



Pathway for recovery of photo-degraded polymer solar cells by post degradation thermal anneal



J. Bhattacharya^{a,*}, P.H. Joshi^a, R. Biswas^{a,b,c}, V.L. Dalal^{a,b}

^a Iowa State University, Department of Electrical Engineering, 2215 Coover Hall, Ames, IA 50011-3060, United States

^b Microelectronics Research Center, Ames, IA 50011, United States

^c Ames Laboratory, Ames, IA 50011, United States

ARTICLE INFO

Keywords:

Organic solar cells
Photo degradation
Shockley Read Hall recombination
Defect density
Capacitance spectroscopy
Thermal stability
Stability

ABSTRACT

The photo-degradation of polymer solar cells is a critical challenge preventing its commercial deployment. We experimentally fabricate organic solar cells and characterize their degradation under solar simulators in an environmental chamber under nitrogen flow, without exposure to oxygen and moisture. We have developed a thermally stable inverted organic solar cell architecture in which light induced degradation of device characteristics can be reversibly annealed to the pristine values. The stable inverted cells utilized MoO_x layers that are thermally treated immediately after their deposition on the organic layer, and before metal cathode deposition. Organic solar cells that are photo-degraded in the presence of oxygen, however show irreversible degradation that cannot be thermally recovered. The decrease of organic solar cell characteristics correlates with increases in mid-gap electronic states, measured using capacitance spectroscopy and dark current. It is likely the photo-induced defect states caused by local H motion from the alkyl chains to the aromatic backbone, can be reversibly annealed at elevated temperatures after photo-degradation. Our results provide a pathway for improving the stability of organic photovoltaics.

1. Introduction

Organic solar cells have attracted broad scientific interest due to their simple processing techniques, flexibility in tuning bandgap, and their ability to be deposited on curved substrates. Recent advances have resulted in organic solar cell (OSC) efficiencies near 11.5% for typical single junction configuration [1], and ~13.5% for multi-junction cells [2]. However degradation remains a critical issue which needs to be understood, and minimized, for a pathway to commercialization.

A large body of work has been performed on extrinsic degradation caused by ingress of oxygen and moisture in the solar cell. Krebs et al. [3] reported degradation in ambient moisture, where moisture intrudes the cell stack through the aluminum cathode layer leading to degradation of the constituent interfaces. Kawano et al. [4] proposed that PEDOT:PSS based hole transport layer reacts with ambient moisture and oxygen leading to the formation of a charge injection barrier at HTL-active layer interface causing degradation in charge collection. Wang et al. [5] proposed the formation of an Al₂O₃ barrier at the cathode side of the device due to the reaction between the Al cathode and ambient oxygen/moisture, hindering efficient electron collection. Reese et al. [6] also proposed that metal cathodes were a source of the degradation of organic cells. For simplicity, all these above degradation

findings are grouped as extrinsic degradation.

In seminal work, Jorgensen et al. [7] detailed the photo-chemical reaction of photo-excited polymers with oxygen leading to the breaking of polymer backbone. This occurs because of the exchange of electron from an excited electronic state of the polymer to the oxygen. There are studies detailing the oxygen induced degradation in polymer based OSCs [8–13]. It was hypothesized by Kawano et al. [4] that PSS (poly 4-styrene sulfonate) groups of PEDOT: PSS layer tend to diffuse into active layer and photo-chemically react with polymer resulting in active layer degradation. Guerrer et al. [10] proposed that molecular oxygen can form polymer-oxygen O₂ complex and the formation of such complexes were directly linked to the drop in photo-current and voltage. Rivaton et al. [14] concluded that oxygen induced photo degradation is due to the reduction in polymer conjugation length and the photo-chemical reaction was termed photo-bleaching or photo-oxidation. Device encapsulation can reduce such extrinsic degradation.

There are also various studies of intrinsic degradation caused by exposure to light itself, in the absence of moisture and oxygen. Intrinsic degradation cannot be reduced by encapsulation alone. Oxygen may be an accelerator in photo-bleaching, but even in its absence, light could cause considerable damage to the performance of organic based solar cells. Street et al. [15,16] and Bhattacharya et al. [17] and recently

* Corresponding author.

