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# Open circuit voltage decay transients and recombination in bulk-heterojunction solar cells

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The internal loss mechanisms in polymer:fullerene bulk-heterojunction solar cells can be fruitfully studied using open circuit voltage decay (OCVD). For OCVD transients of poly (3-hexylthiophene-2, 5-diyl) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) solar cells, we observe that the open circuit voltage as a function time $t$ changes from initially being nearly constant to being proportional to $ln(t)$ for most part of the decay before eventually decaying to zero. We demonstrate that the transients can be fully described over eight orders of magnitude in time using a simple model of decay based on a diode coupled to a capacitor. The fitting to the analytical model solution enables true determination of the diode ideality factor and saturation leakage current. The ideality factor is observed to vary between 1.52 and 1.68 depending on excess carrier concentration and temperature. The technique is used to isolate the diode current in presence of excess carriers, and hence to independently determine the intensity dependence of the light-induced recombination current and shunt resistance.  [http://dx.doi.org/10.1063/1.4879278]

The unique advantages of the bulk-heterojunction polymer-PCBM system,[1,2] especially with P3HT as the host polymer, have made it the work horse of organic photovoltaic research. It continues to be the most intensively studied model system with the hope that efficiency of the cells can be pushed up once one understands well the limiting loss mechanisms.[1–8] The physics of the intrinsic recombination loss processes is yet to be understood sufficiently well to enable distinguishing between various mechanisms such as geminate, bimolecular, and Shockley-Read-Hall (SRH) recombination in a given sample.[1,2,9] The study of competing recombination processes under different operating conditions to isolate dominant pathways of loss in polymer solar cells has taken many forms including steady state,[4,10] transient,[11,12] and ac impedance[7,13] based techniques. The goal has been to obtain the order of reaction in the recombination process from experimentally measured parameters.[14,15] A coherent understanding of the dominant mechanisms of loss is yet to emerge, especially its variation under short-circuit, operational bias, and open circuit conditions.[3]

The current density-voltage ($J$-$V$) characteristics under dark and illumination have been widely analyzed using equivalent lumped circuit models in terms of voltage and intensity dependence of steady state parameters such as ideality factor of the diodes and series and shunt resistances.[16–18] However, the non-linear inter-dependence of such parameters has made interpretation difficult, and there has been recently a lot of effort in developing both conceptual and experimental tools to connect the order of the reaction of the loss mechanisms to the measured parameters.[8,14] For example, there has been a proliferation of definition of ideality factors,[8,19] based on which conclusions are to be drawn about the dominant recombination mechanisms.[20]

Recently, the alternative popular approach has been used to study transient photovoltage (TPV), especially under open circuit conditions,[8,21,22] to focus on recombination processes alone without the involvement of carrier transport and series resistance of the device. The methods based on open circuit voltage decay (OCVD),[15,23,24] though attractive for recombination studies, currently lack a comprehensive model. TPV, with differential light pulse measurements, has been sought to be used to measure the lifetime of excess carriers and relate them to the density of states (DOS) of localized states in the HOMO-LUMO gap responsible for recombination.[23,25] However, measurements from different experiments have been difficult to reconcile. Street[12] has even questioned the ability of such methods to yield the lifetime of carriers and has drawn attention towards the need of accounting for the diode capacitance in the interpretational scheme. The lack of a comprehensive model to study transients can lead to serious difficulties in the interpretation of a wide range of TPV experiments that are used to characterize loss mechanisms and density of states responsible for such losses. Further, there is an urgent need to clearly distinguish between processes that occur under light and dark conditions, and OCVD transients provide such an opportunity.

In this Letter, we unambiguously show that the OCVD transient over eight orders of magnitude in time can be accurately modeled as a combination of a dark diode and a capacitor in well designed samples. This provides an opportunity to reliably characterize the diode characteristics and measure its ideality factors without being influenced by the shunt and series resistances. Based on the transient measurements, we demonstrate the ability to isolate the light-induced shunt resistance from that of excess carrier recombination processes in the dark. We estimate shunt resistance as a function of illumination, and hence unravel important insights regarding recombination pathways of excess carriers in presence and absence of illumination.

