

Origin of Radiation-Induced Degradation in Polymer Solar Cells

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Polymer solar cells have been shown to degrade under X-rays. Here, in situ polymer photovoltaic performance and recombination lifetimes are measured and it is found that charge accumulation is the primary reason for degradation of solar cells. This is affected by the mixing ratio of donor and acceptor in the bulk heterojunction. Both a quantitative understanding and the physical model of the degradation mechanism are presented. Understanding of the degradation mechanism is extended in polymer donor–acceptor bulk heterojunction systems to propose a material combination for making radiation hard diodes that can find important application in fields ranging from memory arrays to organic X-ray detectors for medical imaging.

solar arrays that produce several kilowatts of power. The solar arrays presently in use can be classified into six categories 1) body-mounted arrays; 2) rigid panel planar arrays; 3) flexible panel array; 4) flexible roll-out arrays; 5) concentrator arrays; and 6) high temperature/intensity arrays.^[1] The design and technical requirements vary depending on the mission requirements.

In view of the diverse mission requirements there is currently a tremendous amount of research being directed towards a thin film alternative to traditional crystalline cells. Next generation thin-film

1. Introduction

Since the early work on the electron-induced vulcanization of rubber by Newton in 1929, numerous and extensive studies have been conducted on the effects of space radiation on polymers. Depending on the particular space application, materials are exposed to high vacuum, thermal cycling (commonly about ± 100 C), solar radiation including high energy UV, X-ray, particulate radiation (electrons, protons, heavy ions), and atomic oxygen. However the ability to tailor polymer properties using smart chemistry has yielded a plethora of products for use as multi-layer insulations and adhesives in space. Here we investigate the effect of X-rays on solar cells based on a new group of electrically conductive polymers for space applications.

Several new solar array structures have been developed over the past fifty years since the launch of Vanguard I satellite to improve the array specific power and reduce the stowed volume during launch. Unlike earlier satellites that produced only a few hundred Watts of power, satellites today require low-mass

technologies may involve a revolutionary change in materials to organic/polymer based devices. For space applications, the lightweight and flexibility of polymers are key advantages.^[2] It is these materials that will hold the key to inexpensive, easily deployed, large area, high mass-specific power arrays. This is due in part to the possibility of roll-to-roll processing using low-cost coating or spray deposition or direct-write/printing approaches to producing thin polymer film solar cells on inexpensive lightweight flexible substrates.^[3] Additionally, polymer solar cells (PSCs) take a minimum of storage space and can be inflated or unrolled for deployment.

There are two classes of epitaxial photovoltaics – space and terrestrial. Space cells typically have higher AM0 efficiencies (28%–30%) in production, but have a higher cost per watt. Their “thin-film” inorganic cousins have been developed using lower-cost processes, but have lower AM0 efficiencies (7%–9%) in production and are questionable for space applications. It is here that the versatility of polymer design in PSCs can provide a suitable solution. The thin multi-spectrum layers can be stacked to make tandem solar cells more efficient and cheaper using existing technology based on polymer solar cell and multi-junction technology used by NASA on Mars missions. The first layer has an optical response that absorbs one waveband; this is followed by another layer that absorbs in another waveband that is transmitted by the first layer. Finally there is a layer that absorbs in the infra-red spectrum, the whole now optimizing absorption of as much of the solar spectrum as possible. Current research is being spearheaded by USA's National Renewable Energy Laboratory and various academic universities and companies including Konarka Technologies, Inc., Solarmer Energy, Inc., Plextronics, Inc., and others.

The pace of research focusing on organic photovoltaics (OPVs) has increased significantly over the past few years. The power conversion efficiencies (PCE) has almost been doubled

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DOI: 10.1002/adfm.201000374

in the last 4–5 years and now 8% (device area = 0.1 cm²) under AM1.5 illumination has been achieved.^[4,5] Although this is far less than what has been observed for inorganic solar cells, it is worthwhile to start looking into the possibility of potential application in space. From the point view of space application, a good benchmark for OPV is a PCE of 12%–15% to compete with other technologies, which is also aligned with the prediction of OPV efficiency limit.^[6] This is not too futuristic at the research level as recent progress in design of new materials (with enhanced absorption in the IR region) and progress in tandem architecture solar cell shows. But before such ideas become a reality and turn to mass production, one important consideration is whether or not such organic cells would be adequately radiation tolerant. We have previously observed^[7] a degradation and recovery phenomenon in PSCs based on a typical material blend of regio-regular poly (3-hexyl thiophene) (RR-P3HT) and [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM). We investigate here in detail the effect of radiation on degradation of PSCs and demonstrate that charge accumulation at the interface is the prominent degradation reason for such devices as a result of X-ray radiation. However, we also propose and demonstrate a material combination to make radiation hard diodes for use in future PSC design.

