Origin of the fill factor loss in bulk-heterojunction organic solar cells

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In this paper, the decrease of fill factor with increase of light illumination intensity was investigated through light assisted impedance studies based on ITO/poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate)/[poly(3-hexylthiophene):1-(3-methyloxycarbonyl)-propyl-1-phenyl(6,6)C_{61} (P3HT:PCBM)]/Ca/Al solar cells. It was found that the charge accumulation at the electrode interface causes a decrease in parallel resistance (Rp), consequently a reduction in fill factor. Moreover, it has also been found that the photocurrent loss near the open-circuit voltage through bimolecular recombination also leads to the reduction of fill factor with increasing light intensity in P3HT:PCBM solar cells. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4871582]

Organic solar cells are attracting significant interests as low-cost and flexible energy converting devices with the continuously improved power conversion efficiencies.[1–7] The efficiency of organic solar cell is mainly determined by three parameters, which are open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), and fill factor (FF). However, the FF is the critical parameter that can reflect dynamic transport of the photocurrent in organic solar cells. Much efforts have been done to investigate the fundamental physics behind of FF.[8–13] For example, it was reported that the FF is mainly determined by the quality of the polymer-cathode interface, while the space charge effect is only the secondary effect in organic solar cells.[12] However, Tress *et al.* found that the imbalance of the electron and hole mobilities played an important role on controlling the FF.[11] Another work done by Zhang *et al.* found that the charge recombination processes at high light intensities for organic solar cells can limit the FF and the power conversion efficiency.[13] In a simple equivalent circuit model, it is pointed out that the FF is determined by both series and parallel resistances.[10] However, under device-operating condition, the series and parallel resistances become a function of bulk and interfacial transport of photo-generated carriers. Clearly, understanding the effects of dynamic transport on the FF is an important issue to optimize the device performance. In this work, we use photoinduced dielectric measurement and theoretical analysis of current–voltage (*J–V*) characteristics to investigate the effects of surface-charge accumulation and bulk-charge recombination on the FF based on poly(3-hexylthiophene):1-(3-methyloxy carbonyl)-propyl-1-phenyl(6,6)C_{61} (P3HT:PCBM) solar cells.

The devices studied in this work were fabricated with the architecture of indium-tin-oxide (ITO)/poly(3,4-ethyle-nedioxythiophene):poly (styrene sulfonate) (PEDOT: PSS)/P3HT: PCBM/Ca/Al. The active layer was prepared by spin coating a chlorobenzene solution, containing the P3HT) and fullerene derivative PCBM, on ITO glass substrates pre-coated with a thin layer of PEDOT:PSS (Baytron P 4083) in nitrogen atmosphere. The relative weight ratio of P3HT: PCBM was set at 1:0.8. The bulk-heterojunction organic solar cells were then fabricated by the vacuum deposition of calcium (Ca) and aluminum (Al) electrodes. The device was thermally annealed under 155 °C for 5 min inside glove box. The photocurrent-voltage characteristics were measured by using the Keithley 2400 source meter, and the light source was from Thermal Oriel 96000 300 W solar simulator under AM1.5G (100 mW/cm^2). The light illumination intensity was changed by using neutral density optical filters. Agilent E4980A LCR meter was utilized for the capacitance measurements under an alternating voltage of 50 mV without DC bias.

Figure 1(a) shows the typical *J-V* characteristics for ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al solar cell at different light intensities from 10 to 100 mW/cm^2. We can see that the FF decreases with the increase of photoexcitation intensity. Here, our results indicate that both the series and parallel resistances are a function of photoexcitation intensity (as shown in Table I). In principle, the series resistance of organic solar cells is mainly from the bulk (i) resistance of the active material and electrodes and (ii) the contact resistance of all the interfaces in the device. We noticed that the dynamic transport of photogenerated charge carriers can affect the series resistance through space charge generation. Space charge generation can lead to a space charge limited current (SCLC) during device operation under sunlight illumination. The SCLC will result in a reduction of photocurrent and an increase of series resistance in an organic solar cell. However, it is shown in Table I that the series resistance does not change much with the various illumination intensities. Thus, this indicates that the space charge generation is not a major concern in our device below 100 mW/cm^2.