 

For the current study, diodes having the simple structure ITO|P3HT:PCBM|Al were fabricated by conventional well known unit processes.[26] Under AM1.5G illumination conditions, we routinely achieve an efficiency of ∼2% for the structure. For this study, fabrication of devices (circular active area of diameter 4 mm) has been especially optimized for low leakage current. All light dependent measurements reported here were carried out using a 10 cd white light-emitting diode mounted along with the sample in a closed cycle cryostat (CTI-Cryogenics Model 22), which helps in controlling and measuring the sample temperature. For open circuit voltage ($V_{oc}$) measurements, a home-built high input impedance (∼TΩ) instrumentation amplifier was used to ensure true open circuit conditions. This is important as demonstrated in the supplementary material to avoid confusing any influence of circuit artifact with physical mechanisms.[26] The output of the instrumentation amplifier was recorded on a fast, high resolution digital (Agilent MSO6012A) oscilloscope. The actual $V_{oc}$ decay curves (over eight orders of magnitude in time) were obtained by stitching two successive curves acquired on two different time scales.

Figure 1 shows typical dark and light dependent *J-V* characteristics of the devices. The diodes were specifically optimized (through pixellization and careful fabrication procedures) for low leakage currents. As can be seen from the figure, the dark forward current is exponential over five orders of magnitude, and the light short-circuit current is four orders of magnitude larger than the dark. For a standard junction solar cell, neglecting the series and shunt resistances, the dark current density is given by the usual diode equation

$$J_D = J_0\left[\exp\left(\frac{qV}{n_d k_B T}\right) - 1\right], \tag{1}$$

where $J_D$ is the diode current, $J_0$ is the reverse saturation current, $V$ is the applied voltage, $q$ is the elementary charge, $k_B$ is the Boltzmann's constant, $T$ is the temperature, and $n_d$ is the ideality factor. The ideality factor measured from the dark characteristics is $n_d \approx 1.5$, in our case. The ideality factor under illumination conditions is conventionally studied by monitoring $V_{oc}$ as a function of incident light intensity $\varphi$; it is referred to as $n_l$ here, and is found to be 1.46.[26] It is usually considered to be a better estimate since it is not contaminated by series resistance and supposed to reflect the recombination mechanisms under open circuit conditions.[19]

To understand the excess carrier decay mechanism in more detail, $V_{oc}$ transients were studied as a function of temperature and initial illumination intensities. The variation of $V_{oc}$ decay for different temperatures for the same initial intensity is shown in Fig. 2. The characteristic variation has three different regions: at early times it is nearly constant, and then linearly decreasing with $ln(t)$ for intermediate times, and finally decaying rapidly to zero at very long times. The *nature* of the decay incorporating all the three regions (including their slopes and curvature) matches extremely well with the open circuit voltage decay transient of a diode connected across a capacitor as has been observed elsewhere using standard diode and capacitor circuits for instructional purposes.[27]

The decay transient can be analytically obtained by setting the sum of the diode current and displacement current in the capacitor to zero, and thus writing the recombination current as

$$-C\frac{dV_{oc}}{dt} = I_0\left[\exp\left(\frac{V_{oc}}{n_X V_T}\right) - 1\right], \tag{2}$$

where $C$ is the geometrical capacitance, $I_0$ is the dark saturation current, $n_x$ is the ideality factor, and $V_T$ is the thermal voltage ($=k_B T/q$). The solution can be readily given as[27]

$$V_{oc}(t) = -n_x V_T \ln\left\{1 - \left[1 - \exp\left(-\frac{V_i}{n_x V_T}\right)\right]\exp(-\alpha t)\right\}, \tag{3}$$

where $V_i$ is the initial voltage at $t=0$, and the parameter $\alpha \equiv I_0/n_x C V_T$. It is straightforward to fit the measured data to Eq. (3) with the ideality factor $n_x$, and the dark saturation current $I_0$ as parameters to obtain extremely reliable values for the two quantities. It is also physically instructive and