There may be various factors influencing the degradation in PSCs. In this manuscript, to understand the degradation effect on polymer film and the physics behind it in detail, we varied the w/w ratio of P3HT:PCBM (donor:acceptor) systematically. We first show the effect of radiation on photovoltaic performance and discuss the effect of radiation on various parameters. It is expected that radiation will damage the polymer structure but that will not explain the recovery phenomenon as reported by us earlier. Here we provide evidence to support this hypothesis. Measurement of diode properties of the device revealed important information about built-in-potentials and suggestive mechanism based on p-n junction theory. Coupled with carrier lifetime measurements and other experimental support, we provide both a physical model and a quantitative reasoning to explain our observations.

2. Results and Discussion

PSCs were made at UCLA as given elsewhere.^[8] For the irradiation studies, the solar cells were encapsulated using glass and epoxy and shipped to the Air Force Research Laboratory (AFRL) Kirtland AFB. The performance of pristine devices as measured at UCLA before shipping to AFRL is summarized in Table 1 in the Supporting Information. These efficiencies are among state of the art reported in literature for the model system under consideration. Control samples, not subjected to radiation but stored at AFRL and shipped back to UCLA in exactly the same conditions (as the ones subjected to radiation), showed less than 5% change in efficiencies.

2.1. Photovoltaic Device Performance

Current–voltage (I – V) measurements under light before and after radiation (0.3 Mrad (SiO₂)) are shown in **Figure 1**.

Samples with high PCBM ratio show significant decrease in open-circuit voltage (V_{oc} ; ~0.06 V for poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) = 1:2) while there is no change for P3HT:PCBM = 10:1. As PCBM concentration in the blend film increases the V_{oc} of the device becomes more susceptible to radiation. In situ monitoring of V_{oc} , shown in **Figure 1d**, confirmed this trend. For high concentrations of PCBM, e.g. P3HT:PCBM = 1:1, there is a 30% drop in V_{oc} under 0.3 Mrad (SiO₂) radiation. But for low concentrations, i.e., 10:1 ratio, the change is around 1%, which is within the margin of experimental error. Another significant difference observed is the slope of the I – V curve at forward bias (indicative of series resistance under light). This behavior is contrary to what is seen for V_{oc} . Low PCBM ratios show more significant changes in injection currents as compared to higher ratios. In fact, for P3HT:PCBM = 1:2 the injection current for device subjected to radiation shows no difference with the pristine device beyond 1 V, whereas there is a significant change in the I – V slope for 10:1 device. Another important figure of merit is the Fill factor that has a similar behavior as injection currents (series resistance under light). Increasing the PCBM ratios makes the device more resistant to changes in fill factor. High fill factors have been attributed to balance of mobility^[9] of the two carriers in the device. Ideal diodes (with diode ideality factor (n) = 1) should have fill factors up to 86%. Any decrease in fill factor is also manifested in reduction in n . We will analyze the two reasons in more detail later.

We had reported earlier that at a dose rate of 300 Krad SiO₂ there is a less than 1% loss in the transmission of the polymer film. No change in film absorption or crystallinity was seen. Similar results were obtained for all the w/w ratios of P3HT:PCBM in the present experiments. Discoloration/bleaching in classical polymer upon irradiation has been attributed to formation of conjugated bonds or to trapped free radicals/ions in the polymer bulk. Experimental measurements^[10] done earlier on the radiation-induced radical yields in different polymers (at a dose rate of 0.02 to 1 Mrad s⁻¹) demonstrated that the radical yield decreases with increasing conjugation in a molecule. We conjecture that the high delocalization in electrically conducting polymer of P3HT also renders it less susceptible to such processes. Hence, structural change in polymer material itself is unlikely.

To explore in detail the role played by radiation on the degradation rate, the dose rate was varied for P3HT:PCBM = 1:1 sample. **Figure 2a** shows the effect of radiation on normalized short circuit current (J_{sc}). The loss in J_{sc} is independent of the dose rate. Further **Figure 2b** shows that the amount of loss in J_{sc} is the same for different P3HT:PCBM weight ratios. This further suggests that there are no structural changes taking place in the polymer film that should be visible in the films with different blend ratio and different dose rates.

To investigate if the change in fill factor was due to changes in mobility of the film, we performed light intensity dependent J_{sc} measurements. For a typical polymer/fullerene based solar cell, J_{sc} does not scale exactly linearly with light intensity (I).^[11,12] Instead, a power law relationship is found given by $J_{sc} \sim I^\alpha$. The deviation of α from unity is attributed to the build-up

