

Photo-induced changes in fundamental properties of organic solar cells

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We report on the measurement of fundamental properties such as deep defects and hole mobility in poly-3-hexyl-thiophene (P3HT)/[6,6]-phenyl-C60-butyric acid methyl ester (PCBM) solar cells when the cells are exposed to solar radiation without any atmospheric exposure. It is found that the midgap defect density in P3HT and the interface density between P3HT and PCBM increase significantly upon light soaking along with a reduction in hole mobility in P3HT. The increase in defect density leads to a corresponding increase in reverse saturation current of the diode, and the corresponding decrease in open circuit voltage of the cell upon light soaking. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4711806>]

Organic solar cells based on polymers are an important class of materials for photovoltaic energy conversion. Recent advances in the field have resulted in conversion efficiencies exceeding 8%.^{1,2} However, the solar cells degrade rapidly when exposed to light, and to the environment, particularly to moisture and oxygen.^{3–8} A recent work on poly-3-hexyl-thiophene (P3HT) suggests that the primary degradation is due to moisture and oxygen exposure and that the exposure to light does not seem to change the photo-conductivity of the film and, therefore, by implication, the fundamental material properties such as the midgap and interfacial defect densities.⁹ In this paper, we report on a careful investigation of the influence of light exposure on fundamental material properties of P3HT/[6,6]-phenyl-C60-butyric acid methyl ester (PCBM) solar cells, which shows that there are significant changes in midgap defects in P3HT and at the P3HT/PCBM interface, which in turn change both the dark I-V characteristics and the open circuit voltage. We also show that there are changes in hole mobility in P3HT under photon-induced degradation.

The P3HT/PCBM device samples were prepared using standard spin coating techniques on ITO coated glass.¹⁰ The thickness of the P3HT/PCBM layer was 150 nm. The initial conversion efficiency of the cell was 3.6%. After fabrication, the device was immediately measured for its light I-V characteristics and then rapidly transferred to a vacuum system capable of pumping down to a pressure $<1 \times 10^{-6}$ Torr. After evacuation, high purity nitrogen gas was introduced into the light testing chamber. A xenon source solar simulator with appropriate filters to simulate AM1.5 sunlight was used as the source for studying the degradation of the solar cells. During degradation, high purity nitrogen was continuously flowing in the light testing chamber. The chamber was provided with appropriate instrumentation to measure dark I-V, light I-V, and defect densities *in-situ* without exposing the sample to air. Absolute quantum efficiency (QE) was measured before and after degradation. The intensity of light could be changed by using a lens. For the results reported here, we used an intensity of 200 mW/cm^2 ($2 \times \text{sun}$) for 96 h from a full spectrum solar simulator.

In Fig. 1, we show the light I-V curve for a cell before and after photo-induced degradation. We also measured sub-gap quantum efficiency before and after degradation so as to determine changes in Urbach energies of tail states near HOMO levels and changes in midgap defects.¹¹ A representative data for the sample before and after degradation is shown in Fig. 2. The sharp tail in quantum efficiency corresponds to excitation from tail states near the HOMO level, and the shallow portion at very low photon energies ($\sim 0.8 \text{ eV}$) corresponds to excitation from midgap states in P3HT. From Fig. 2, we can observe that the midgap defect density in P3HT has increased significantly after degradation, whereas there is virtually no change in tail state densities.

We also measured the midgap defect density using the capacitance-frequency-technique described in Ref. 11. In this technique, one measures capacitance (C) vs. frequency (f), and then calculates the defect density as a function of energy from a measurement of dC/df .^{12,13} In Fig. 3, we plot the measured defect density vs. defect energy above the HOMO level of P3HT for our sample at three different times, original, and for two degradation times. The data of Fig. 3 show that the defect density keeps increasing as a

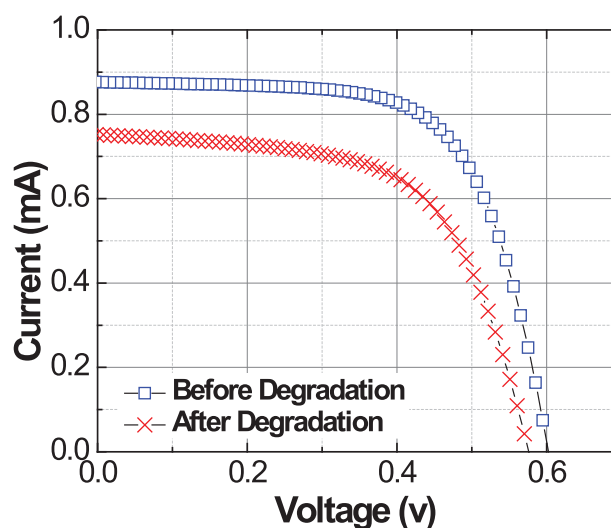


FIG. 1. I-V curve of a P3HT solar cell measured at 1 sun intensity before and after photo-induced degradation under 200 mW/cm^2 of full spectrum simulator. The area of the cell is $\sim 0.1 \text{ cm}^2$.

