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Influence of series resistance on the photocurrent analysis of organic solar cells

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ABSTRACT

The series resistance of a bulk heterojunction solar cell diode affects the measurement of the voltage dependence of the diode photocurrent, $P(V)$. An empirical model for the effect is described and shows that $P(V)$ can be significantly modified, particularly at high bias voltages. Experimental measurements on PCDTBT:PCBM solar cells with added series resistance demonstrate the effect and confirm the model. The model provides a method to correct the photoconductivity data using measured quantities.

1. Introduction

Organic solar cells are formed from a nanostructured composite of electron donor and acceptor domains with a bulk heterojunction (BHJ) diode structure [1]. Excitons which are optically excited in one or other domain are split by the band offset at the BHJ interface so that the electrons move in the acceptor and holes in the donor. The charge is collected by the internal voltage of the diode. The cell structure comprises metal contacts which are usually an indium tin oxide (ITO) anode and a suitable metal cathode, a hole contact layer which is typically poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and is principally in electrical contact with the donor, the BHJ diode and sometimes an additional optical spacer layer of TiO_x in electrical contact with the acceptor [2]. The diode built-in potential arises from the difference in the effective Fermi energy on either side of the diode.

The recombination of the electrons and holes is of great interest because it has a detrimental effect on the solar cells efficiency and because it is fundamentally interesting to understand the role of the nanostructure on the optoelectronic properties. There are several possible recombination mechanisms and considerable disagreement over which mechanism dominates in any particular cells [3–7]. A useful measure of the recombination is the voltage dependence of the cell photocurrent [7–9]. Barring contact injection or avalanche gain, both of which are negligible at low electric fields [10], the diode is limited to unity gain in reverse bias. Hence, the photocurrent normalized to the effective generation rate, $P(V)$, measures the fraction of carriers that reach the contacts, and $1 - P(V)$ is the fraction that recombine.

A knowledge of $P(V)$ therefore allows different recombination models for the BHJ diode to be tested. Since the recombination occurs at the interface in the BHJ structure, it is important that $P(V)$ correctly reflects the internal photocurrent of the diode and the electronic properties of the junction. The purpose of this paper is to point out that this is not necessarily the case. Generally it is expected that $P(V)$ will drop monotonically to zero when the applied voltage equals the built-in potential, V_{BI}, because at this voltage the internal field changes sign.

It is well known that a series resistance influences the current in a solar cell and reduces the fill factor as shown in BHJ cells by recent work [11]. The physical origin of the series resistance in any particular cell is not obvious

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because there are several possibilities. Most cells use an ITO transparent conductor and its resistance between the cell stack and the contact leads can be significant. Within the cell stack the PEDOT:PSS layer and the TiO_x (if used) have higher resistivity than the metal contacts, and could be the origin. Any of the junctions between the layers could also add resistance. For example, ITO and PEDOT:PSS have different work functions, and the alignment of the Fermi energy across the junction occurs by charge transfer at the interface. The resulting dipole layer at this or other junctions may introduce a series resistance. The internal resistance of carriers in the BHJ diode itself may also be the origin of the series resistance.

This paper describes how the resistance specifically affects the cell photocurrent. An empirical model is described that does not presuppose any specific physical origin of the series resistance. Indeed we show that some measured forms of $P(V)$ are a consequence of a series resistance that could be of any origin. Analytical expressions relating the experimentally measured and internal $P(V)$ are developed in Section 2 and compared to experimental data in Section 3.

2. Series resistance model

The photocurrent is the difference between the current measured under illumination, J_L, and the dark current, J_D,

$$J_L(V) = J_D(V) - e \cdot G \cdot P(V), \tag{1}$$

where G is the effective carrier generation rate (the concentration of optically excited excitons that are split at the BHJ interface), and the sign of the photocurrent is chosen so the $P(V)$ is positive under solar cell operating conditions. The diode dark current is described by [12,13],

$$J_D(V) = J_0 \exp\left(\frac{e(V - J_D(V)R_S)}{nkT}\right) = J_0 \exp\left(\frac{eV_{IDJ}}{nkT}\right), \tag{2}$$