<http://dx.doi.org/10.1016/j.solmat.2017.02.012>

Received 4 September 2016; Received in revised form 18 January 2017; Accepted 9 February 2017

Available online 16 February 2017

0927-0248/ © 2017 Elsevier B.V. All rights reserved.

Tamai et al. [18] reported that even in the absence of ambient oxygen and moisture, prolonged light illumination can degrade the efficiency of the organic solar cells by creating mid-gap electronic states, resulting in increased rate of trap-assisted recombination, and lower open circuit voltage and short circuit current due to the deterioration of the charge transport of photo-generated charge carriers. The origin of charge traps was discussed with ESR measurements and density functional theory. The same work demonstrated the completed recovery of performance of photo-degraded cell upon post-degradation thermal annealing [18]. Furthermore photo-degraded solar cells that were thermally annealed, showed reductions in sub-gap photo-absorption indicative of the reduction in mid-gap defect density [15]. Previous studies by Toshihiro et al. [19] showed a recovery of OPV performance upon post degradation thermal treatment. The author attributed photo degradation to charge accumulation at cathode-organic interface as an interpretation of performance recovery. Katz et al. also reported the recovery of OPV performances after concentrated light exposure and attributed the change of the performance to anode HTL series resistance caused by O₂ desorption/adsorption respectively [20–22]. Other groups also reported the impact of thermal treatment on the performance of degraded cells [23,24]. It is possible to prevent the interaction of atmospheric moisture/oxygen with the cell stack by encapsulation materials. However this does not protect the solar cell when the active material itself is unstable under light. So understanding the pathway of photo degradation becomes critical for developing pathways to stabilize OSCs.

In this paper, we fabricate a P3HT (poly 3-hexylthiophene-2,5-diy) based bulk heterojunction solar cell with an inverted n-i-p architecture with specialized processing sequence containing MoO_x hole-transport layer. We characterize the degradation of the solar cell under light illumination in a nitrogen filled atmosphere. We then show that, it is possible to completely recover the solar cell efficiency and device characteristics that were photo-degraded by thermal annealing. Detailed measurements of mid-gap defect states by both capacitance spectroscopy and dark current are presented to demonstrate the complete recovery of the performance of the solar cell. In contrast, we find that the p-i-n cells cannot be thermally annealed after light degradation because of metal cathode instability due to temperature treatment. The mechanisms underlying degradation under light illumination and thermal recovery is discussed using these measurements.

2. Experimental details

Organic solar cells (OSCs) were fabricated from regio-regular P3HT (Sigma Aldrich/Average Mw 54,000–75,000 and PDI≤2.5 (product code- 698997) with 99.995% trace metal basis) based donor and PC₆₀BM (Nano-C) in both regular (p-i-n) and inverted (n-i-p) type bulk-heterojunction architectures. We have obtained ITO-coated glass substrates with sheet resistance $\sigma=16 \Omega/\square$ (Colorado concepts). To serve as a hole transport layer in p-i-n cells, a 30 nm PEDOT:PSS is deposited on the ITO coated glass by spin coating at 5000 rpm for 40 s followed by baking on hot-plate at 120 °C for 15 min. Alternatively for n-i-p cells, Cs₂CO₃ is spin coated on ITO coated glass at 4000 rpm for 40 s followed by a 15 min baking on a hot-plate for 150 C in air. This was followed by spin coating of P3HT:PC₆₀BM (1:1) blend solution at 400 rpm for 40 s inside the glove-box. This ensured ~200 nm of absorber layer. After the deposition, the films are dried slowly inside glove-box. Once the film is dried completely, it was annealed at 160 °C for 2 min followed by 110 °C for 10 min. Finally the metal cathode (Ca/Al) for p-i-n cell was deposited using thermal evaporation. For the n-i-p cell, MoO_x was thermally evaporated on the active layer. This is followed by an aluminum deposition using thermal evaporation. All thermal evaporations performed through a shadow mask with a circular aperture with area of 0.106 cm². More details of fabrication are included in the [Supplementary material](#). The [Supplementary material](#) includes the description of the annealing steps in the various

stages of experiment - starting from device fabrication to the post-degradation anneal.