Figure 2(a) shows the capacitance-frequency relationship under different light intensities at short-circuit condition. It is clearly seen that the capacitance at short-circuit
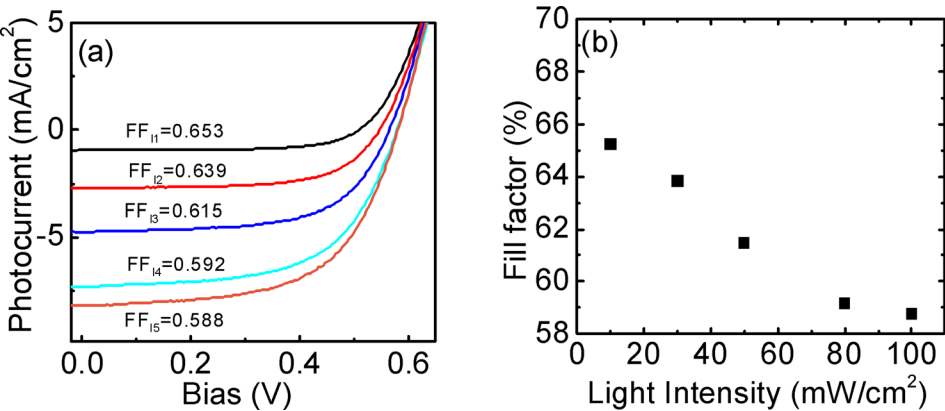
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FIG. 1. (a) *J-V* curves under various illumination intensities for P3HT/PCBM solar cells; (b) Fill factor as a function of light intensity.

TABLE I. Effects of illumination intensity on fill factor and series, parallel resistances.

	Intensity (mW/cm^2)	FF	Rp (KΩ cm^2)	Rs (Ω cm^2)
I1	10	0.6527	25906.7	1.59
I2	30	0.6386	8417.5	1.57
I3	50	0.6149	2780.9	1.54
I4	80	0.5920	1851.2	1.58
I5	100	0.5879	1561	1.52

condition increases with light intensities. It is known that the device capacitance is directly determined by the charge densities at the electrode interfaces in organic solar cells under-operating condition.[6,14,15] Thus, the increase of device capacitance with light intensity (Figure 2(b)) clearly indicates that there are more charge carriers accumulated at the electrode and active layer interface. This means that the charge accumulation at electrode interfaces can limit the dynamic transport of photogenerated charge carriers. This can cause an increase on the resistance under device-operating condition. It is known that the main contribution to series resistance (R_s) comes from the base contact resistance

and bulk resistance from the solar cell device. However, with the consideration of the minor change of series resistance under different light intensities, the series resistance is not the major parameter in the reduction of FF. On the other hand, the parallel resistance (R_p) is correlated with the amount and character of the impurities and defects in the active organic semiconductor layer because impurities and defects can cause leakage current.[16] Figure 1(c) shows the equivalent circuit for a solar cell, the R_s and R_p are series and parallel resistance, respectively. Clearly, both the resistances can affect the J-V behavior of the device and, consequently, on the FF. The R_p shown in Figure 2(d) can be simply calculated by the slope of the *J-V* curve at the reverse bias voltage of 0.5 V (Figure 1(a)). In contrast to R_s (shown in inset of Figure 2(d)), the R_p reduces dramatically from 10 to 100 mW/cm^2. As the amount of photoinduced charges in the blend layer increases along with the photoexcitation intensity, a larger leakage current can be produced by a photo-conductive shunt pathway from the accumulated charge carriers between partially selective device contacts, especially after thermal annealing, and consequently causes a decrease in the R_p.[17,18] Thus, the decrease of R_p with increasing light intensity can lead to an inefficient charge transport
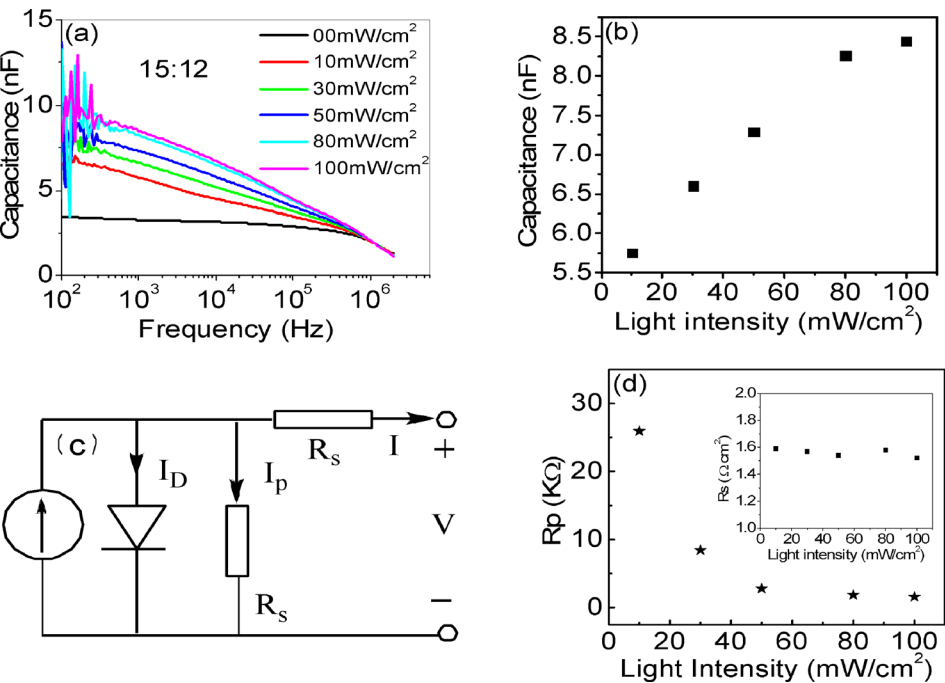