where n is the diode ideality factor, R_S is the ohmic series resistance (in units of $\Omega\,\mathrm{cm}^2$) and the shunt resistance is not included. $V_{IDJ} = V - J_DR_S$ is the internal diode junction voltage with the voltage drop across the resistance subtracted, and is the voltage that defines the diode junction. This conventional form of the dark current applies well to many BHJ solar cells at the voltages of interest [7,13]. Inserting Eq. (2) into Eq. (1) gives the experimentally measured $P_{EXP}(V)$,

$$eGP_{EXP}(V) = J_0 \exp\left(\frac{e(V - J_D(V)R_S)}{nkT}\right) - J_L(V) \tag{3}$$

$P_{EXP}(V)$ is the difference between the experimentally measured dark current and the experimentally measured current under illumination. However, inspection of Eq. (3) indicates that it cannot be the correct expression for the photocurrent, since the right side of the equation has the current J_L in one term and J_D in the other. The problem is that the voltage drop across the series resistance must reflect the current under illumination rather than the current in the dark. Consequently the photoconductivity derived experimentally from Eqs. (1) and (2) is not the correct internal photoconductivity when there is significant series resistance. The voltage drop across R_S has a different magnitude in the dark and under illumination and also changes sign with the current, and is therefore of opposite sign for the dark current and the photocurrent for $V < V_{OC}$.

There is a second related problem with the use of Eq. (3) to extract the internal $P(V)$. The term $(V - J(V)R_S)$ in the diode equation (Eq. (2)) arises because the internal voltage across the diode differs from the external applied voltage. The physically interesting $P(V)$ also reflects the internal diode voltage V_{IDJ}, rather than the external voltage. The internal diode photocurrent, $P_{INT}(V)$, is therefore described by Eqs. (1) and (2), in which V is replaced by V_{IDJ} in the expression for $P(V)$, which gives

$$eGP_{INT}(V_{IDJ}) = J_0 \exp(eV_{IDJ}/nkT) - J_L(V) \tag{4}$$

Inserting the value of V_{IDJ} gives,

$$eGP_{INT}(V - J_L(V)R_S) = J_0 \exp\left(\frac{e(V - J_L(V)R_S)}{nkT}\right) - J_L(V) \tag{5}$$

Combining Eqs. (3) and (5), relates the experimental and internal $P(V)$,

$$eGP_{INT}(V - J_LR_S) = eGP_{EXP}(V) - J_0 \times \exp\left(\frac{eV}{nkT}\right)\left[\exp -\frac{J_D(V)R_S}{nkT} - \exp -\frac{J_L(V)R_S}{nkT}\right] \tag{6}$$

or alternatively,

$$eGP_{INT}(V - J_LR_S) = J_D(V) \exp\left(\frac{eGP_{EXP}(V)R_S}{nkT}\right) - J_L(V) \tag{7}$$

The internal and experimental values of $P(V)$ are the same only when $J_L(V)R_S \ll V$ over the whole voltage range, otherwise they are different. The experimentally measured quantities are $J_L(V)$ and $J_D(V)$ from which $P_{EXP}(V)$ is obtained from Eq. (1). With the additional knowledge of R_S, which can be obtained from $J_D(V)$ using Eq. (2), $P_{INT}(V)$ can be deduced from these equations.

Calculations of $P_{EXP}(V)$ for a given $P_{INT}(V)$ with different series resistance and different illumination intensities were made to illustrate the effect. The parameters of the dark diode current calculation are chosen to correspond to the data for a PCDTBT/PCBM solar cell and we set $J_0 = 3 \times 10^{-12}\,\mathrm{A/cm^2}$, $n = 1.7$ and $V_{BI} = 0.86\,\mathrm{V}$. The internal $P_{INT}(V)$ in Eq. (7) is modeled by the charge collection equation used in Ref. [7], since it gives a good fit to the photoconductivity data but any suitable form could be used. The procedure for modeling the effect of series resistance to obtain $P_{EXP}(V)$ is to calculate the dark diode current from Eq. (2), the illuminated diode current, $J_L(V)$, from Eq. (5), and use these to calculate $P_{EXP}(V)$ from Eq. (3). The dark current is shown in the inset to Fig. 1, for a series resistance of $12\,\Omega\,\mathrm{cm}^2$ and is a good fit to the data from Ref. [7].

