



Ionizing radiation exposure reveals instability of purified domains in polymer/fullerene solar cells

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ARTICLE INFO

Keywords:

Ionizing radiation
Solar cells
Morphology
Aggregates

ABSTRACT

Solar cells based on conjugated polymer and fullerene blends exhibit morphology-dependent stability towards ionizing radiation exposure. Blend thin film solar cells of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₀-butyric acid methyl ester (PCBM) were irradiated up to 1 Mrad with X-rays (10–60 KeV) and investigated with resonance Raman and photocurrent/photovoltage modulation spectroscopy and imaging. Bulk blend morphological characteristics were pre-selected by controlling film processing conditions (i.e., solvent and thermal annealing). As-cast P3HT/PCBM devices with a large fraction of a well-mixed phase display improvements in performance upon application of post-irradiation annealing treatments. On the other hand, devices annealed prior to irradiation showed irreversible performance degradation that could not be recovered following annealing treatments after exposure. Resonance Raman spectroscopy and imaging following irradiation up to 1 Mrad reveals virtually no changes in the P3HT structural and packing integrity for both types of devices. Intensity modulated photocurrent/photovoltage spectroscopy measurements indicate that radiation-induced performance degradation is concentrated in the vicinity of device contacts, evident from large alterations in charge extraction kinetics. We propose that charge transfer from the aluminum cathode leads to formation of a space charge zone which becomes more pronounced in devices with greater phase purification (i.e., larger PCBM crystallites in the vicinity of the cathode). Importantly, well-mixed P3HT/PCBM regions, which are more plentiful in as-cast devices, appear to mitigate radiation-induced performance degradation since application of post-irradiation annealing treatments restores device performances to pristine levels. Our results suggest that greater morphological stability, such as polymer/fullerene systems forming co-crystals, is key for suppressing performance losses from ionizing radiation exposure.

1. Introduction

Solar cells based on blend thin films of conjugated polymers and soluble fullerene derivatives have seen significant improvements in performance and stability in recent years [1,2]. Device packaging technology, in particular, has extended lifetimes by excluding oxygen and moisture leading to photodegradation usually mediated by low-lying triplet or charged defect states [3,4]. Although polymeric solar cells have tremendous advantages for terrestrial applications mostly in terms of cost and ease of processing, there is now increasing interest for employing these devices to power small space vehicles (e.g., cube satellites) [5–9]. Unlike conventional inorganic solar cells, the intrinsic lightweight and flexibility of polymer solar cells makes them attractive as power sources despite their intrinsically lower power conversion efficiencies. However, it is not yet clear if design rules developed for terrestrial applications (i.e., AM1.5 conditions) will directly translate

into acceptable performance and stability for space applications. For example, strategies for harvesting a greater fraction of NIR photons have extended polymer/fullerene solar cell power conversion efficiencies (PCE) beyond 10% [10]. The greater flux of UV–vis photons under AM0 conditions encountered in low Earth orbits offers new opportunities for harvesting these photons, in addition to NIR photons. Before polymer solar cells can be introduced as low-cost alternative to space vehicle power sources, a detailed knowledge of stability in space environments is first required. In particular, repeated exposure to high-energy ionizing photons, energetic protons and electrons as well as large temperature fluctuations may result in irreversible chemical and morphological changes that degrade performance to unacceptable levels [11]. In this paper, we investigate the stability of polymer solar cells exposed to large levels of ionizing X-ray radiation (up to 1 Mrad) and determine the predisposition of specific morphological features and regions of device architectures to degradation.

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<http://dx.doi.org/10.1016/j.solmat.2016.10.017>

Received 18 July 2016; Received in revised form 13 September 2016; Accepted 6 October 2016

Available online 24 October 2016

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Thin film solar cells of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (1:1 w/w) blends are excellent benchmarks for understanding ionizing radiation effects on organic active layers because of their well-characterized structure-function relationships. The semi-crystalline nature of both components also facilitates spectroscopic studies due to the distinct physical and electronic properties of these ordered regions. Furthermore, correlations between morphology and performance and changes with ionizing radiation exposure are possible owing to the unique spectroscopic signatures of morphological zones with different compositions characteristics. Earlier studies on P3HT/PCBM devices found significant performance degradation upon X-ray irradiation, which was proposed to originate degraded charge transport due to increased levels of radicals [12]. Kumar et al. investigated P3HT/PCBM blend solar cells with varying loadings using standard device characterization techniques (i.e., current-voltage measurements) for radiation dosages up to 300 Krad and observed different degradation rates. Street et al. further investigated radiation effects on P3HT/PCBM and other solar cells over a broad spectral range (i.e., X-ray up to NIR wavelengths) and proposed that hydrogen abstraction on the solubilizing alkyl side chains of P3HT as the primary degradation mechanism [9]. These authors further noted this mechanism is reversible based on restoration of pristine device performance levels by post-irradiation annealing treatments. However, it is not yet clear how the heterogeneous morphological landscape of polymer/fullerene blends and the presence of morphology-dependent polymorphs influences radiation-induced degradation mechanisms and their efficacies. For example, the blend composition varies greatly over the entire material active layer, which should modulate degradation pathways and kinetics. Because morphological characteristics also change with temperature and time, extracting reliable mechanistic details of degradation processes can often be fraught with many pitfalls. In order to both understand and possibly mitigate chemical and morphological changes in response to ionizing radiation exposure, morphology-sensitive physical probes are required to correlate the blend structure and composition to performance characteristics.