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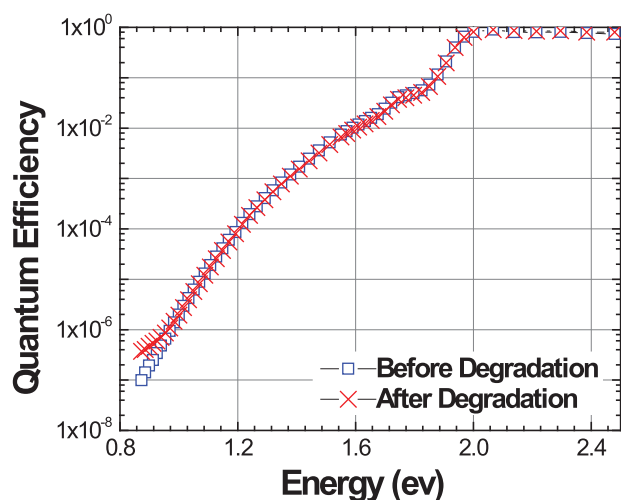


FIG. 2. Subgap quantum efficiency of the solar cell before and after degradation. For ease of comparison, the two curves are normalized in the higher energy range.

function of light soaking time and has increased by a factor of 2 at ~ 0.3 eV above the valence band after 96 h of light soaking, but by a factor of 5 in the 0.5 eV–0.6 eV region after photon exposure. This is a different energy region than the midgap of P3HT (~ 0.8 –1.0 eV) and corresponds to an energy region which is about half the energy between the LUMO level of PCBM and the HOMO level of P3HT. This fact strongly suggests that these states are located at the interface between P3HT and PCBM.

A necessary consequence of the increase in interface defect density is that the dark I-V curve must change as a result of degradation, with an increase in reverse saturation current I_0 .¹⁴ In Fig. 4, we show the dark I-V curve before and after degradation. The dark I-V curves show a very interesting development, namely, that the I-V curve after degradation not only shows a higher value for dark current, but actually has an inflection point, clearly showing two distinct regions of dark I-V, one at low forward voltages (< 0.3 V) and one at higher voltages, in addition to the usual shunt and series resistance regions. The two regions in the I-V curve after degradation strongly suggest that the current at low voltages corresponding to the generation-recombination factor,

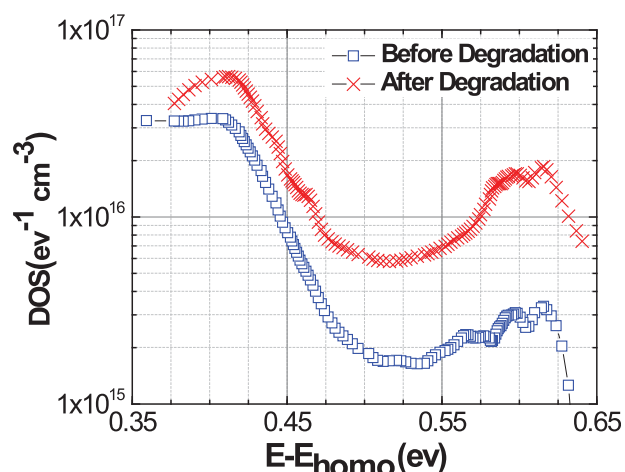


FIG. 3. Defect density vs. energy in the cell measured using capacitance-frequency technique before and after degradation.

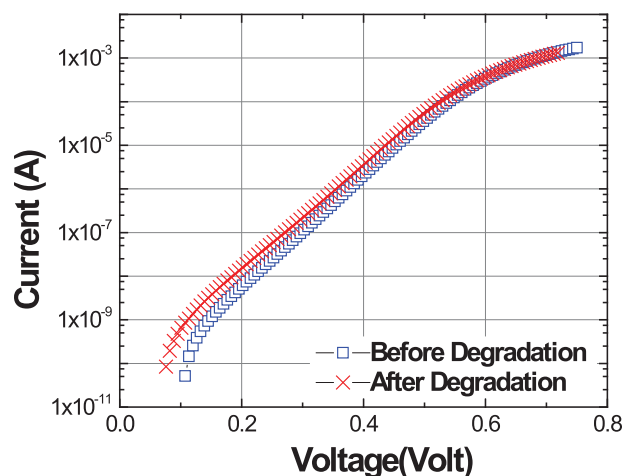


FIG. 4. Dark I-V curves of the cell before and after degradation.

