Kinetics of light induced defect creation in organic solar cells

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(Received 19 November 2012; accepted 16 January 2013; published online 30 January 2013)

The kinetics of light-induced recombination centers in bulk heterojunction organic solar cells are measured as a function of exposure time, intensity, and the illumination photon energy. The density of induced centers increases with exposure but stabilizes partially due to self-annealing. UV exposure is roughly 50 times more effective for defect creation than white light or yellow-filtered white light. Light-induced breaking of C-H bonds to create H-related localized states is proposed as the underlying mechanism.

With the continuing increase in the efficiency of organic bulk heterojunction (BHJ) solar cells, it becomes increasingly important to measure and understand their long term degradation kinetics, to predict their expected lifetime and find ways to improve stability. Various reports have measured the solar cell stability in sunlight. In particular, poly(carbazole-dithienyl-benzothiadiazole):phenyl C70-butyric acid methyl ester (PCDTBT:PC70BM) is found to degrade by about 20% in the first 100–200h of sunlight and then to stabilize, while poly(3-hexyl thiophene) (P3HT):PCBM is found to be relatively more stable. Evidently different materials have different stability properties and hence a deeper understanding of the mechanisms might help the design and fabrication of long lifetime materials.

The photocurrent spectral response (PSR) measures the short-circuit photocurrent as a function of the photon energy of monochromatic light. At an energy below the polymer or fullerene band gap of about 1.7 eV, the PSR signal arises from charge transfer (CT) optical absorption at the bulk heterojunction interface between the polymer valence band and fullerene conduction band. At still lower energy, below 1–1.2 eV, the PSR arises from optical excitations through deep localized states located near the heterojunction interfaces and provides a measure of the state density. An increase in the localized state density as measured by the low energy PSR, as a result of both white light and x-ray exposure was previously reported. Other measurements also observe an increase in deep state density with prolonged illumination.

About 10 PCDTBT:PCBM and P3HT:PCBM solar cells were exposed to various light sources. The cell structure is glass/indium tin oxide (ITO)/poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/BHJ/TiOx/Al with glass encapsulation: further details of fabrication are described elsewhere. Typical initial cell efficiency is 5%–6% for PCDTBT:PCBM and 2%–3% for P3HT:PCBM. The BHJ thickness was usually about 100 nm but a few cells were up to 200 nm thick and had lower efficiency. UV exposure used an arc-lamp with emission from 300–450 nm. The lamp exposed a large area and caused significant heating of the substrate but exposures were for 90 s each with an interval in between to allow cooling. White illumination used a halogen lamp with an infra-red absorbing filter to reduce the heat, and yellow-filtered white light used the same source with a 450 nm long-pass cut-off filter. An aperture prevented the halogen illumination from extending beyond the device, to minimize heating. Active cooling with an air stream was used in some cases. The incident power for the different illumination was in the range 0.3–1 W/cm² and for some measurements neutral density filters were used to reduce the intensity. Samples were exposed for various times and monitored by PSR using lock-in techniques as described elsewhere.

Figure 1 shows the low energy region of the PSR for exposure to UV and white light for PCDTBT:PCBM and P3HT:PCBM. Only the lowest energy region of the spectrum increases with exposure. The high energy regions are virtually unchanged although the overall signal strength decrease slightly after long exposures due to a reduction in charge collection at short circuit. We interpret the low energy region as optical transitions through deep localized states near the heterojunction interface. The photocurrent is generated by photon energies well below the interface band gap (~1.4 eV for PCDTBT:PCBM and 1.1 eV for P3HT:PCBM), which leaves...
little room for any other explanation. The relative deep state density can, therefore, be measured from the PSR data.

Figure 2 shows the relative induced state density as a function of total exposure for UV, white light and yellow-filtered white light for PCDTBT:PCBM and P3HT:PCBM using illumination of approximately the same intensity in each case. These data are normalized to the PSR signal at 1.3 eV in PCDTBT:PCBM and to 1.11 eV for P3HT:PCBM, which have photocurrents of similar magnitude, to correct for the small changes in overall intensity, and the initial signal before exposure is subtracted. The deep state density increases with exposure but the rate of increase slows and the density eventually stabilizes. The UV exposure induces states at a rate that is about 50 times faster than white or yellow light for the same exposure, and the saturation is correspondingly faster. Yellow exposure is comparable to white exposure, but one measurement in which the sample was exposed alternately to white and yellow lights found that the yellow light had a lower rate of trap creation by about a factor 2. Sample to sample variations are 20%–50%, possibly due to different optical absorption profiles and thickness dependence. The P3HT:PCBM cells have a lower rate of defect creation and also saturate at a lower level. The white light P3HT:PCBM data include measurements after one and two annealing cycles, showing that the generation and annealing cycle is repeatable.

The light-induced states are reversible and are removed by annealing. The annealing effect occurs for both UV and visible light exposure and for both cell materials. The induced states anneal with a combination of a fast and a slow time constant which are about 1 h and 50 h, respectively, for PCDTBT:PCBM annealed at 90 °C and are about 5 × shorter in P3HT:PCBM. Presently, we reported that the fast time constant dominates the annealing after x-ray exposure but the slow time constant dominates after white light exposure. Present data indicate that the difference between x-ray and light exposure is not an intrinsic difference. The faster annealing is suppressed in samples which were either exposed for a long time or warmed significantly during exposure (e.g., UV exposure), but not in samples with short exposure times or with active cooling. The heating of the sample during exposure causes self-annealing of the induced states and hence contributes to the saturation effect.