FIG. 2. (a) Capacitance as a function of frequency at different light intensities. (b) The device capacitance as a function of light intensity under short-circuit condition at 1 kHz. (c) The equivalent electric circuit for an organic solar cell. (d) The series (inset figure) and parallel resistance as a function of light intensity.
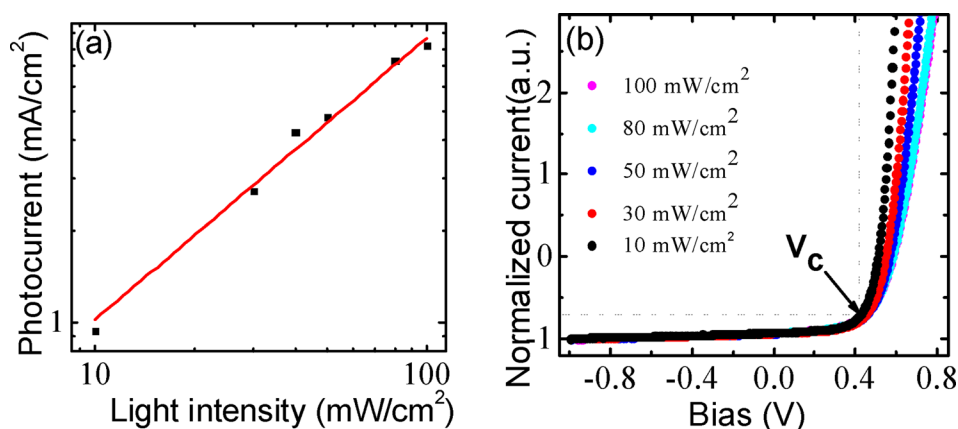
FIG. 3. (a) Short-circuit current as a function of light intensity; (b) Normalized *J-V* curves at short-circuit current under various illumination intensities.

in the bulk-heterojunction and low charge collection efficiency at the electrode interfaces. This clearly indicates that the capacitance measurement with light intensity can reveal the charge transport, collection processes, and thus the reduction of FF.

To further understand the reduction of FF with increasing the light intensity, we investigated the dependence of J_{sc} and V_{oc} on light intensity. Figure 3(a) shows the J_{sc} as the function of light intensity in a double logarithmic scale. The J_{sc} follows the power law dependence $J_{sc} = P_{Light}^{\alpha}$ with scaling exponents $\alpha = 0.93$. The nearly linear dependence of the J_{sc} on P_{Light} indicates that charge carrier losses at short-circuit condition are dominated by monomolecular recombination.[19] Separate evidence in favor of monomolecular recombination at short-circuit condition comes from the normalized *J–V* curves under different incident light intensities.[16] The normalized *J-V* curves at short-circuit current show two interesting parts: Light intensity-independent component below the voltage V_c and light intensity-dependent component above the critical voltage V_c, shown in Figure 3(b). The critical voltage is defined as the point where it corresponds to the maximum of $(J\text{-}V)_{max}$. The light intensity-independent component in the normalized *J-V* curves below the critical voltage indicates a monomolecular recombination. However, above the critical voltage, the light intensity-dependent component in the normalized *J-V* curves shows clear spreads in the normalized currents for different light intensities near open-circuit voltage. The light intensity-dependent spreads suggest that the dominant recombination near open-circuit condition evolves into bimolecular recombination.[16] The literature work has shown that the recombination coefficient of bimolecular recombination process depends on charge density: $k(n) = k_0 n^{\delta}$, where k_0 and δ are both constants, n represents the average charge density in active layer.[20,21] The increase of charge density due to the higher illumination intensity in the bulk heterojunction indicates that the bimolecular recombination coefficient increases; thus, from the normalized J-V analysis, the FF inevitably decreases with increasing of the light intensity due to the dominated bimolecular charge recombination over the transportation of photogenerated carriers to the electrodes.

In summary, the FF was studied at different light intensities based on ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al solar cells. The V_{oc} and J_{sc} both increase with increasing the light intensity, while the FF decrease with light intensity. We found that the decrease of FF with the increase of light intensity is attributed to following two main parameters: (i) Light intensity induced change on parallel resistance; and (ii) the more significant bimolecular recombination, due to the charge accumulation. Therefore, our studies on the origin of FF in organic solar cells provide a deeper understanding to further increase the energy conversion efficiencies in organic solar cells.

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