

# The identification of recombination centers in organic solar cells

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## ABSTRACT

Recombination in bulk heterojunction organic solar cells is explored by observing the result of prolonged white light illumination and thermal annealing. The photocurrent spectral response, the steady state photocurrent-voltage characteristics and transient photoconductivity measurements on PCDTBT:PCBM and P3HT:PCBM solar cells provide information about recombination centers. Illumination generates deep traps while thermal annealing broadens the band tail localized states. Both types of state act as recombination centers. The evidence suggests that hydrogen abstraction, migration and re-bonding is responsible for the creation and recovery of recombination centers.

**Keywords:** organic solar cells, recombination, traps.

## 1 INTRODUCTION

Bulk heterojunction organic solar cells are a promising technology because of their anticipated low fabrication cost, but the cell efficiency is still too low to be commercially viable for large scale power production. Recombination is one limitation on performance, and so it is important to identify and eliminate the recombination mechanisms in order to increase cell efficiency. There is prior evidence that trap states near the heterojunction interfaces provide the dominant recombination, at least in some cell materials, but there is little information about the electronic or chemical nature of the traps.[1-3] Here we report measurements of the photocurrent spectral response and other opto-electronic experiments to obtain the density of states distribution and the trap characteristics. These measurements show that prolonged light illumination induces deep trap states while high temperature annealing broadens the disorder-induced band tail states.[4] Each type of state acts as recombination centers with different characteristic properties.

## 2 MEASUREMENTS AND RESULTS

PCDTBT:PCBM and P3HT:PCBM solar cells are studied. The photocurrent spectral response is measured at zero bias on the solar cell, using a 9 kohm load resistance and with a lock-in amplifier and a chopped monochromatic light source as described elsewhere.[5] The transient photocurrent is measured with a nitrogen pulsed dye laser operating at 520 nm. The signal across a series of load resistors is measured on a digital oscilloscope.[6]

## 2.1 Photocurrent spectral response

The photocurrent spectral response (PSR) measures the photocurrent as a function of illumination wavelength, normalized to the incident light intensity. When the optical absorption within the device is weak, the PSR measures the optical absorption of those optical transitions that excite carriers into mobile photoconducting states. Since optical absorption is proportional to the number of absorbing states, the experiment provides a measurement of the density of states (DOS) distribution. The absorption is a convolution of the initial and final state distribution, and so the precise DOS can be difficult to extract, but broad features are more clear.

Figure 1 shows the photocurrent spectral response for a PCDTBT:PCBM cell at different stages of white light soaking. Different types of optical transitions contribute to the PSR in different energy ranges. Above 1.8-2 eV there is bulk absorption into either PCDTBT or PCBM. Below 1.8 eV is absorption at the heterojunction interface, between the PCDTBT HOMO levels and the PCBM LUMO levels as shown in Fig. 1. The exponential region between 1.2-1.4 eV is due to the disorder-induced band tail states of the cell materials.[4,5] Finally the broad absorption band below 1.2 eV corresponds to transitions between deep trap states and the HOMO or LUMO levels. The increased PSR intensity in the energy range 0.8-1.2 eV provides a measure of the deep trap density induced by light. The trap density increases 10-fold after illumination.

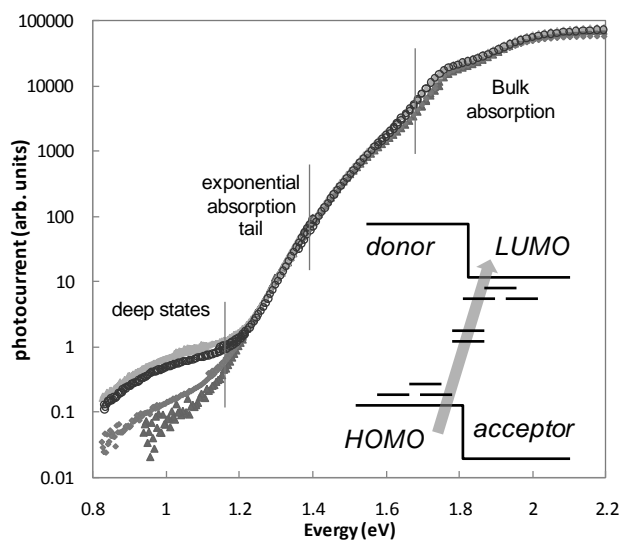


Figure 1. Photocurrent spectral response of PCDTBT:PCBM at various stages of prolonged light exposure, showing an increased response at 0.8-1.2 eV arising from deep traps.[4]

Evidence that these deep traps are the dominant recombination centers is obtained from the voltage dependence of the photocurrent  $J_{PC}(V)$  (in effect the solar cell fill factor) which is analyzed to give the relative density of recombination centers. Figure 2 shows that  $J_{PC}(V)$  flattens out with prolonged illumination. The change in  $J_{PC}(V)$  indicates that there is increasing recombination as a result of prolonged light illumination. The measurements in Fig. 2 are made at sufficiently low light intensity that bimolecular recombination or contact series resistance do not affect the results.