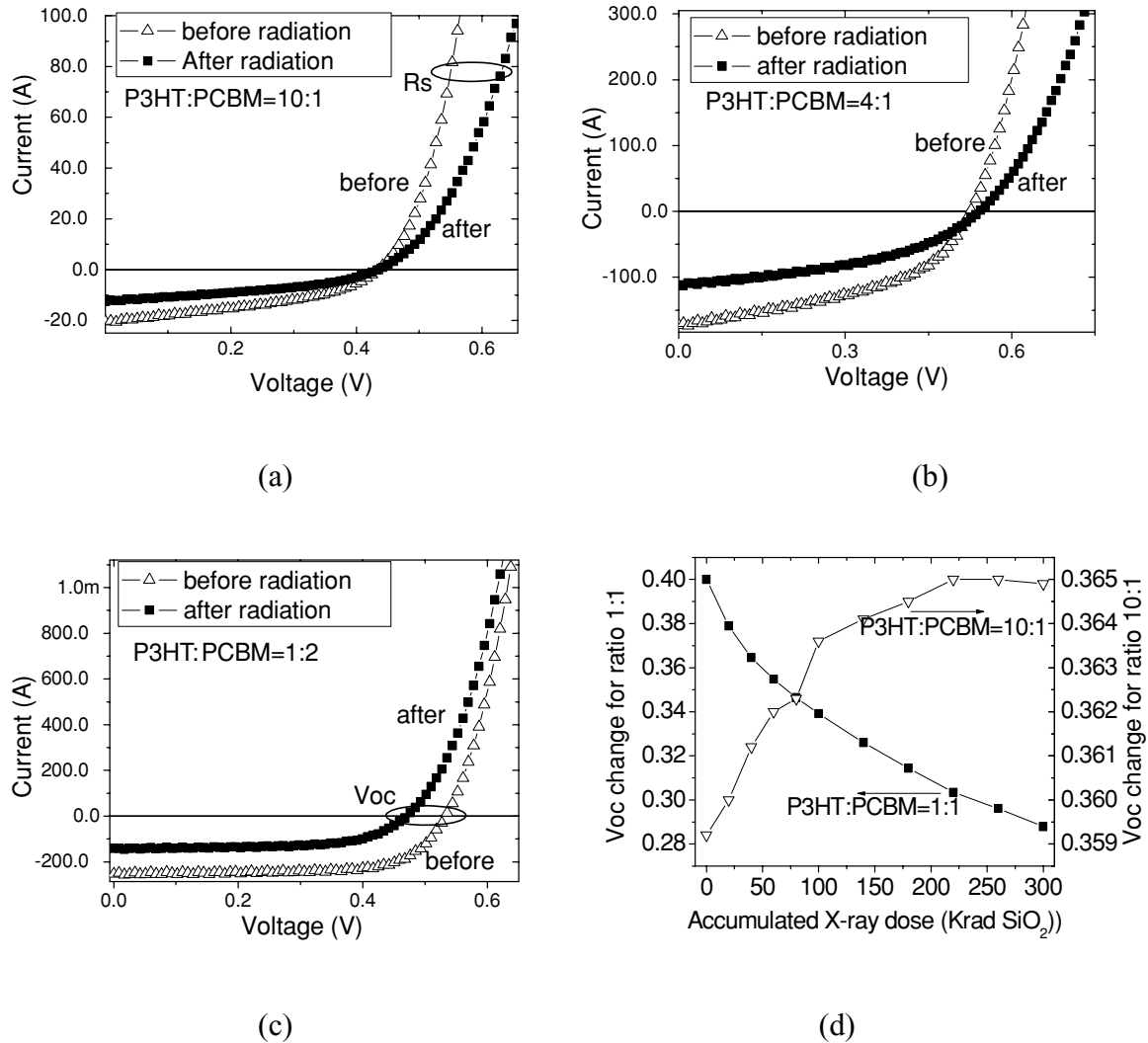


Figure 1. Photovoltaic performance of different w/w ratio P3HT:PCBM based solar cells. The Figure shows I - V curves obtained before (open triangle) and after (solid square) 0.3 Mrad (SiO_2) X-ray radiation for P3HT:PCBM corresponding respectively to a) 10:1, b) 4:1, and c) 1:2. d) In situ measurements of V_{oc} for P3HT:PCBM = 10:1 (open triangle) and 1:1 (solid square) when subjected to radiation.

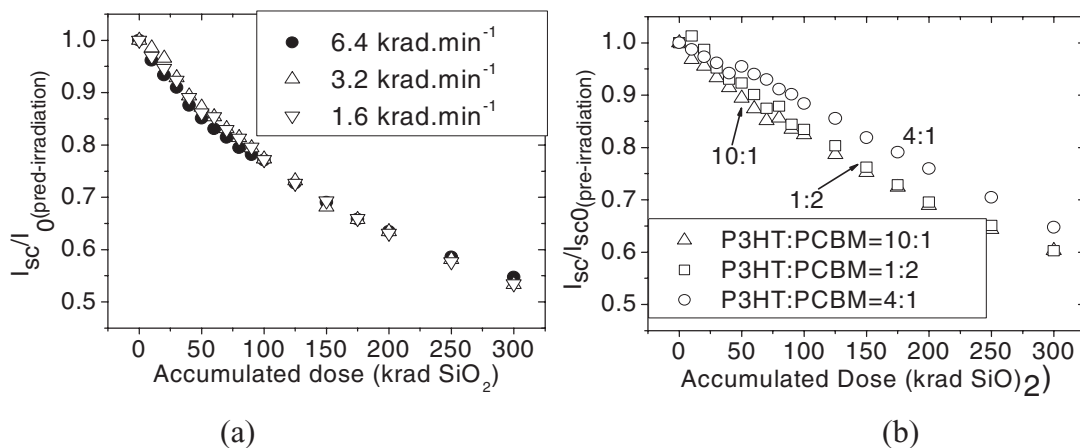


Figure 2. Effect of X-ray dose on normalized short-circuit current (I_{sc}) a) for different dose rate for P3HT:PCBM = 1:1 and b) for different w/w P3HT:PCBM ratios at a fixed rate of 6.4 krad min⁻¹.

