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Multiple stress degradation analysis of the active layer in organic photovoltaics

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ABSTRACT

Under general working conditions, organic solar cells are exposed to a multitude of degradative stresses, including light, oxygen, temperature and humidity.

We selectively exposed the layer stacks of three different material systems, P3HT, PCDTBT and AnE-PVcc in bulk heterojunction with fullerene, to different combinations of stresses, starting from one single stress and then iteratively adding a new stress to the combination. This allowed us to determine how harshly different polymers get affected by individual stress factors.

P3HT based devices show an overall higher stability compared to PCDTBT or AnE-PVcc. All of the devices are affected the most by combined influences of light, oxygen, humidity and temperature, and they cease functioning within a couple of hours of exposure. A thermodynamically driven formation of a thin PCBM layer at the anode is observed with the prolonged storage, which causes an increase in the current densities for the large reverse voltages. We explain this phenomenon by tunneling from the fullerene HOMO to the LUMO, as a result of a large gradient in the electric potential over this layer. The increase of open circuit voltage of the pre-annealed P3HT devices upon UV photolysis was investigated, and attributed to the UV irradiation facilitated destruction of the face-on P3HT layer grown on the surface of the active layer.

The effect of the sequence in which the annealing step is performed with respect to evaporation and degradation on the performance upon degradation is discussed.

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1. Introduction

Solar cells have in last decades established their importance as an eco-friendly, sustainable energy source. Organic solar cells, in specific, are low-cost [1–3], highly scalable [4–6], flexible [7], light-weight [7], with a short energy payback time [8–11], and consequently of high commercial interest.

Since 1994 when Yu, Zhang and Heeger for the first time presented the concept of bulk heterojunction cells [12], a variety of polymers, starting from MDMO-PPV and MEH-PPV, over P3HT, to the novel 3rd generation PCPDTBT, PCDTBT, PSiF-DBT, PTB7 and PBDTTPD, has been developed in search of higher efficiencies [13–17]. The recent record in power conversion efficiency is held by Mitsubishi with a high 9.2%, using a yet not disclosed molecule [18]. Still, improving the lifetime of the devices remains a serious issue that has to be resolved in order to make them commercially feasible. Their organic nature makes them especially sensitive to light, oxygen, heat and water. As all of the mentioned factors are present in normal working

environment of the solar cells, big efforts should still be undertaken to understand the degradation mechanisms and to find ways to reduce these effects [19–21].

In contact with air and light, the polymer reacts with oxygen, which produces different oxidized polymer species and breaks the polymer chain, leading to irreversible failure in functioning of the devices. [22–27] Recently it has been shown by Hintz et al. that two concurrent mechanisms take place in degradation process, depending on the irradiation conditions [28,29]. Under the UV irradiation, the degradation proceeds as a radical reaction [22,24–26] starting at the α carbon of the alkyl sidechain, and results with simultaneous degradation of the π conjugated system and the sidechain. Under visible illumination, however, the reaction involves a photosensitized species, possibly singlet oxygen [30–34] that primarily destroys the π conjugated system of the polymer, leaving the sidechain almost unaffected. In white light conditions, both of the mechanisms are active, but since the radical chain mechanism has a higher effectiveness, it dominates even when only a low UV irradiation fraction is present [28,29].

Besides the irreversible degradation mechanisms, an additional reversible process takes place. It was reported the first time by Abdou et al. [33] that when exposed to oxygen and light, P3HT gets

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reversibly doped via a polymer-oxygen charge transfer complex. This finding has since been further confirmed by many other groups [35–39].

In this study we investigated the stabilities of anthracene containing PPV-type copolymer poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (referred to as AnE-PVcc) [40–44] and a representative of the 3rd generation materials poly[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (in further text, PCDTBT) [45], and compared them to the reference poly(3-hexylthiophene) P3HT devices [46].

In the first part we tested the effect that the sequence in which the reference P3HT:PCBM devices are fabricated and exposed to various degradation stresses has on the decay in the performance. As solar cells are multi-layered structures, the decay in their performance reflects not only the degradation of the photoactive layer, but of each of its constituent layers. As we noticed an especially strong influence arising from the degradation of the cathode, the stability tests of the three material systems in the second part of experiment were performed on layer stacks prior to the cathode deposition.

In the stability comparison test we selectively exposed the layer stacks to different combinations of stresses, starting from one single stress and then iteratively adding a new stress to the combination. Testing conditions include ambient and inert atmosphere, at different temperatures, in the dark and exposed to different types of illumination. This allowed us to determine how harshly different polymers get affected by individual stresses.

2. Experimental

The first part of the study was performed on P3HT:PCBM [60] solar cells, prepared as described in Section 3. All of the ITO coated glasses were etched using Zn powder and aqueous solution of hydrochloric acid. After that, they were ultrasonicated in toluene, acetone and isopropanol consecutively, for 15 min in each. An approximately 40 nm thick PEDOT:PSS (Heraeus Clevios PH) hole transport layer was spin coated on top of the ITO substrates and then annealed in air at 140 °C. After 20 min of annealing, the still hot samples were transferred to the nitrogen filled glove box. There, an approximately 90 nm thick active layer, was spin coated from chlorobenzene solution of P3HT:PCBM 3:2 [60].