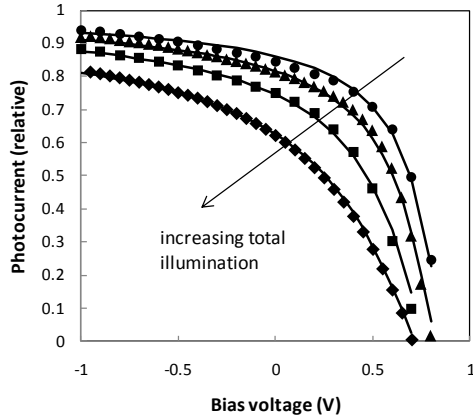


Figure 2. Voltage dependence of the photocurrent after increasing amounts of white light exposure. The solid lines are a fit to the charge transport model.

The relative density of recombination centers can be obtained from the data in Fig. 2, based on the voltage dependence of the relative probability of recombination and charge collection.[7] The model we use extracts the mobility-lifetime  $\mu\tau$  product of carriers which is related to the density of recombination centers  $N_R$  by,

$$\mu\tau = \text{const} / \sigma N_R \quad (1)$$

so that the relative value of  $N_R$  is obtained.

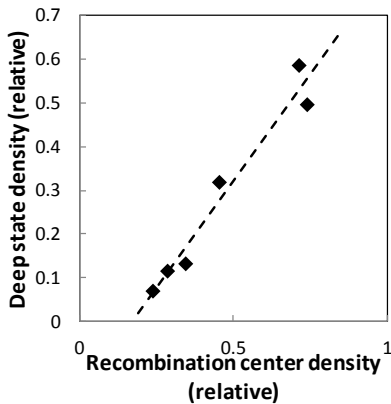


Figure 3. Plot showing a linear dependence of the relative trap density and recombination center density for various stages of light exposure.

A linear relation between the trap density as measured by PSR, and the recombination center density as measured

by  $J_{PC}(V)$  is shown in Figure 3. The result confirms that the deep states that are observed in the PSR are the recombination centers.

Figure 4 shows that a large fraction of the low energy PSR signal after prolonged illumination recovers upon annealing at about 100C, indicating that the induced states are metastable and can be removed. Recently we have made similar measurements on solar cells exposed to low energy (8 keV) x-rays, with very similar results.[8] The x-ray irradiation induces the same low energy absorption band in the PSR spectrum and the states are removed by annealing. Measurement of the annealing kinetics of either light or x-ray induced states find two thermally activated rates corresponding to activation energies of 1.1-1.3 eV.

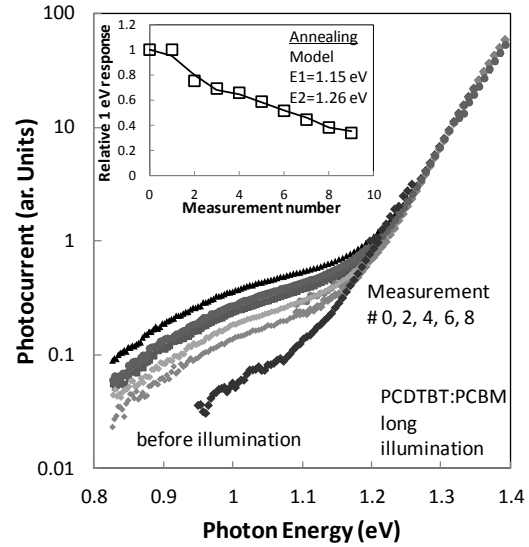


Figure 4. Photocurrent spectral response of PCDTBT:PCBM before and after exposure to white light and after annealing to about 100C.[5]

The PSR measurement combined with  $J_{PC}(V)$  therefore allows the light-induced degradation mechanism of the solar cell to be characterized both with regard to the electronic states and the defect creation and annealing kinetics. Illumination and x-ray exposure create qualitatively similar deep recombination centers.