Fig. 1 shows the calculated $P_{EXP}(V)$ for different series resistance at fixed generation rate and Fig. 2 shows the same as a function of the generation rate at fixed R_S. When the series resistance is zero, the internal and experimental $P(V)$ are identical. At low illumination levels, $P_{EXP}(V)$ differs from $P_{INT}(V)$ primarily at high forward voltages when $J_D(V)$ is large and $J_D(V)R_S$ is significant compared to V. At high

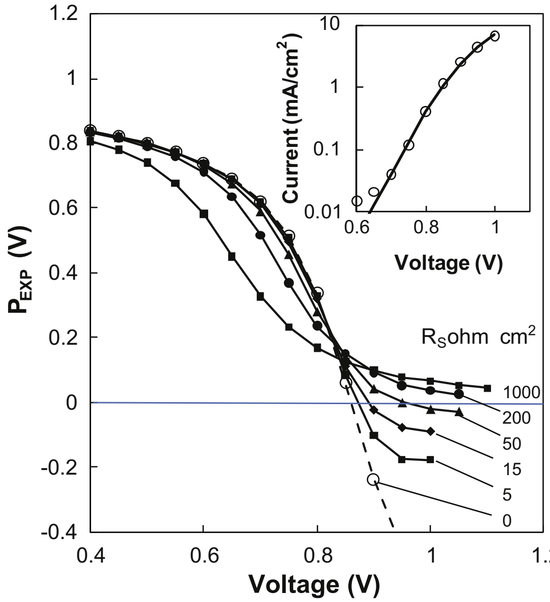

Fig. 1. Calculated $P_{EXP}(V)$ for fixed illumination and various series resistances as shown. The parameters of the calculation reflect data obtained for PCDTBT:PCBM cells, with V_{BI} = 0.86 V. $P_{INT}(V)$ is the dashed line. The illumination corresponds to a reverse saturation current of ~0.1 mA/cm^2. The inset shows the measured dark current for a PCBTBT:PCBM cell (data points), and the corresponding model (solid line) with R_S = 12 Ω cm^2, $J_0 = 3 \times 10^{-12}$ A/cm^2 and n = 1.7.

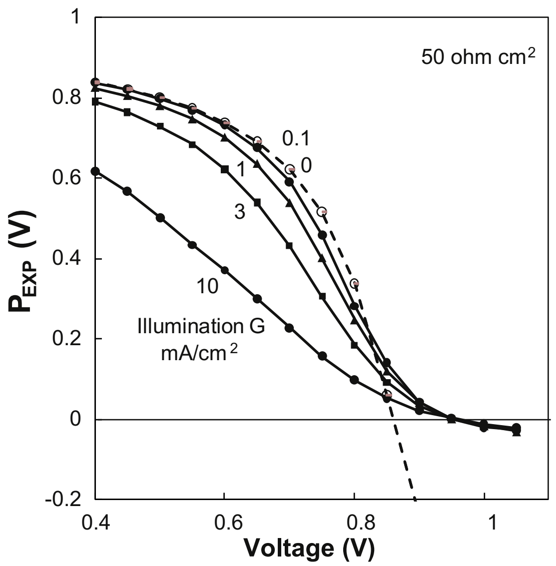

Fig. 2. Calculated $P_{EXP}(V)$ for a fixed series resistance and various illumination intensities as shown, with the same parameters as for Fig. 1.

light intensity $P_{EXP}(V)$ differs from $P_{INT}(V)$ over a wider range of voltages because $J_L(V)R_S$ is also large. Focusing on the high voltage behavior, there is an extended tail of $P_{EXP}(V)$ to high voltage, so that the zero crossing (the value of $V = V_X$ when $P_{EXP}(V_X) = 0$) moves to higher voltage with increasing R_S. Inspection of Eq. (6) shows that when $P_{EXP}(V_X)$ is zero, which occurs by definition, when $J_L = J_D$, then the right side of Eq. (6) is zero, so that $P_{INT}(V_X - J_L R_S)$ is also zero. This occurs when the internal voltage is the built-in potential, V_{BI}, so that,

$$V_X = V_{BI} + J_D(V_X)R_S \tag{8}$$

The voltage at which $P_{EXP}(V_X)$ crosses zero is therefore larger than V_{BI} and according to Eq. (8), should be independent of illumination, since none of the terms in the equation depend on the illumination intensity.

