from 10 mW/cm^2 to 100 mW/cm^2. We should note that the V_{peak} shift (ΔV_{peak}) is essentially caused by the surface charge accumulation in organic solar cells.[37,38] Specifically, when the photo-generated charge carriers are accumulated on the surfaces of a photovoltaic film, it can form local electric fields nearby respective electrodes in the same direction with applied bias in the C-V measurement. When the applied bias reaches V_{peak} value, the charge injection can be induced from respective electrodes. The injected charge carriers will then recombine with photo-generated charge carriers in the D:A structures, decreasing the capacitance of an organic solar cell. The surface charge accumulation can then lead to a reduction on the critical bias (V_{peak}), which is required to inject charge carriers from each electrodes. Therefore, the V_{peak} shift (ΔV_{peak}) can reflect the amount of charge accumulation (Q_a) on the surfaces of photovoltaic film when the light intensity is varied. Larger and smaller ΔV_{peak} values correspond to more and less interfacial accumulation of photo-generated charge carriers at electrode interfaces. We can then suggest from Fig. 3 that un-annealed and annealed PBTTPD:PCBM devices exhibit less and more surface
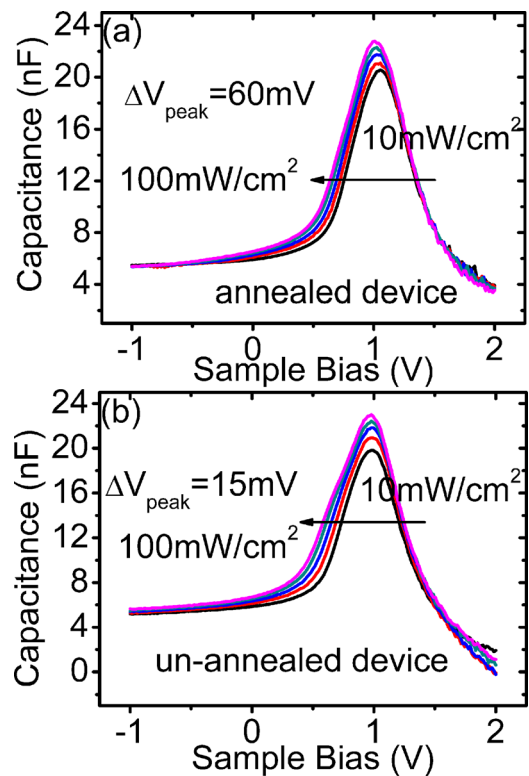

FIG. 3. Capacitance-voltage (C-V) characteristics for the ITO/PEDOT/PBTTPD:PCBM/Al devices by un-annealed or thermally annealed under varied light illumination intensity with alternating voltage 50 mV at 1 kHz: (a) annealed device; (b) un-annealed device.

accumulation, respectively. This confirms our argument that bulk accumulation and recombination play an important role in the determination of *FF* when high density of bulk traps and weak charge transport exist. However, surface charge accumulation functions as a major factor in the determination of *FF* when low density of bulk traps and strong charge transport exist. In general, the *FF* can be largely controlled by the series resistance (R_s) in organic solar cells (Fig. 4). Here, our experimental studies indicate that the R_s consists of two components: (1) bulk accumulation and recombination and (2) interfacial accumulation. The former and latter are the main processes accountable for the determination of *FF* for un-annealed, where the morphological transport channels are partially developed, and annealed devices, where the morphological charge transport channels are fully developed, respectively.
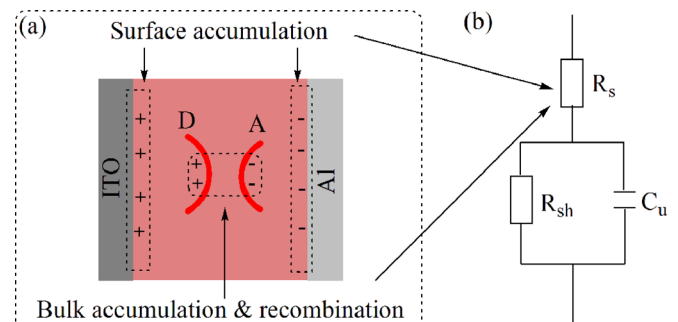

FIG. 4. (a) Schematic diagram to show bulk accumulation and recombination in D:A structure as well as surface accumulation at organic/electrode interfaces in organic solar cells; (b) the circuit model of organic solar cells.

In summary, we observe from light intensity-dependent I-V characteristics that the *FF* shows non-monotonic changes: positive and negative dependences when light intensity is increased in the un-annealed PBTTPD:PCBM solar cell. In contrast, the *FF* in the annealed PBTTPD:PCBM solar cell exhibits a monotonic change: negative dependence of light intensity. The C-V results indicate that bulk and surface charge accumulations dominate the un-annealed and annealed devices. We can thus suggest from the non-monotonic dependence of *FF* on light intensity that both bulk accumulation and recombination are involved in the determination of *FF* when organic solar cells are fabricated with more bulk traps and weak charge transport. The monotonic dependence of *FF* on light intensity implies that surface charge accumulation plays a critical role in the development of *FF* when organic solar cells are fabricated with less bulk traps and strong charge transport. Clearly, our light intensity-dependent I-V and C-V studies provide further understanding on the development of *FF* in organic solar cells.

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