## 2.2 Transient photoconductivity

Transient photoconductivity (TPC) provides an alternative measure of the density of localized states. TPC relies on thermal excitation from trap states and is therefore useful to compare with the optical excitation data provided by PSR. The density of trap states is obtained from the transient photoconductivity measured over an extended time scale.[6] The laser pulse creates mobile charge and a certain fraction of the charge is captured by trap states, and subsequently released with a characteristic release time,  $t_R$  that depends on the trap depth,  $E_D$ ,

$$t_R = \omega_0^{-1} \exp(E_D / kT) \quad (2)$$

where  $\omega_b$  is an attempt to escape prefactor of order  $10^{12} \text{ s}^{-1}$ . Eq. 2 relates the thermal excitation of trapped carriers at a particular time after the laser pulse to the trap energy. A broad energy distribution of states  $N(E)$  then leads to a photocurrent  $J_{PC}(t)$  arising from the release of carriers from traps, given by,[6]

$$N(E) = \frac{t J_{PC}(t)}{e v f k T} \quad (3)$$

where  $v$  is the sample volume and  $f$  the fraction of states that are filled. Eqs. 2 and 3 give  $N(E)$  from a measurement of  $J_{PC}(t)$ . Figure 5 shows the density of states distribution derived for PCDTBT:PCBM.[6] There is an exponential density of states with 45 meV slope, which exactly corresponds to the slope of the PSR between 1.2 and 1.4 eV. There is also a broader distribution of deeper trap states that are consistent with the broad low energy band in the PSR (see Fig 1). Similar agreement between PSR and TPC is found for P3HT:PCBM, confirming that there is an exponential distribution of band tail states and a broader distribution of deeper traps.

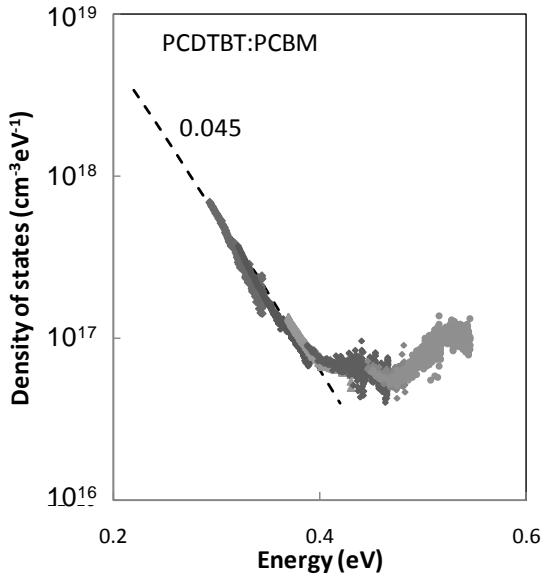


Figure 5. Density of states distribution as measured by transient photocurrent measurements showing the exponential band tail and the deeper states.[6]

### 2.3 Effects of thermal annealing

The data in Fig. 1 and 4 show that prolonged exposure to illumination increases the density of deep states that act as recombination centers. We have found that thermal annealing of the solar cells to high temperature also increases recombination, and it is therefore interesting to compare the two recombination mechanisms.[4] Figure 6 shows the PSR for PCDTBT:PCBM at different stages of annealing up to 210C. The magnitude of the PSR above 2 eV decreases because there is an increase in the recombination and a large reduction in fill factor as measured by  $J_{PC}(V)$ .

Thermal annealing causes a broadening of the band tail as shown in Figure 7, but there is no obvious increase in the density of deep states as there is for prolonged illumination (see Fig. 6). Strongly increased recombination is observed by the shape of  $J_{PC}(V)$  from which we measure a 10-fold increase in the density of recombination centers at the highest annealing temperature.

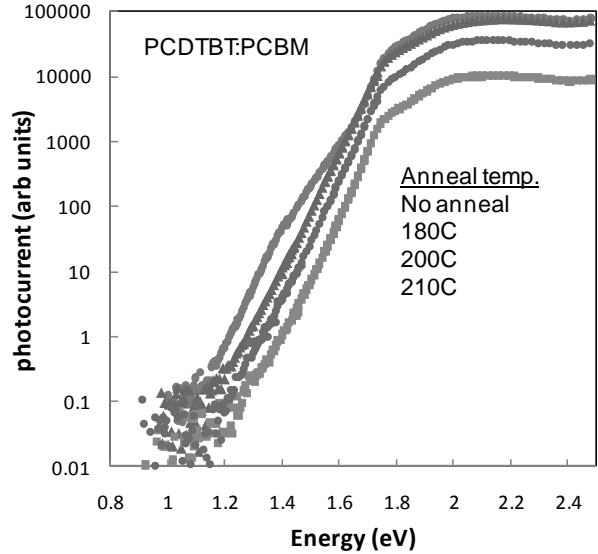


Figure 6. Photocurrent spectral response measurements for PCDTBT:PCBM annealed to various temperatures.[4]