Further into forward bias than V_X, the increasing forward current results in a larger voltage drop across R_S, and the internal voltage is an increasingly small fraction of the applied voltage. $P_{EXP}(V > V_X)$ will therefore tend to a constant with absolute value <1 determined by the small residual internal voltage. Its value can be calculated from Eq. (3) and should decrease as R_S increases. If the series resistance is large enough to completely dominate the diode current, then $J_D \sim V_X/R_S$ and Eq. (8) has no solution. In this case $P_{EXP}(V_X)$ tends to zero asymptotically and never crosses zero, as is seen in the high resistance model calculations in Fig. 1.

The open circuit voltage V_{OC} occurs when $J_L(V_{OC}) = 0$, when from Eqs. (3) and (5),

$$eGP_{EXP}(V_{OC}) = J_0 \exp\left(\frac{e(V_{OC} - J_D(V)R_S)}{nkT}\right) \tag{9}$$

$$eGP_{INT}(V_{OC}) = J_0 \exp\left(\frac{eV_{OC}}{nkT}\right) \tag{10}$$

so that,

$$\frac{P_{INT}(V_{OC})}{P_{EXT}(V_{OC})} = \exp\left[-J_D(V_{OC})R_S/nkT\right] \tag{11}$$

Eq. (11) shows that $P_{INT}(V)$ is smaller than $P_{EXP}(V)$at V_{OC}, because the exponent is negative. However, at low illumination intensity and small V_{OC}, the right side of Eq. (11) becomes very close to unity.

3. Experimental measurements

To further illustrate the effects, we have measured $P_{EXP}(V)$ for BHJ solar cells in which an additional external series resistance is included. The cells are fabricated from a PCDTBT/$PC_{70}BM$ blend [14], and are similar to those used in the previous recombination studies [7]. Details of cell fabrication are given elsewhere [2]. The measurements are made using illumination chopped at 230 Hz, and a lock-in amplifier to record the photocurrent with the dark current automatically subtracted. The input to the lock-in amplifier is the voltage developed across a resistor, which was varied from R = 5 Ω–10 kΩ, and this resistor also acts as the added series resistance of the cell. The use of chopped illumination prevents possible effects of a temperature difference between measurements in the dark and under illumination.[15] The cell has an area of about A = 0.04 cm^2, and $R_S = R{\cdot}A$ for comparison with the model.

Fig. 3a shows the measurements of $P_{EXP}(V)$ for different added series resistance, and Fig. 3b shows measurements for different illumination intensities. The data also shows