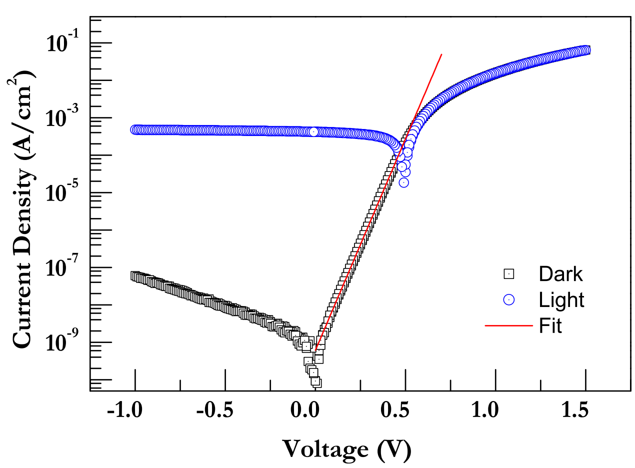


FIG. 1. Dark and light *J-V* characteristics for ITO|P3HT:PCBM|Al device. The ideality factor for the dark characteristics is ∼1.5 for the exponential regime.

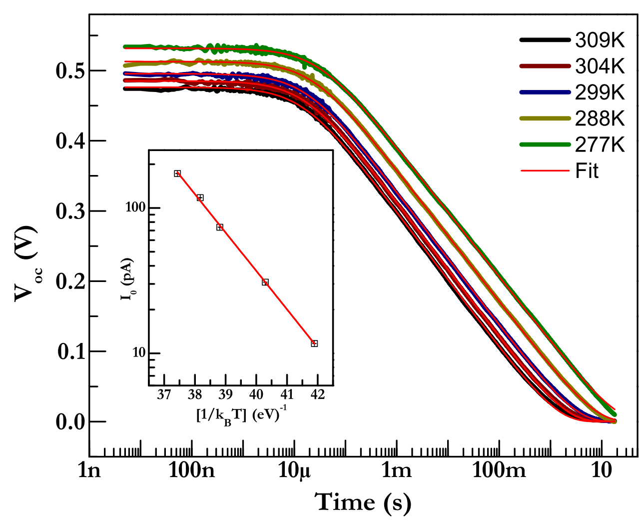


FIG. 2. $V_{oc}$ decay at different temperatures. The fitting to Eq. (3) with dark saturation current ($I_0$) and ideality factor ($n_x$) as parameters for each case is shown as a red continuous line. Inset shows Arrhenius plot of $I_0$ so obtained.

fairly easy to see, following Hellen,[27] that the most significant part of the decay, i.e., linear decrease with $ln(t)$ during intermediate times, is given by the requirement that $\exp[-V_i/n_x V_T] \ll \alpha t \ll 1$, and that it can be expressed as

$$V_{oc}(t) = -n_x V_T \ln(\alpha) - n_x V_T \ln(t), \tag{4}$$

and hence, the ideality factor $n_x$ can be inferred from the slope alone quite reliably without using other experimental parameters such as the capacitance value.[28] The parameters $\alpha$ (hence $I_0$) and $n_x$ can be obtained using either Eq. (3) or Eq. (4) with equal ease. The ideality factor changes from 1.678 to 1.574 for temperatures 277–309 K. The temperature dependence of the corresponding dark reverse saturation current $I_0$ is shown in the inset as an Arrhenius plot. The slope so obtained when multiplied with $n_x$ yields an energy barrier of 0.986 eV, which agrees well with other estimates in the literature[8] and corresponds to the heterojunction barrier at the interface of the polymer and PCBM.

Next, we turn to OCVD transients for different initial values of $V_{oc}$ obtained by varying the steady state illumination level prior to the decay keeping the temperature constant. This is shown in Fig. 3, where the transients correspond to a variation of two orders of magnitude in relative intensity at room temperature. Irrespective of the initial value, the decay transient hits the same decay curve showing that the evolution of the excess carrier profile follows the same mechanism and route in each case. The reverse saturation current is nearly constant between 63 and 75 pA in this case, whereas the ideality factor increases from 1.527 at the lowest intensity to 1.601 to the highest level.

To discuss the significance of the physical consequences of the model, we consider the simplest relevant equivalent circuit in Fig. 4. Since our case corresponds to open circuit, no series resistance needs to be considered. Note that as mentioned earlier, the dark shunt resistance is too high to be considered during the decay. This is confirmed from the dark $J$-$V$ characteristics. This is also borne out by the absence of $R$-$C$ time constant response till more than 100 s of decay time, with the sample capacitance being in $nF$ range. The latter reasoning can be fruitfully used to measure the dark shunt resistance,[26] if present. The highly reliable value of the ideality factor $n_x$, obtained by fitting to OCVD transients, then becomes true representation of losses in the diode in presence of excess carriers under *dark* conditions. Of the three ideality factors $n_d$, $n_l$, and $n_x$, obtained, respectively, from dark $J$-$V$, $V_{oc}$-$ln(\varphi)$, and OCVD, $n_x$ is the most reliable in estimating the current through the diode.