which is closely related to increases in defect density in the midgap region including changes at the interface between the two materials, has increased significantly after degradation. Since recombination due to mid-level interfacial states leads to an I-V curve with a diode factor close to 2, whereas the band-to-band recombination leads to a diode factor of ~ 1 , an increase in the midgap recombination must increase the average diode factor of the I-V curve. Data analysis shows that the average diode factor of the curve increased from 1.26 before degradation to 1.35 after degradation. The I_{01} (reverse saturation) current corresponding to this early voltage part of the curve after degradation increased to 6.0×10^{-11} A, from 1.2×10^{-11} A prior to degradation, a factor of 5 increase. This increase in I_{01} is directly due to the increase in mid-gap defect density at the interface.¹⁴ Note that the increase in midgap densities, measured using C-f method, was also a factor of ~ 5 , showing very good agreement between the two *independent* measurements of the increase in defect density upon light soaking.

The change in open circuit voltage upon degradation can be calculated from the dark current values and the effective diode factor before and after degradation. The effective diode factor changed to 1.35 after degradation from 1.26 before, with the average I_0 increasing from 9.7×10^{-12} A to 4.5×10^{-11} A. Using the standard voltage equation, $V_{oc} = (nkT/q) \ln(I_{sc}/I_0)$, gives an initial calculated voltage of 600 mV and voltage after degradation 583 mV, in good agreement with the measured values in Fig. 1.

It is useful to note that these results are not a single sample result. Many similar devices were measured in a similar fashion, and all devices showed very similar behavior, with an increase in dark current and in midgap and interfacial defects, with a strong correlation between the two measurements.

The change in short-circuit current upon degradation cannot be explained by changes in optical absorption.¹⁵ However, we observed a significant change in mobility of holes in P3HT after photon exposure (see Fig. 5). Space-charge limited current measurements on P3HT films sandwiched between PEDOT:PSS [Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)] and gold hole injecting contacts were used to measure mobility. The large change in mobility will lead to reductions in carrier collection efficiency and this may be one

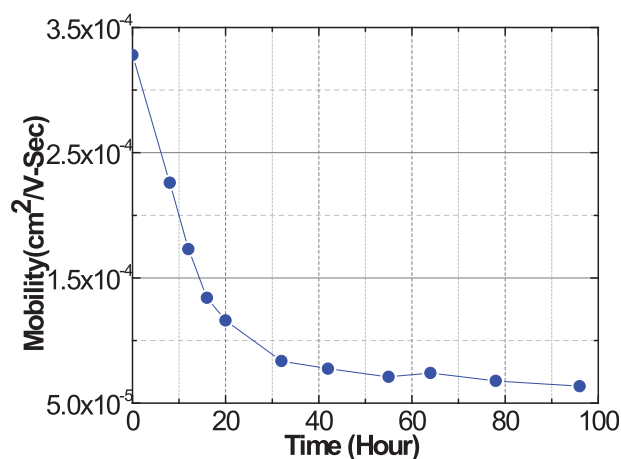


FIG. 5. Change in hole mobility in P3HT material deposited on PEDOT:PSS hole transporting layers as a function of time of photo-induced degradation.

reason for changes in current upon light soaking. Another reason for the decrease in current may be increased recombination at the interface between P3HT and PCBM, and indeed, the change in slope in I-V curve near short circuit conditions strongly suggests a voltage-dependent current collection, a classical signature of increased recombination.

The change in fill factor can be easily explained by noting the change in resistance due to changes in mobility and in carrier collection, due to increased recombination.

Our results convincingly demonstrate that *fundamental properties* of the active photovoltaic material are changing upon exposure to photons, and that it is inaccurate to ascribe changes in device properties to changes in just the contact layers, or to the influence of oxygen and moisture alone. The significant changes in the midgap densities occur both in the P3HT material (~ 0.8 – 1.0 eV above the HOMO level of P3HT) and at the interface between P3HT and PCBM (~ 0.5 – 0.6 eV above the HOMO level).

In summary, there are measurable increases in midgap defects and decrease in hole mobility in P3HT/PCBM solar cells when exposed to light alone, and that the decrease in current and voltage upon light exposure, as well as changes in dark diode I-V curves, can be explained using these changes. There may also be additional changes in the materials when exposed to atmosphere.

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