All the thermal treatments were performed on hot plate at above-mentioned temperatures. The fabricated devices were tested inside a nitrogen filled environmental chamber for initial measurement of light IV (current-voltage), dark IV and capacitance spectroscopy. Two solar cells (i.e. metal top contacts) were identified which had similar photovoltaic performance. One of the selected cells was exposed under 2X intensity (200 mW/cm²) of the ABET solar simulator that matches the AM 1.5 spectrum of sun, inside the chamber while the rest of the cell area was covered with metal foil to shadow other metal contacts from light exposure. The unexposed contact were used as reference for comparing the effect of photo-degradation. Light IV, dark IV, EQE (external quantum efficiency), C-F (capacitance-frequency) were measured on the degraded contact to measure the impact of light soaking on electrical parameters. Finally the entire device were thermally annealed at various temperatures for different times and both the degraded and non-degraded metal contacts were characterized after each thermal annealing step. During the photo exposure the temperature of the device was maintained at room temperature (25 °C) by using a cooling fan, and monitored with a temperature probe.

In this work we utilize the same starting material from a single source, with the same initial concentration of additives and chain terminators for all studies. We then study the role of light in changing the density of defects. P3HT:PC₆₀BM solar cells made with different additives or using different sources do produce somewhat varying solar cell efficiencies due to additives and also are known to accelerate the photo-degradation of the respective cells with the inclusion of additives such as diiodooctane(DIO) and octane dithiol(ODT) as described in previous publications [25,26].

It must also be noted that there is a distinct possibility that there can be trace amount of Bromine present as an impurity introduced during the polymerization process which may act as a possible recombination center. There are two previous report which studied the effect of termination of the end groups by capping the end group of regio-regular P3HT by incorporating *additional* Br (i.e. P3HT-Br) rather than the conventional H-termination (P3HT-H) [27,28]. P3HT-Br shows slightly lower light absorption than P3HT-H, possibly due to the larger size of Br, and altered electrostatic interaction that affects chain packing, and the modified morphology of the P3HT domains. The short circuit current, fill factor, and EQE of P3HT-Br were lower than that of P3HT-H, interpreted by the authors [27] as due to increased charge trapping in P3HT-Br based devices. Photo-degradation has been suggested [27] to lead to increased charge trapping in P3HT-Br than P3HT-H, but further experimental and theoretical studies are required to investigate this effect.

In the present work, the P3HT material used is electronic grade, regio-regular P3HT with average Mw 54,000–75,000 and PDI≤2.5. It has a purity of 99.995% and not expected to have significant amount of impurities such as Br. Impurities and x-ray fluorescence (XRF) of P3HT has been extensively studied by Bannock et al. [29]. Their XRF measurements show that Br is only present in the crude P3HT, but acetone washing or chloroform extraction reduces the Br content to negligible values, which is the case for the P3HT used in these experiments. Furthermore the MoO_x interlayer we utilize in this paper, prevents the inter-diffusion of Al from the cathode to the active layer- a mechanism that is independent of the details of the absorber layer. The current work is stressing on the role of mid-gap defect states originating because of prolonged light exposure and their recuperation due to post degradation thermal treatment. Any external treatment both photo and thermal, are unlikely to change that concentration of bromine impurity in the polymer and hence the density of traps contributed by them. We anticipate further work of characterizing bromine content present in the polymer using X-Ray fluorescence technique would yield results similar to those in [29], and to further study the role of deliberate introduction of bromine as an end-cap for

Download English Version:

<https://daneshyari.com/en/article/6457102>

Download Persian Version:

<https://daneshyari.com/article/6457102>

[Daneshyari.com](https://daneshyari.com)