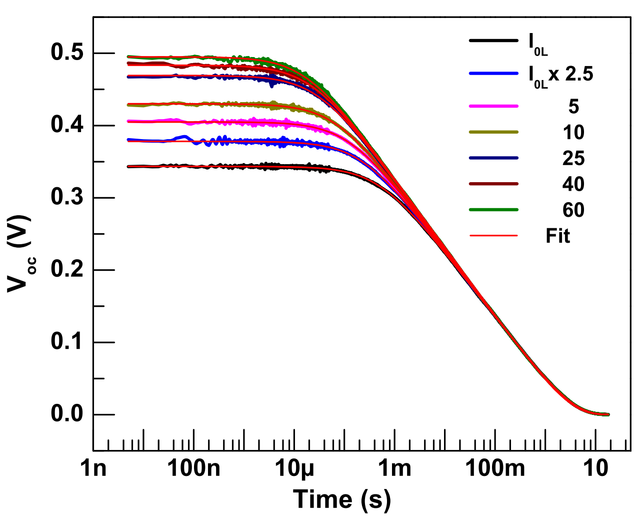


FIG. 3. $V_{oc}$ decay for different initial light intensities. Fit to Eq. (3) is shown as red continuous line in each case.

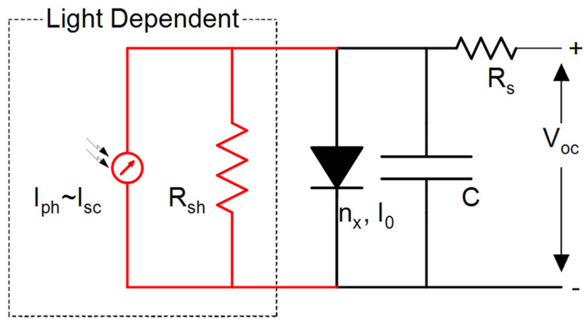


FIG. 4. A schematic equivalent circuit with light dependent components marked (red). In the steady state, the photocurrent gets divided into current through the $I_D$ and the $I_{sh}$.

In the steady state open circuit condition under illumination, the generated photocurrent ($I_{ph}$), which can be reasonably approximated to be the short circuit current ($I_{sc}$),[29] is divided between the diode ($I_D$) and a shunt resistance ($I_{sh}$), which represents an additional recombination mechanism in the presence of light (Fig. 4). Immediately after the cessation of light, the measured $V_{oc}$ is due to excess carrier profile alone. Under steady state illumination, the same $V_{oc}$ is due to the balance between the generation and recombination rates. From OCVD transient conditions, we already know the diode current ($I_D$) at any bias, and hence the rest must be through the mechanism of recombination under illumination alone represented by the light-induced shunt resistance $R_{sh}$, shown in the equivalent circuit (Fig. 4). Therefore, OCVD analysis helps us in isolating the fraction of the current carried by the two paths, and the value of $R_{sh}$ can be obtained by measuring independently the short circuit current $I_{sc}$ for each level of illumination. Figure 5

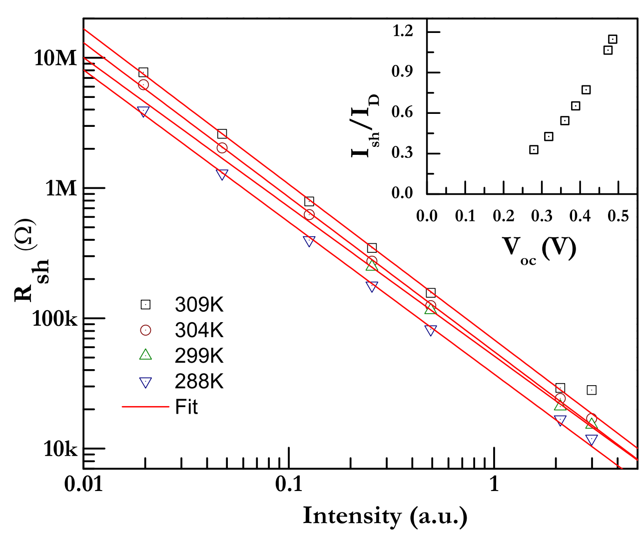


FIG. 5. Equivalent shunt resistance estimated in the presence of light as function of the light intensity. The inset shows the shunt contribution to the loss current increasing with light. The slope, i.e., the exponent of intensity dependence, varies between 1.15 and 1.19.