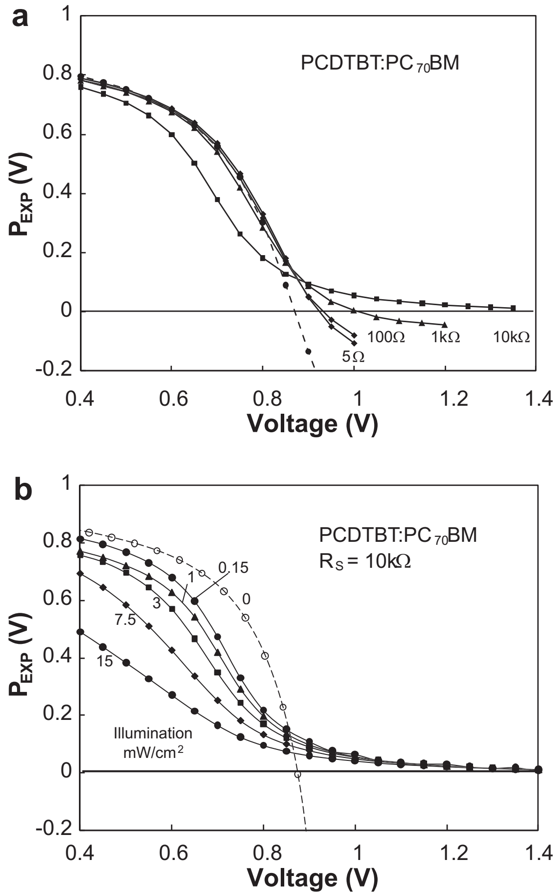

Fig. 3. (a) Measurements of $P_{EXP}(V)$ for a PCDTBT:PCBM solar cell with (a) added series resistance as shown and a constant light intensity, and (b) a fixed added series resistance of 10 kΩ, and for different light intensity, as shown. The measurements use a lock-in amplifier which automatically subtracts the dark current. The area of the cell is ~0.04 cm^2.

the charge collection model as used in the simulations of Figs. 1 and 2, with parameters chosen to fit the particular data set. Comparison of the data with the models in Figs. 1 and 2 shows qualitative and quantitative agreement. The change in shape of $P_{EXP}(V)$ for different resistance and light intensity is evident. The data shows no change in the $P_{EXP}(V)$ until R exceeds about 100 Ω ($R_S \sim 4\ \Omega\,\mathrm{cm}^2$). The zero crossing voltage increases with series resistance, and at sufficiently large R, $P_{EXP}(V)$ remains positive and approaches zero asymptotically, as expected from the model. The data in Fig. 3a have a zero crossing at 0.92 V for the 5 Ω resistance and is almost the same for 100 Ω. The data in this voltage range deviate from the charge collection equation and have a higher zero crossing than we found previously (0.92 V versus 0.86 V). The curvature near the zero crossing indicates that there is a significant series resistance in this device even in the absence of the added resistance.

The variation with illumination intensity shown in Fig. 3b similarly agrees with the model, and demonstrates the expected decrease in $P_{EXP}(V)$ at lower voltages when G is sufficiently large. A large resistance was used for this experiment to accentuate the effects. The results illustrate that $P_{EXP}(V)$ can differ greatly from $P_{INT}(V)$.

The built-in potential and the corrected $P_{INT}(V)$ can be extracted from the measurement of $P_{EXP}(V_X)$ using set of equations given above. Fig. 4 shows measured $P_{EXP}(V_X)$ data for the PCDTBT/PCBM cell and the calculated $P_{INT}(V)$. The dark current, which is measured separately, provides a value of R_S, J_0 and n, and these parameters are shown in Fig. 4. The built-in potential can be obtained from the measured crossing point using Eq. (8). For the data in Fig. 4, the zero crossing voltage is 0.9 V and decreases to 0.87 V after the correction. The calculated $P_{INT}(V)$ in Fig. 4 differs from $P_{EXP}(V)$ mostly near the crossing point, and to a lesser extent at lower voltages, as expected. Cells with a much larger internal series resistance prove to be difficult to correct accurately, probably because R_S has a small voltage dependence rather than being constant, and the correction relies on an increasingly accurate model for J_D.

Previous data on similar PCDTBT cells had a zero crossing at 0.86 V and did not show significant curvature near the zero crossing [7]. The inset of Fig. 1 shows that the dark current data from Ref. [7] has a series resistance of 12 Ω cm^2 and the current at 0.86 V is about 1 mA/cm^2. The zero crossing voltage V_X is shifted by $J(V_X)R_S \sim 0.01$ V, which shows for that particular sample, that the measured P(V) is minimally affected by the series resistance. The cell in Fig. 4 has a larger internal resistance and hence a slightly different shape and crossing point. However the corrected values of the built-in potential for the two devices agree well.

The analysis of Fig. 4 shows that the series resistance measured in the dark leads to a function $P_{INT}(V)$ which is consistent with theoretical expectations and with measurements of $P_{EXP}(V)$ in similar devices with a lower resistance [7]. It is possible that the series resistance varies with light intensity in some solar cells [16]. In such cases the resistance can be treated as a free parameter and obtained from a best fit to any known property of $P_{INT}(V)$.