of space charge in the device.^[13] The occurrence of space-charge stems from the difference in charge carrier mobility of electrons and holes. To explore this we measured the light intensity dependence of J_{sc} for devices exposed to progressively increasing amounts of radiation (see Supporting Information for figure). No significant changes were seen in the values of α for all the devices under study. This suggests that the reason for change in fill factor should correlate to the ideality factor of the devices. This necessitates an investigation of the $I-V$ curves under dark.

2.2. Diode Analysis

To understand the diode behavior of the cells the $I-V$ curves under dark were analyzed. The $I-V$ curves measured under dark are extremely important for the extraction of diode parameter, which in turn explains the loss mechanism based on the p-n junction theory and the circuit model for solar cells.^[14] Use of dark $I-V$ curves separates the effect of photo-generated current. **Figure 3** shows the dark $I-V$ curves for different ratios of P3HT:PCBM before and after radiation. It can be seen that diodes with smaller amount of PCBM in the pristine blend had a bigger loss in injection currents as compared to diodes with higher PCBM composition. This is in agreement to the trend seen for $I-V$ curves under light as seen in Figure 1. Dark currents can give useful information about the built-in-potential in the device by looking at the injection barrier (the turn-on-region). There is a larger change in injection barrier for higher PCBM ratios as compared to lower PCBM ratios ($\sim 0.8V$ for P3HT:PCBM = 1:2 as compared to almost zero for P3HT:PCBM = 10:1). Interestingly, this is consistent with the $I-V$ measurements under light (Figure 1). This suggests that change in V_{oc} seems to arise from a change in the built-in potential of the devices, which should be a direct result of change in electric field/energy alignment inside the device. It rules out the effect of any kind of photo-generated carriers. Devices with higher PCBM ratios have a significant change in built-in-potential when subjected to radiation; in contrast to what is seen for low PCBM ratio devices. To get a deeper understanding of this, analysis of dark $I-V$ curves obtained in situ during radiation is needed.

In order to extract the parameters in the most accurate and reliable way, we developed a new software system that differs from the conventional method. The analysis of dark $I-V$ curves was based on a commonly accepted one-diode circuit model.^[15] While the conventional methods normally fits the dark $I-V$ curves and get the parameters of the p-n junction and series (R_s)/shunt (R_{sh}) resistance directly, we first calculate the R_s based on the comparison between dark and light $I-V$ curves.^[16,17] According to theoretical as well as experimental studies,^[18] the R_s extracted this way is more accurate compared to the one obtained by fitting the slope at the high voltage end, since it considers the different current flow patterns under dark and under illumination, and the multi-dimensional effect of the R_s . The diode parameters and shunt resistance were calculated from curve fittings. The fitting method we used combined both the least square error searching (higher numerical accuracy) and slope fitting (better physical meaning presentation).