Figure 3 shows measurements of the intensity dependence of the defect creation rate in PCDTBT:PCBM. The cells are alternately illuminated with high and low intensity white light (closed and open symbols in Fig. 3) using a neutral density filter with 25% transmission. These data are plotted as a function of total exposure. For a linear dependence on illumination, the data should lie on a common curve while a non-linear dependence should exhibit a different slope for high and low intensity. These data are plotted this way to adapt to the overall non-linear dependence on total exposure. Sample A shows no evidence of non-linear intensity dependence, while sample B shows some evidence of a super-linear dependence. Sample A is about twice the thickness of sample B, which accounts for the generally faster increase in defect density.

Previous results show that the increase of the low energy PSR transition is proportional to the density of recombination centers as measured by the cell current-voltage characteristics, hence showing that the deep states are important recombination centers. Our measurements of the deep state generation kinetics and annealing are consistent with long term studies of solar cells in sunlight. The initial degradation (burn-in) and subsequent stabilization of PCDTBT:PCBM in sunlight is qualitatively consistent with the increase in state density in Fig. 2 followed by saturation. The smaller creation rate of P3HT:PCBM and the more rapid annealing combine to limit the induced state density and make P3HT:PCBM a more stable solar cell as observed.

Table I shows the estimated deep state creation efficiency, defined as the ratio of the number of states created to the number of photons absorbed in the active layer, obtained from the present measurements and from previous measurements of x-ray exposure. These data are corrected for the measured absorption of the cell and the glass/ITO/PEDOT:PSS layers, which start to absorb at ~350 nm and

FIG. 2. Plot of the relative induced localized state density as measured by the PSR, versus exposure for UV (squares), white light (diamonds), and yellow-filtered white light (triangles). Filled symbols are PCDTBT:PCBM and open symbols are P3HT:PCBM. Solid lines indicate the initial increase of defects with exposure.

FIG. 3. The PSR localized state signal for PCDTBT:PCBM solar cells versus total white light exposure using two different light intensities.
are completely absorbing at 300 nm. The relative induced state density of PCDTBT:PCBM and P3HT:PCBM is made by comparing the magnitudes of the PSR signal. The absolute creation efficiency is based on a previous calculation that during x-ray exposure 1% of the secondary electrons creates a deep state. The values are approximate due to the various assumptions in the calculation, but the range covers many orders of magnitude. It is not surprising that UV exposure induces states at a higher rate than visible light, and that x-ray exposure has a very much higher rate given the different excitation energy.

The low energy PSR defect absorption band is similar for the light, UV, and x-ray exposure, and the annealing kinetics are also indistinguishable. Consequently, the data strongly suggest that the induced localized states are identical in each case. There is good evidence that x-ray exposure breaks C-H bonds, and theoretical studies show that excess cal in each case. There is good evidence that x-ray exposure strongly suggests that the induced localized states are identical for the light, UV, and x-ray exposure, and the annealing kinetics. The defect pair comprising a hydrogen vacancies and hydrogen forming overcoordinated sites on the polymer chain provides a viable model for the deep states and their property of reversible annealing.

The C-H bond strength is 4–5 eV, which is well within the range of the secondary electrons resulting from x-ray exposure and close to the energy of the UV excitation. The 2–3 eV energy of yellow or white light is considerably smaller than the C-H bond strength raising a question about the bond-breaking mechanism. The bond could be broken by 2-photon excitation but the two-photon cross-section is much too low, and the expected dependence on the square of the intensity is not observed. A two-step process in which a photon excites a previously excited electron or hole is another possibility. Due to the presence of band tail states, the density of excited carriers increases relatively slowly with excitation intensity, so that the two-step process should have an intensity (G) dependence of \( \sim G^{1.3} \), which is possibly consistent with the intensity dependence data. However, the calculations in Ref. 8 showed that the formation energy of the defect pair is about 2.2 eV, so that in principle, single white light photons could form the states. A possible mechanism is the formation of the defect pair on adjacent sites followed by diffusion apart to a more stable configuration. The very low white light defect creation efficiency allows for low probability processes to create the states.

In summary, prolonged light excitation produces deep localized states that act as recombination centers in some bulk heterojunction solar cells. The evidence indicates that a reversible hydrogen-related defect is the underlying origin of the states.

The authors are grateful to A. Heeger and S. Cowan for providing the solar cell samples, J. Northrup for valuable discussions, and C. Paulson for technical assistance.


<table>
<thead>
<tr>
<th>Exposure</th>
<th>PCDTBT:PCBM Defects/e-h pair</th>
<th>P3HT:PCBM Defects/e-h pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>White light</td>
<td>(6 \times 10^{-11})</td>
<td>(3 \times 10^{-11})</td>
</tr>
<tr>
<td>UV</td>
<td>(3 \times 10^{-9})</td>
<td>(4 \times 10^{-10})</td>
</tr>
<tr>
<td>x-ray</td>
<td>(1 \times 10^{-2})</td>
<td>(1 \times 10^{-2})</td>
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