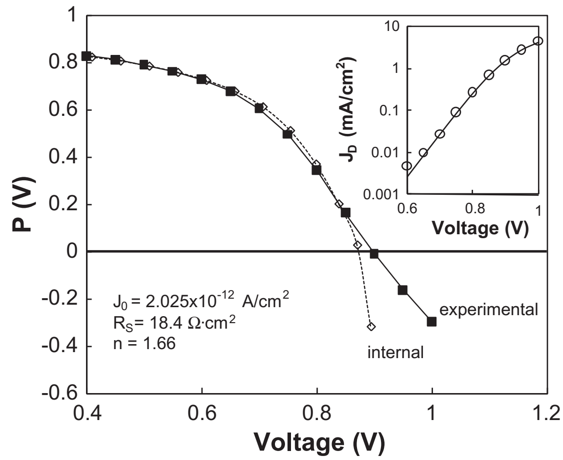

Fig. 4. Measurements of $P_{EXP}(V)$ for the same PCDTBT:PCBM cell as in Fig. 3, using dc illumination, and the calculation of $P_{INT}(V)$ as derived from Eq. (4). The series resistance and other diode parameters are obtained from the dark forward bias current, as shown in the inset (points are data and the line is the model). The reverse bias photocurrent is 0.7 mA/cm^2.

4. Discussion

The model and experiments show that $P(V)$ can be significantly modified by a series resistance. The data can be corrected to give the internal $P(V)$, provided that the series resistance can be determined and is not too large. The best test of whether there is a significant series resistance effect is to measure the dark forward bias characteristics, $J_D(V)$. If the exponential region of $J_D(V)$ continues up to at least the built-in potential, then the measured $P(V)$ is not influenced by series resistance at low illumination intensity, but otherwise will be increasingly distorted at high voltages. At high illumination intensity there is a series resistance effect whenever $J_L R_S$ is significant.

Other publications discuss the cell photoconductivity, $P(V)$, and exhibit a form of $P(V)$ that is similar to those that we demonstrate are influenced by series resistance. For example, Ooi et al. described P3HT/PCBM cells with a symmetric photocurrent response that is similar to the calculations in Fig. 1 and the data of Fig. 3 [16]. Ooi et al. correct for the possible change in temperature when the cell is illuminated which has a different effect on J_D and therefore on the experimental $P_{EXP}(V)$. The data by Ooi et al. show the same general shape as given by Fig. 1, as well as a zero crossing of $P_{EXP}(V)$ which is independent of illumination, and the saturation of $P_{EXP}(V)$ in forward bias at a value much lower than in reverse bias. Their data therefore closely follow the predictions expected for a cell with significant series resistance. Indeed the paper shows a forward current that is almost ohmic above $\sim$0.7 V, and a zero crossing at $\sim$0.9 V, which is much higher than other P3HT cells. Ooi et al. explain their results in terms of different extraction barriers at the two contacts, but a significant series resistance effect may be a more likely explanation.

Since our analysis of the series resistance is empirical, the effects described are independent of the physical mechanism that provides the series resistance. The shape of $P_{EXP}(V)$ can demonstrate that a series resistance effect is present, and the corrected value of $P_{INT}(V)$ provides insight into the photoconductivity of the cell diode, but neither measurement can give direct evidence for the origin of the series resistance, which requires additional experimental information.

5. Conclusions

The series resistance has a significant effect on the voltage dependence of the photocurrent, such that the measured result is different from the internal photocurrent of the diode. When the photocurrent is used to deduce the properties of the solar cell, it is important that the internal $P_{INT}(V)$ is determined. The presence of a significant series resistance effect can often be deduced from the form of $P_{EXP}(V)$ and the magnitude of the R_S can be obtained from the dark diode characteristics. It is possible to extract V_{BI} and $P_{INT}(V)$ from the experimental measurements, although the accuracy decreases with increasingly large values of the series resistance.

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