shows the light induced $R_{sh}$ so obtained as a function of relative illumination intensity in a log-log plot for different temperatures, and the inset shows the ratio of the current carried by the diode to that of the shunt. As the intensity is increased, the current contribution through the light-induced shunt increases rapidly with $V_{oc}$ as shown in the inset.

The ideality factor derived from dark *J-V* characteristics ($n_d$) is affected by the presence of series and shunt resistances which themselves depend on voltage and other parameters such as thickness. Its variation has been recently studied in detail by Kirchartz *et al.*[19] The ideality factor obtained from the steady state $V_{oc}$, i.e., $n_l$, though unaffected by series resistance, would be definitely influenced by the light induced shunt path. It is only the OCVD transient which provides the "true" ideality factor ($n_x$) reflecting the intrinsic losses of the diode in presence of excess carriers, but in absence of series or light induced shunt resistances. The values of $n_x$ (between 1.52 and 1.67 depending on temperature and concentration of excess carriers) clearly point to the dominance of SRH recombination through localized states in the dark.

The recombination in the presence of light can now be separately studied by investigating the intensity dependence of the light induced shunt current alone (subtracting the current through the diode $I_D$ from $I_{sc}$). The exponent of intensity dependence (obtained from the slope of a log-log plot) turns out to be ∼1.31 in our case. For pure bimolecular recombination, it is expected to be 0.5 and 1 for dominantly trap assisted recombination. The supra-linear dependence points to the possible involvement of "sensitization" of shallow defects in the presence of light.[30] It is important to recognize that the dark recombination in the diode represented by the ideality factor $n_x$ (∼1.5–1.6), and the light-induced recombination current having an intensity exponent (∼1.31) owe their origin to different mechanisms, though both appear to be dominantly trap-assisted recombination. The latter involves additional path of recombination in presence of light. The mechanism of light induced pathways may involve a photo-ionization step or conversion of traps to recombination centers due to the movement of quasi-Fermi levels. The possible role of PCBM acting as a quantum dot site[31] for such recombination needs further detail studies.

The analysis given above constitutes demonstration of the power of OCVD technique in isolating the recombination current in the diode due to excess carriers from that of light induced mechanisms of recombination. Our results also support the argument of Street[12] that it is difficult to associate time constants observed in TPV experiments directly with lifetime of carriers. The TPV transient would contain indirect information about changes in the recombination path through differential change in shunt resistance. The OCVD analysis basically provides reliable steady state parameters and the transient model to calculate time-constants in TPV and related experimental situations. The life-time need be gleaned out through a proper analysis of the transient including the capacitor, diode, and the light induced steady state shunt resistance. Our model will help in redesigning experiments and interpreting the results in such an approach.

In summary, we have used well designed low leakage P3HT:PCBM bulk-heterojunction solar cells to study OCVD, and provide a full account of the transient over eight orders of magnitude by proposing a simple model of diode in combination with a capacitor. The model helps in obtaining true characterization of the underlying diode characteristics in terms of its ideality factor and reverse saturation current in presence of excess carriers. This is used to isolate light induced shunt path of recombination that comes into existence in the presence of light. The diode ideality factor varied between 1.52 and 1.64, increasing with increase in excess carrier concentration and decreasing temperature. The exponent of the intensity dependence of the light-induced recombination current and shunt resistance was found to be 1.31 and 1.19, respectively. The OCVD technique has the potential to determine a sample's shunt resistance both under dark and light conditions and to study the underlying mechanisms of recombination in operating conditions. It should be possible to suitably redesign OCVD transients or its differential form to study localized deep DOS and carrier kinetics at these centers, and examine the possibility of photo-ionization as a mechanism of sensitizing the recombination centers through spectral resolution.

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