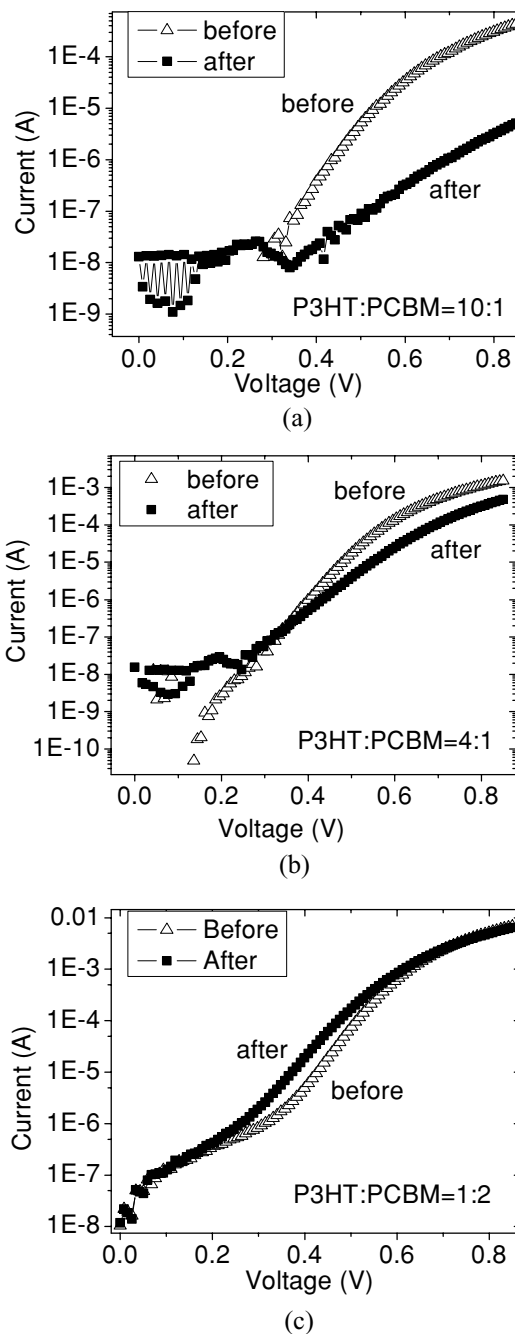


Figure 3. $I-V$ curves under dark demonstrating the diode behavior of different w/w ratio P3HT:PCBM based solar cells. The Figure shows $I-V$ curves obtained before (open triangle) and after (solid square) 0.3 Mrad (SiO_2) X-ray radiation for P3HT:PCBM corresponding respectively to a) 10:1, b) 4:1, and c) 1:2.

The error between the fitting curves and the actual $I-V$ data was maintained below 5% even while the measurement data at low voltage range is very noisy due to the special measurement condition.

Figure 4 shows the behavior of R_s , n , and dark saturation currents (I_0) as a function of time when subjected to 0.3 Mrad (SiO_2) radiations. It was confirmed that with decrease in PCBM

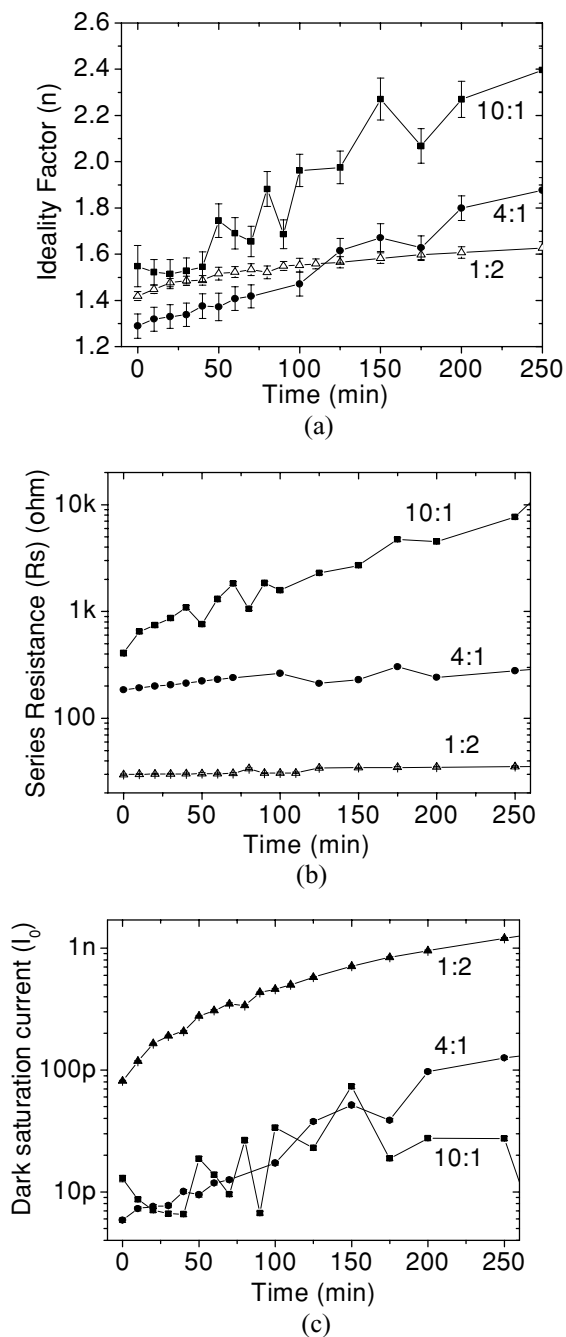


Figure 4. Diode parameters as a function of degradation time (at a dose rate of $6.4 \text{ Krad min}^{-1}$) extracted using the novel modeling method for different w/w ratio P3HT:PCBM based solar cells. The parameters extracted are a) ideality factor, n , b) series resistance, R_s , and c) dark saturation current, I_0 . a) Error bars calculated using least square fitting marked on it.

ratio the series resistance of the diode becomes more sensitive to radiation. Although the R_{sh} of the devices showed no clear trend with radiation time, the dark saturation currents became less sensitive to radiation on decreasing the PCBM (donor) ratios. With increasing PCBM concentrations the ideality factors became less sensitive to radiation making the diodes more

stable to radiation. This is also consistent with trend for fill factors we observed earlier from I - V curves under illumination.