The sequence in which the further steps - annealing at 150 °C for 10 min in the glovebox (A), evaporation of approximately 100 nm thick aluminum cathode (E) and exposure to different degradation conditions (D) were performed was permuted, and for each of the degradation conditions, 6 differently treated devices were obtained (ADE, AED, DAE, DEA, EAD, EDA).

The conditions in the degradation step (D) include exposure to 150 °C in dark glove box for 2 h, 150 °C in dark air for 2 h, 50 °C in dark air for 1 day, and 50 °C under 1 sun intensity solar simulator in air for 1 day.

As a reference, two non-degraded cells have been used, one cell annealed prior to evaporation (AE), and the other one in the presence of cathode (EA).

After these three steps, the cells were sealed under glass using a UV curable glue, and characterized using an AM 1.5 solar simulator from Solar Light Co. The same simulator was used as a source of UV-vis illumination in the degradation experiment. UV irradiation degradation was performed using an OmniCure S1000 mercury vapor lamp (intensity 2 W/cm²) and a band pass optical filter (transparency window 320–500 nm).

The second part of the study was performed on P3HT:PCBM [60], PCDTBT:PCBM [70] and AnE-PVcc:PCBM [60] solar cells. The etching, cleaning and the spin coating of PEDOT:PSS and the active

layers were made as in the first part of the experiment. The active layers were spin coated from chlorobenzene solution of P3HT:PCBM [60] 3:2, 1:1 mixed ortho-dichlorobenzene:chloroform solution of PCDTBT:PCBM [70] 2:3 and 1:1 mixed chlorobenzene:chloroform solution of AnE-PV:PCBM [60] 1:1.

Before the degradation step, P3HT:[60]PCBM samples were annealed prior to evaporation, at 150 °C for 10 min in the glove box.

The degradation stresses were the same as in the first part of the experiment, only the time of exposure was varied in case of UV light degradation 4 min, 8 min, 16 min and 32 min, and for the rest of the stresses 1 h, 2 h, 4 h and 8 h. For each data point, a separate cell was used.

Finally, after the degradation step, the aluminum top cathode was thermally evaporated at a pressure lower than 10⁻⁶ mbar, and the cells were sealed in the same manner as in the first part of the experiment.

After sealing, the cells were taken out of the glove box, and electrically characterized. *J* (V) curves were obtained with a AM1.5G solar simulator with intensity of 1 kW/m² and a Keithley 2400 Source Measure Unit.

Influences of UV exposure on the surface composition and electronic properties of P3HT:PCBM [60] were examined implementing X-ray and UV photoelectron spectroscopy (XPS, UPS). The measurements were performed under Ultra-High-Vacuum (UHV) conditions employing X-ray (monochromated Al K α ; *hν* = 1486.7 eV) and ultraviolet radiation (He I/II; *hν* = 21.2/40.8 eV) as mentioned in detail in [47]. For performing XPS and UPS investigations, P3HT:PCBM [60] thin films were prepared under identical conditions, on PEDOT:PSS coated ITO substrates by spincoating and annealing at 150 °C. After that they have been transferred, as prepared or after additional illumination by mercury-vapor UV lamp for 16 min in the glove box, to the load lock chamber of the UHV system. Additional measurements were performed after UV irradiation of the sample in the UHV chamber for 15 min employing a mercury discharge lamp.

3. Results and discussion

3.1. P3HT based solar cells – The influence of the sequence in which annealing, evaporation and degradation are conducted on the stability

In the first part of the experiment, we investigated how the sequence in which annealing and evaporation of P3HT:PCBM [60] devices are performed affect their performance when exposed to different degradative stresses.

As shown in Fig. 1, the main difference between the pre- and post-cathode annealed P3HT:PCBM devices is in their open circuit voltage (*V_{oc}*), which is much higher in the latter case, whereby the short circuit current (*J_{sc}*) is almost the same. This phenomenon was investigated by several groups. When the devices are annealed prior to the deposition of the aluminum, a thin layer of face-on P3HT is formed on top, representing a barrier to electron transport [48–51]. When the annealing is conducted after the aluminum deposition, the aluminum cap confines the organic material, resulting in a less rough surface morphology and less crystalline and less specific oriented bulk, which improves the formation of the interpenetrating networks [49,52–54]. Due to the aluminum diffusion into the organic layer, a stronger interaction between the aluminum and the organic layer is achieved, manifested in formation of covalent bonds between the metal and the polymer, e.g. C–Al, C–O–Al, which result in stronger contacts and increased contact area, thus reducing the series resistance [55–59]. This difference is reflected in the value of *V_{oc}*, which is found to be lower in pre-evaporation annealed devices.

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