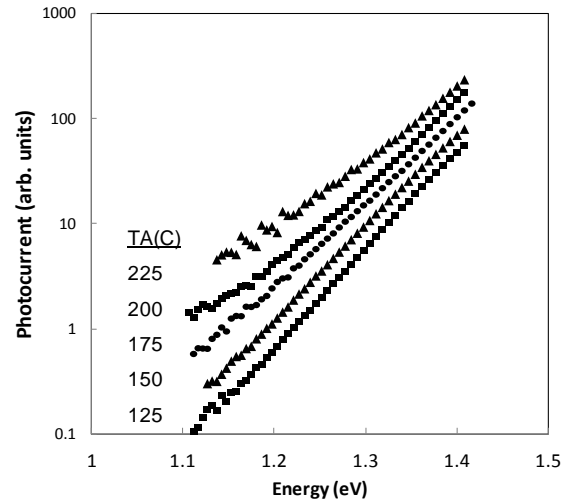


Figure 7. Detail of the photocurrent spectral response showing the increase in band tail width with thermal annealing at the temperatures indicated.[4]

The increased recombination, with no apparent increase in deep trap density, strongly suggests that in this case the deeper band tail states act as the recombination centers. The number of band tail states deeper than an energy  $E_B$  is,

$$N_T(E > E_B) = N_o E_0 \exp(-E_B / E_0) \quad (4)$$

Assuming that these tail states are the recombination centers then,

$$\ln(N_R) = \text{const.} - E_B / E_0 \quad (5)$$

Figure 8 plots the thermal anneal data in the form of eq. 5 and shows that it is consistent with band tail states deeper than about 0.3 eV acting as recombination centers.

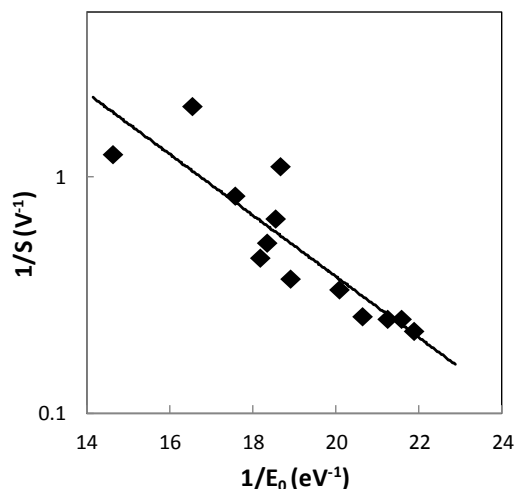


Figure 8. Plot of the relation between density of recombination centers and the slope of the band tail, plotted according to eq. 5. The line is a fit to Eq. 5 with  $E_B=0.3$  eV.

### 3 DISCUSSION

The light exposure and thermal annealing data show that there are two types of recombination centers in these solar cells – band tail states and deep traps. Light exposure increases the deep trap density and thermal annealing increases the band tail state density. Measurements of the dark current shows that the diode ideality factor increases with the increased recombination,[4] but that the relative increase is different for light exposure and thermal annealing, providing further evidence that different recombination centers are involved.

The conclusion that there are two types of recombination center explains the data in Fig. 3 which shows that there is some residual recombination even when the deep state density drops to zero. Band tail states provide the residual recombination centers. However, Fig. 1 also shows that there are deep traps even before significant light exposure.

While the electronic states associated with recombination centers can be characterized by these measurements, the atomic and chemical structure of the states is not revealed. However, the experimental evidence that the light-induced states can be at least partially annealed away shows that the structure must be metastable. Furthermore, measurements on x-ray irradiated organic solar cells observe induced recombination centers with very similar properties to the light induced defects, including the observation of thermally activated defect recovery, suggesting that the same type of defect state is involved.[8]

X-ray irradiation studies find that hydrogen abstraction from C-H bonds is the main form of radiation damage at low exposure.[9] This leads us to investigate further the possibility that the recombination centers are the result of hydrogen abstraction. First principles theoretical calculations find that a carbon atom in the alkyl chain that is missing an H atom, and an additional H atom attached to the conjugated polymer ring (a  $\text{CH}_2$  defect), both form gap states.[8] The latter configuration is shown in Fig. 9. The extra H atom could be placed on atoms 2, 3, 5 or on the S atom (see Fig. 9), but these structures have higher energy. Furthermore, hydrogen migration either along the alkyl chain or along the conjugated rings is calculated to have a migration energy of 1.2-1.4 eV,[8] which is close to the measured activation energy for defect recovery after irradiation of light exposure. These calculations therefore provide evidence that hydrogen chemistry is the fundamental mechanism determining the formation and annealing kinetics of the recombination centers in these organic solar cells.

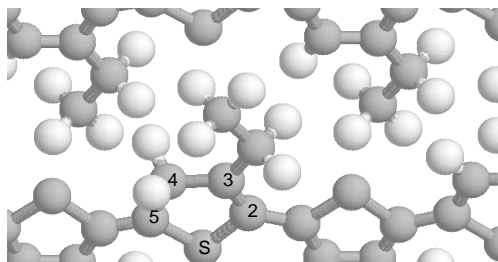


Figure 9. An atomic model of a  $\text{CH}_2$  defect in which the added H atom is located on carbon atom 4.[8]

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