2.3. Quantitative Discussion of V_{oc} Change

Although there is lack of complete understanding as to the origins of V_{oc} in PSCs, recently Vandewal et al.^[19] demonstrated that charge-transfer absorption and emission are related to each other and to V_{oc} in accordance with the assumptions of the detailed balance and quasi-equilibrium theory. Their results show the validity of the often used expression for V_{oc} , where K is the Boltzmann constant, T is the temperature and q is the elementary charge:

$$V_{oc} = \frac{nKT}{q} \ln \left(\frac{I_{sc}}{I_0} + 1 \right) \quad (1)$$

Figure 2b shows that for a particular radiation dose the fall in normalized J_{sc} is almost independent of the ratio of P3HT:PCBM. Figure 4c shows that the rise in I_0 after radiation will be larger for higher PCBM concentrations (for P3HT:PCBM = 1:2 I_0 rises by approximately 2 orders of magnitude) whilst the change in n will be larger for smaller PCBM concentrations (notice y-axis in Figure 4a for n is on the linear scale while that for I_0 in Figure 4c is on the log scale). It is this increase of I_0 by approximately a factor of two that is responsible for the V_{oc} decrease). Inserting the values in the V_{oc} equation predicts the trend in V_{oc} as observed experimentally earlier in Figure 1. Hence, the trend in V_{oc} can be explained easily from a purely mathematical point of view. Still a physical picture is lacking and we try to explain it here.

Following the photovoltaic (PV) theory,^[20] the physics of a solar cell, namely the separation of the photo-generated charges, lies in two parameters, I_0 and n . The saturation current density I_0 determines the absolute size of the diode current around zero bias, while the exponential behavior is dominated by the diode's ideality factor n . A microscopic model of I_0 and n in bulk heterojunction PSC is missing and hence we follow a qualitative discussion to understand the findings. For bulk heterojunction devices, I_0 represents the minority charge density in the vicinity of the barrier, which is at the donor/acceptor interface for bulk heterojunction solar cells. We do not expect any change in morphology of the films here. Increase of I_0 can however be explained by increased doping or a source of additional minority carriers created near the interface.

As suggested by Waldauf,^[21] the ideality factor reflects the "opening behavior" of the diode with the applied voltage with respect to its recombination behavior. Recombination will take place at interfaces where carriers with opposite charges can meet. In traditional diode theories, an ideality factor close to one suggests that the dominating recombination is at the junction, while a value close to two would indicate a more bulk-wise recombination. Some studies on thin film solar cell devices also proposed that a higher ideality factor could be related to the tunneling effect. Therefore, a change in the ideality factor could be an evidence for a different type of mechanism for the recombination loss, which is in general unfavorable. The decreased sensitivity to radiation might be suggesting that the device

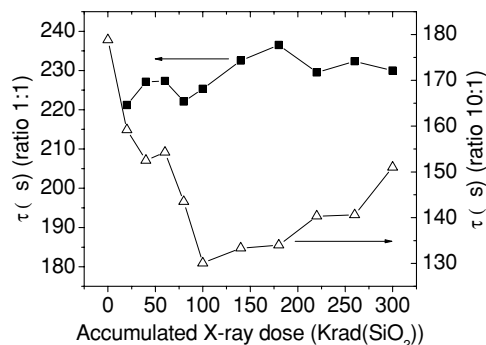


Figure 5. Carrier lifetime (τ) measured as a function of accumulated X-ray dose for solar cells based on two different P3HT:PCBM w/w ratio corresponding to 10:1 (open triangle) and 1:1 (solid square).

(with higher PCBM) is more reliable in limiting the recombination sources.