The primary motivation for our present study is to ascertain the response and stability of blend morphologies and phase purity to ionizing radiation exposure. In particular, we are interested in characterizing the response of specific P3HT polymorphs (i.e., aggregates and amorphous chains) as well as local blend composition (i.e., PCBM content) to varying dosages of X-rays. The miscibility characteristics of PCBM in each of these forms (i.e., well-mixed amorphous P3HT/PCBM regions and complete exclusion from π -stacked P3HT aggregates) will be further exploited to understand how morphological features are affected by radiation exposure. Because X-rays are not resonant with valence electronic transitions involved in photovoltaic processes (i.e., charge generation and transport), it should be possible to interrogate device performance changes while the cell is still operational. It is also noteworthy that recent studies have found evidence of cross-linking in P3HT thin films in addition to alterations in PCBM crystallinity possibly from degradation of the C₆₀ cage from prolonged X-ray exposure [13,14]. Ionization of core electrons is possible although cross-sections are expected to be small at the photon energies used to expose devices.

In the following, we attempt to bridge the gap in understanding of possible degradation pathways between pristine and blend solar cell materials, which are expected to significantly different due to the miscibility characteristics in various P3HT polymorphs. Both conventional (e.g., current density-voltage (J-V) measurements) as well as more specialized experimental techniques, such as intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS), to assess the response of carrier extraction and recombination kinetics to radiation exposure. These frequency domain measurements are particularly useful for resolving interfacial versus bulk charge recombination processes, which have different intrinsic kinetics and possibly different

degradation mechanisms from ionizing radiation exposure. Resonance Raman spectroscopy and imaging are next used to identify and map the local composition of the P3HT/PCBM blend within the device active layer that can be directly correlated to device performance metrics. This technique is particularly effective for discerning blend morphology and stability by taking advantage of strong resonance enhancements of the P3HT Raman scattering cross-sections that also reveals local PCBM content due to its miscibility characteristics in different polymer conformers [15–17].

2. Materials and methods

2.1. Device fabrication and characterization

Model P3HT/PCBM solar cell devices were fabricated on glass coverslips (VWR) coated with indium-tin oxide (ITO). Substrates were rigorously cleaned by sonication in trichloroethylene, acetone and methanol followed by UV-ozone treatment for ~20 min. A hole-transport layer of PEDOT: PSS (Sigma Aldrich, 3–4% high conductivity grade) was spin coated on cleaned substrates (2000 rpm for 2 min) then heated at 120 °C on a hot plate for 1 h to drive off residual moisture. MoO₃ (~10 nm) was also used as a hole transport layer on select devices to verify the radiation stability of the PEDOT: PSS/ITO contact.

Chlorobenzene solutions (10 mg/mL) of P3HT (Sigma Aldrich) and PCBM (Sigma Aldrich) were filtered using a 2 μ m pore size filter to remove undissolved material. P3HT and PCBM solutions were blended (1:1 w/w) and heated at 80 °C on a hot plate for 4 h and stirred. Blend solutions were spin-cast onto ITO coated substrates (600 rpm) inside a nitrogen circulating glovebox. P3HT/PCBM thin film thicknesses were ~110 nm measured by profilometry. Aluminum contacts (25 mm²) were deposited by thermal deposition at a base pressure of $\sim 2 \times 10^{-7}$ Torr.

Completed P3HT/PCBM devices were thermally annealed (110 °C, 6 min) to optimize blend morphologies prior to irradiation. In some cases, as-cast devices were investigated to compare the effect of processing conditions. A total of 36 annealed and 22 as-cast devices were examined, including irradiated and control devices. Several annealed and as-cast devices were subjected to post-irradiation annealing treatments using the same conditions above to determine recoverability of performance metrics following X-ray irradiation. Devices were stored in a dry nitrogen circulating glovebox to prevent unwanted degradation until use. Electrical characterization measurements (i.e., open-circuit voltage, V_{OC}, short-circuit current densities, J_{SC}, fill factors (FF), and power conversion efficiencies, PCE) were performed in the glovebox under AM1.5 conditions using a Keithley 2400 source-measure unit and calibrated AM1.5 solar simulator (Oriel).

2.2. Instrumentation

Irradiation of P3HT/PCBM solar cells was performed at the ARACOR X-ray source located at the Air Force Research Laboratory (Kirtland Air Force Base, Albuquerque, NM). This system produces X-ray photons with energies ranging from 10 keV to 60 keV and dosage rates between 2 and 200 Krad/min (SiO₂). Radiation dosage and absorption rates were calibrated relative to SiO₂. Devices were typically irradiated up to 1 Mrad and performance metrics were monitored in-situ by temporarily halting radiation exposure.

Resonance Raman spectroscopy and imaging was performed on P3HT/PCBM devices before and after irradiation exposure using a scanning confocal microscope spectrometer system described previously [15,16]. Briefly, excitation wavelengths were chosen to resonantly excite P3HT absorption transitions, which consist of contributions from aggregated and amorphous chains. Raman images were generated by exciting the P3HT/PCBM blend thin in-situ within functioning devices by raster scanning the device (typical scan ranges

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