Modeling of the X-irradiation response of the carrier relaxation time in P3HT:PCBM organic based photo-cells

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X-irradiation generated trapped charge induces open-circuit voltage (Voc) variations and carrier relaxation time. This is modeled using a standard drift/diffusion program. Voc shifts and anomalous behavior of relaxation time are accounted for.

The requirement for inexpensive, dependable, light weight solar cells for use in space applications has led to attention being focused on organic polymer solar cells. They are light weight, flexible and are potentially useful in conformal coverage applications. While these solar cells are less efficient (presently ~ 8%) than traditional silicon or III-V based solar cells this is compensated for by their lower weight which leads to a higher specific power and a lower fuel cost for launch. Furthermore their flexibility may be a specifically positive attribute since this renders them less vulnerable to vibration damage during the launch process. However, for them to be used in space a complete evaluation and understanding of the radiation hardness of organic photocells is essential. We have carried out preliminary studies of the behavior of P3HT:PCBM based photocells and a reduction of the open circuit voltage, V_{oc}, due to X-ray exposure up to 300 krad (SiO_2) was measured whilst the optical photo-carrier relaxation time, τ, was observed to remain unchanged [1]. To explain these phenomena the hypothesis was advanced that radiation resulted in charging at the photo-cell contacts and that this charge acted rather like fixed oxide trapped charge in MOSFETs by varying V_{oc} analagous to threshold voltage shifts. Implicit to understanding the experimental data (Fig. 1a) for the photo-induced carrier relaxation, τ, was the assumption that the trapped charge did not influence it. In an effort to place these assumptions on a more physical foundation and to further our ability to model them we have extended our experimental data range (primarily to significantly higher total dose) and used traditional device modeling methods usually applied to the study of inorganic devices.

The experimental set-up has been described elsewhere [1] and is briefly described as follows. The P3HT:PCBM 1:1 by weight cells were exposed with an uncalibrated background light source which established a mean open-circuit voltage at a chosen value in the range 0 – 0.45 V. Superimposed on the background was a pulse of light from a halogen flashtube (also uncalibrated). The duration of the pulse was ~ 2μs which was substantially shorter than any of the estimated photo-induced carrier relaxation times we measured. These pulses, at a repetition frequency ~ 1Hz, induced small fluctuations (ΔV_{oc}) of the cell open circuit voltage as measured using a high input impedance, digitizing oscilloscope. The pulse intensity was adjusted during the experiment so that $\Delta V_{oc}/V_{oc}$ was ≤ 0.05—the photo-induced carrier density was then only slightly perturbed by the addition of the pulse. The relaxation of the induced ΔV_{oc} was assumed to follow an exponential time decay consistent with other authors (see [1] and references therein) with the approximation that $\Delta V_{oc} \propto \Delta n$ where n is the photo-induced carrier density. Relaxation times and open circuit voltages were determined for different background light levels and following different levels of X-irradiation. All measurements were performed in-situ in an ARACOR 4100 irradiation system using a tungsten targett 50 kV with different current levels chosen to explore possible dose rate effects.

The organic photocells were simulated using Silvaco Atlas [2] as a 200 nm thick material representing the P3HT:PCBM blend with anode and cathode contacts attached on the top and bottom. The effective built-in potential was generated by the difference in the work functions between the two contacts analagous to the method used by Hwang and Greenham [3] and a zero current boundary condition used to calculate V_{oc}. In order to simulate the experimental extraction of the carrier relaxation time (based on the work of Shuttle and others[1,4,5]) the following methodology was adopted. First, the device was exposed to a spatially uniform electron-hole, e-h, pair generation rate and allowed to equilibrate, this emulated the effect of the background light source. Then a short duration (~ 2 μs) additional pulse of e-h pairs was injected causing the V_{oc} to rise by an amount ΔV_{oc} during the pulse and then decay back to the initial level. As for the experimental situation fitting assumed an exponential dependence of ΔV_{oc} with time and a relaxation time extracted.

By varying the background e-h pair generation rate, the equivalent of raising or lowering the light intensity, it is possible to extract the relaxation time as a function of V_{oc}. The experimental results (Fig. 1a for unirradiated devices) suggest $\ln(\tau)= \ln(\tau_o)-\beta\, qV_{oc}/kT$, where theoretically $\beta=1$ but experimentally is often significantly less than one. Similar results were obtained from the simulations as shown by the △ symbols in Fig. 1b. When comparing the experimental data to the simulations we note there is qualitative matching between the two for biases between 0.25 and 0.45 volts, the primary region of interest. For lower V_{oc} values (i.e. where ΔV_{oc} becomes significant with respect to V_{oc} because one cannot obtain a large enough signal by maintaining $\Delta V_{oc}/ V_{oc}$ constant) the experimental results show a saturation effect which is not presently predicted in the simulations.