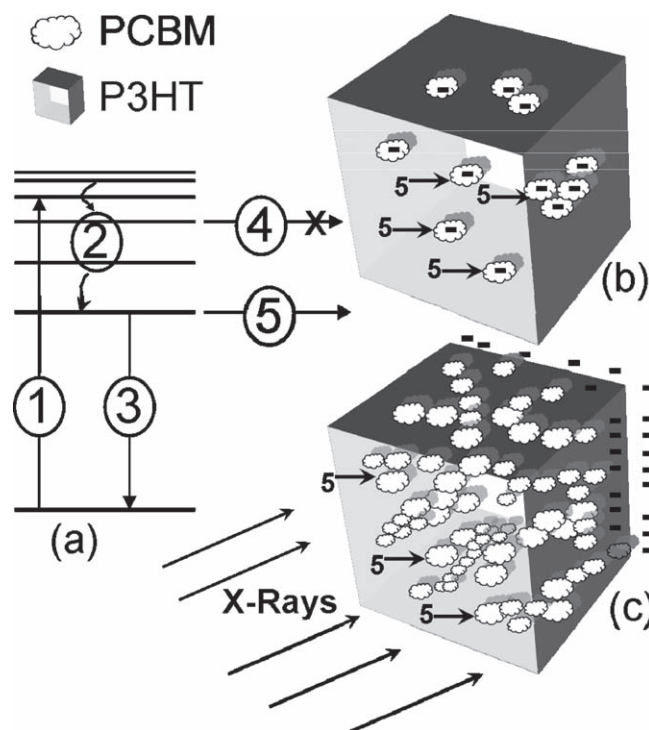
2.4. Carrier Lifetime Analysis

To study the recombination mechanism, we measured the recombination lifetime of carriers under continuously illuminated open-circuit conditions using transient photo voltage (TPV) measurements as reported by Schuttler et al.^[22] for P3HT:PCBM solar cells. Fitting the fall of photovoltage to first order rate gives the recombination lifetime of carriers. **Figure 5** shows the change in the measured recombination lifetime of carriers as a function of radiation time for a fixed light intensity. P3HT:PCBM = 1:1 shows no change in carrier recombination lifetimes. This is surprising since lifetime is normally a function of V_{oc} since one would expect that increase in light intensity (causing an increase in V_{oc}) will increase the number of photo-generated electron-hole pairs, thus causing a decrease in lifetime of carriers (see Supporting Information for figure). If the V_{oc} drop with radiation (Figure 1) is associated with a smaller number of carriers generated, an increase in lifetime was expected. Lifetime measurements performed on 1:1 ratio under different open circuit conditions (different light intensity illumination to generate different starting V_{oc}) consistently showed no change in lifetime (see Supporting Information). This indicates that although the V_{oc} falls with radiation, it is not due to a smaller number of carriers generated. This is consistent with our earlier prediction that probably change in the built in potential of the device is responsible for change in V_{oc} . For devices with low PCBM compositions, a faster recombination of carriers after radiation is seen. Physically this can be explained by the fact that there is no good interpenetrating donor/acceptor (D/A) network available for the transport of both carriers and hence a higher degree of geminate recombination. The change in lifetime is approximately of the same order as seen for pristine devices when varying light intensity (and hence open circuit voltage) (see Supporting Information). The data is clear evidence that no electronic/structural defects are created in the polymer film. This strongly suggests that the bulk of the polymer film is not changing. Our earlier assumption regarding charge accumulation is the only possible answer. This is not surprising since

recently Kawano et al.^[23] showed using thermally stimulated current technique that when P3HT:PCBM PSCs are subjected to 1 sun radiation (100 mW cm^{-2} electromagnetic radiation), charge accumulation is a severe problem. Results from tests conducted under identical conditions on classical polymers have suggested that, regardless of the type of radiation used, "equal amounts of energy absorbed produced equal changes in the properties of the polymers under identical conditions."^[24]

3. Physical Model and Explanation

Recently Raval et al.^[25] showed that when P3HT transistors are subjected to high energy ^{60}Co radiation (1 Krad min^{-1}), the thiophene molecule in the chain of this polymer goes to a polaron state and gets stabilized to a bipolaron and a neutral state. Based on the evidence we have we conjecture the following physical picture as surmised in **Scheme 1** to explain the effect of radiation. Organic molecules may be excited to different levels during X-ray radiation beginning with the first excited level and extending up to levels immediately adjacent to the ionization boundary. However molecules from higher excited levels (S_n , $n > 1$) pass to the first excited state (S_1) in the picosecond timescale. This is a radiation-less process, transition 2, due to the so-called internal conversion. Transition 3 from the first excited



Scheme 1. Physical model of the effect of X-rays on polymer solar cells. a) Scheme of electronic levels and transitions in a molecule: 1) excitation, 2) internal deactivation, 3) transition to the ground state, 4) dissociation from higher excited states, 5) dissociation from the first excited level. b) A low PCBM % bulk P3HT:PCBM film showing isolated PCBM domains. c) A high PCBM % bulk P3HT:PCBM film showing well connected PCBM network resulting in good charge transport.

level to the ground state is usually accompanied by the emission of a quantum of light and occurs within no less than 10^{-8} s to 10^{-9} s. As transition 2 is a very fast process, it can be suggested that the creation of charged species from higher excited electronic levels would be improbable and, consequently, the radiation-induced yield would depend essentially on the probability of dissociation from the S_1 (transition 5). P3HT:PCBM forms a very good donor acceptor system energetically. PCBM due to its cage structure is one of the best known electrons accepting organic material. At a high concentration of PCBM, the PCBM forms a very good network within the blend film. An efficient charge transfer from P3HT to PCBM from the S_1 level is possible that are then transported at the interface. This creates a gradual build up of charges at the polymer active film and the electrode interface. This results in a “reverse” electric field to the built in potential, in turn affecting the final V_{oc} . But when the PCBM network is scant as in P3HT:PCBM = 10:1 (which in effect is almost a pure P3HT) the charges in the P3HT have no path to travel towards the interface resulting in a study recombination of the type 3. Constant radiation will cause dynamic charge equilibrium within the bulk film. This charge resides with the bulk of the film. However when adequate reverse electric field is applied these charges can be extracted as minority carriers (demonstrated by an increase in dark saturation current I_0). A similar concept of radiation induced conductivity (in dark) in polymers has been known since as long as experiments done by Fowler and Farmer.^[26,27] It is known that it can be highly localized and transient. The presence of trapped electrons in γ -irradiated conducting polymers like polyethylene (PE) in the dark at 77 K was demonstrated by Keyser et al.^[28,29] They further showed that higher crystallinity (85%–95%) high density PE has more charges than low-density PE (50% crystallization). This clearly explains the dark I - V curves. Charge accumulation at the interface in 1:2 case will cause a decrease in injection barrier but once injected the charges do not see any additional resistance to movement and hence the R_s is unaffected. While for cases corresponding to low PCBM; in the bulk there is a dynamic amount of charge carriers (mainly electrons) activated by irradiation that acts as a “speed-brake” to injected charge movement (however no change in potential barrier for injection) causing the R_s to increase. This is also supported by the recombination lifetimes as observed for the two extreme cases.