(a) (b)

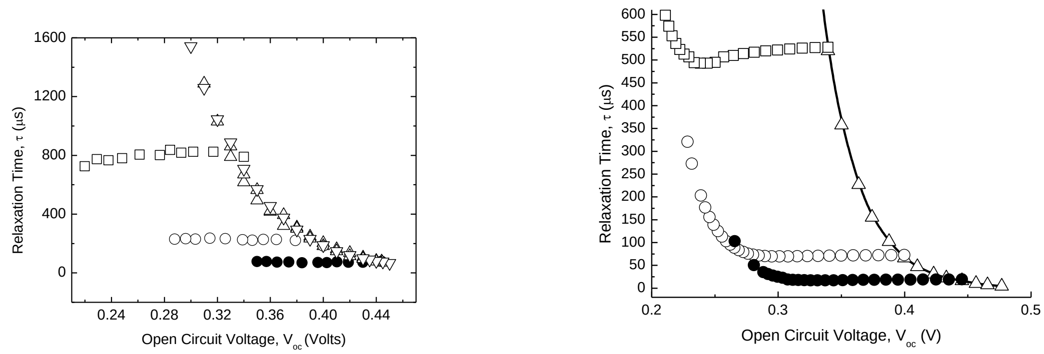

Figure 1: The experimental (a) and simulated (b) relaxation times as a function of the open circuit voltage. Triangles (△, ▽) are the results where V_{oc} is varied by changing the light level/generation rate. Squares, open circles, and solid circles are the results when V_{oc} is changed by irradiation(a)/adding trapped hole charge(b).

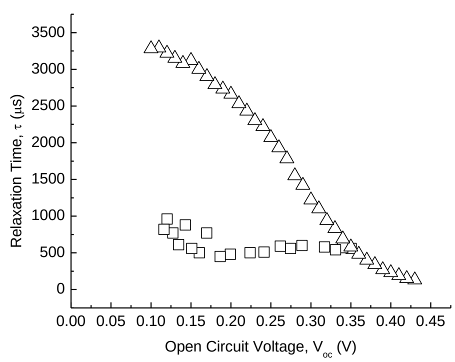

Figure 2: The experimental relaxation time as function of the open circuit voltage. The interpretation of the symbols is the same as in Fig. 1a.

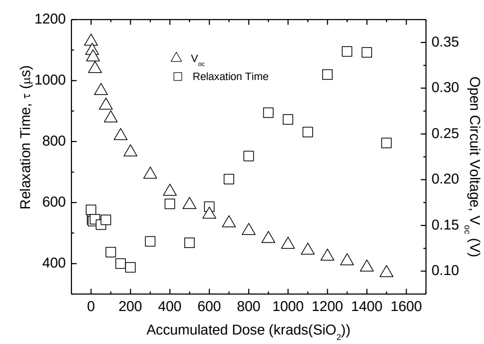

Figure 3: The relaxation time and a open circuit voltage as a function of the accumulated dose when the light level produces a V_{oc}=0.35 V background before irradiation.

As shown in Fig. 1a, the experiment shows an unusual effect when the device is irradiated with X-rays [1](illustrated using symbols □,○ and ●). The open circuit voltage decreases (corresponding to the effect of irradiation) without a variation in the relaxation time—we argue this to be due to charge trapping. To test the influence of charge using the modeling, a uniform trapped hole density was placed just inside the anode contact and the amount of charge was increased to see what effect this would have on the calculated V_{oc} and τ. For all three curves in Fig. 1b (□,○ and ● differing by variation of the background photo-induced e-h generation rates leading to different initial V_{oc} values) V_{oc} decreased without having sizeable effect on the relaxation time until an upswing occurred at lower V_{oc} levels (corresponding to higher charge). The theoretical upswing at higher charge levels/lower V_{oc} shown in Fig. 1b is not observed in the initial experiments (Fig. 1a).

New experiments have been carried out in order to observe whether or not the upswing in the relaxation time exists at higher accumulated X-ray doses. In the initial experiments, the samples were exposed to an accumulated x-ray dose of approximately 300 krad (SiO_2), while in the new experiments the samples were exposed to approximately 1.5 Mrad (SiO_2). It was necessary to limit the accumulated dose to 1.5 Mrads (SiO_2) since higher accumulated dose repeatedly caused catastrophic failures of the photo-cells. Preliminary experimental results (Fig. 2) show behavior similar to the theoretical results shown in Fig. 1b, where the relaxation time does indeed change with induced radiation and an upswing is apparent. As can be seen in Fig. 3, there is a clear dependence of relaxation time on accumulated dose at higher doses.

Summarizing:

1) Device modeling has been used to simulate the behavior of P3HT:PCBM based photo-cells.
2) Qualitative description of the V_{oc} and τ variation with incident light level is achieved.
3) Approximating the effects of irradiation by a build-up of charge near the anode contact leads to a satisfactory description of the experimentally observed behavior of V_{oc} and τ.

Work is continuing on understanding the complex role of the radiation induced charging and why it results in unusual behavior of photo-induced carrier lifetime. Further large accumulated dose radiation studies are being conducted for devices subjected to different background light levels (i.e. different initial V_{oc} values) analogous to those shown in Fig. 1a. The results of these measurements will be presented at the conference.

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