4. Conclusions

We demonstrated here that no structural changes take place in the polymer solar cells when subjected to high radiation doses. However, charge accumulation can be a severe problem resulting in temporary degradation in solar cell performance. However, we believe it can be mitigated by engineering smart polymer-electrode interfaces. The research is still in its infancy and there is a lot that can be done. We provide reason for the seen degradation of PSCs from both a quantitative as well as physical point of view. Interestingly, we also found that diodes (based on the donor-acceptor kind of system) are more stable to radiation when the amount of acceptor is higher. This allows construction of novel radiation hard organic diodes that can be

used in the so called “1T1R” structure suggested by semiconductor industry to avoid “cross talk” between word line and bit line, having a huge impact in integration of polymer memory devices into actual all organic electrical circuit for space applications. Another potential impact of this paper can be for improved organic X-ray detectors. X-rays are used widely in the field of medicine, dentistry and security to provide a non-invasive probe of internal structure. If organic semiconductor devices are to provide a genuinely useful method of imaging X-rays, such systems need to have a high level of radiation stability. In fact there have already been some reports trying to fabricate a detector based on an organic photovoltaic device or optical sensor that is coupled to a scintillator.^[30,31]

To the best knowledge of the authors, the reported measurements are one of the first in-depth studies of the effect of X-ray radiation on polymer solar cells for space applications. The results are far reaching and provide an impetus to study the effect of the unforgiving environment in outer space on PSCs. Solar cells based on highly conjugated electrically conducting polymers seem to be inherently stable to high radiation doses. Coupled with the relaxation effect they seem good candidates for such applications depending on mission critical requirements. To prevent color-centre formation inorganic solar cells require a cover glass of 50–500 μ m thickness, usually borosilicate glass containing a few percent CeO_2 . Our results open up new avenues surpassing such stringent requirements and hence, give more flexibility with cell packaging and installation in space.

5. Experimental Section

Solar Cell Fabrication: RR-P3HT and PCBM were separately dissolved in 1, 2-dichlorobenzene, then blended together in different wt/wt ratio to form a 2 wt% solution. The four (w/w) ratios of P3HT: PCBM were 10:1, 4:1, 1:1 and 1:2. The polymer solar cells were made using a slow growth approach as described elsewhere.^[7] The device area was 0.12 cm^2 . Electrical contacts to the photocell structures were made via indium pads to the Al cathode and ITO anodes. I - V measurements at UCLA were performed under a nitrogen atmosphere using a Keithley 2400 source meter unit. The photocurrent was measured under an AM 1.5G illumination at 100 mW cm^{-2} using an Oriel 96000 150 W solar simulator source. The light intensity was determined using a silicon detector (with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL).

Radiation Tests at AFRL: The devices were installed on the chuck of an ARACOR 4100 X-ray system (W target) equipped with W probes to contact the In pads on the cell. During irradiation, the anode and cathode were always short circuited to avoid the risk of charge buildup due to stray fields. Light from an un-calibrated 150 W halogen lamp was introduced into the ARACOR box using a silica fiber light guide and side coupled into the photocell stack.

Transient Photovoltage Measurements: Additional, light could be introduced into the ARACOR system from a pulsed Xenon arc lamp (General Radio 1531AB Strobotac operating at 650Hz with 2 μ s optical pulse duration) in parallel with the continuous halogen source. In this way the continuous light could be used to optically “bias” the photocell to some open circuit voltage level, V_{oc} and a pulsed light level “modulation” superimposed. V_{oc} was measured directly using a Keithley high input impedance voltmeter; the values were confirmed for a few specific points by measuring complete current/voltage curves using an HP 4155 and determining the voltage for which the cell current became zero. Typically the ΔV_{oc} induced by the pulsed source was $\sim 2 \text{ mV}$ peak whereas the V_{oc}

values studied were substantially larger and ranged from 0.29 V to 0.5 V. Following the light pulse the photocell open circuit voltage decayed with time due to excess carrier relaxation and this was measured using a Tektronix model TDS 640 digitizing oscilloscope.

Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

Acknowledgements

A. Kumar, B. Lei and Prof. Y. Yang would like to thank Dr. Ziruo Hong and Li-Min Chen for fruitful scientific discussions. This work is supported by the Air Force Office of Scientific Research (grant # FA9550-09-1-0610, Program manager-Dr. Charles Lee).

Received: February 25, 2010
Published online: June 25, 2010

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