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# Characterization of the degradation process of Si-PCPDTBT:PC<sub>70</sub>BM(1:2) blend layers deposited on ITO/glass substrate

M. Seck<sup>a,b,\*</sup>, A. Vincze<sup>a,b</sup>, A. Satka<sup>a,b</sup>, D. Hasko<sup>a</sup>, F. Uherek<sup>a,b</sup>, A. Tournebize<sup>c</sup>, H. Peisert<sup>c</sup>, T. Chasse<sup>c</sup>

<sup>a</sup> International Laser Centre, Ilkovicova 3, 841 04 Bratislava, Slovakia

<sup>b</sup> Institute of Electronics and Photonics, Slovak University of Technology, Ilkovicova 3, 812 19 Bratislava, Slovakia

<sup>c</sup> Eberhard Karls Universität Tübingen, Institut für Physikalische und Theoretische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany

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## ABSTRACT

In organic photovoltaic (OPV), the photoactive layer is the main part, where the energy conversion process takes place. In our work we focus on Si-PCPDTBT:PC<sub>70</sub>BM (1:2) photoactive blend layers, where Si-PCPDTBT and PC<sub>70</sub>BM are the poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2,3-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)] and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester, respectively. The mixture of these materials was deposited on the ITO/glass substrate and investigated using different analytical methods such as secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) before and after the degradation. The different degree degradation of layers measured as % of UV absorbance loss was performed under the illumination at ambient air using a solar simulator (AM 1.5, Xenon arc lamp). SIMS depth profiles reveal a diffusion of atmospheric oxygen through the photoactive layer leading to the photooxidation of organic materials as unveiled from the distribution of selected ions fragments (SO<sup>-</sup>, NO<sup>-</sup>, SO<sub>2</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and CO<sup>-</sup>). AFM and SEM images of the non-degraded sample show a relatively smooth surface. SEM investigations of the degraded layers reveal a homogenous formation of dispersed fibril-like nano-objects at the surface. The formation of such nano-objects may explain the increase of the layer surface oxidation and volatilization during the long-term degradation.

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## 1. Introduction

Recently, a new range of polymers with a low energy bandgap ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ) were developed resulting in a better efficiency of OPV devices, essentially by increasing the absorption fraction of the solar spectrum. Among them, Si-PCPDTBT whose energy bandgap below 1.4 eV is well suited for the use as an electron-donor polymer in bulk heterojunction (BHJ) solar cells [1]. However, the fact that this polymer poses a low bandgap is not the only reason that it is subject to several studies [2–5]. It was also described as an example that the disadvantageous charge transfer exciton (CTE) emission observed in a related BHJ system may be suppressed using Si-PCPDTBT:PC<sub>60</sub>BM (PC<sub>60</sub>BM: [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) with the additive octane-dithiol (ODT) [5]. In the present work, we study Si-PCPDTBT as the donor material in BHJ solar cells (OSCs) and the fullerene [6,6]-phenyl-C<sub>71</sub>-

butyric acid methyl ester (PC<sub>70</sub>BM) was used as electron-acceptor material. The chemical structures of the used materials in the present work are illustrated in Fig. 1. Fullerenes in general are often used in BHJ OSCs, since the HOMO and LUMO energy levels are in the optimal range for many systems [6]. Also, it was mentioned in the literature that fullerenes can stabilize many  $\pi$ -conjugate polymers used in the photoactive layer of organic solar cells [7] quenching the polymer exciton by an electron transfer which reduces the lifetime of the excited singlet. Distler et al. studied the photooxidation behavior (kinetics) of poly(3-hexylthiophene) (P3HT), poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothia-diazole)] (C-PCPDTBT) and Si-PCPDTBT in neat polymer films and in blend with fullerene. Authors found that an enhanced generation of triplets (in the blend via the charge-transfer state) in C-PCPDTBT is observed upon blending with fullerene leading therefore to a destabilizing effect of fullerene. Indeed, in the presence of oxygen, the triplet state may sensitize the formation of chemically active oxygen species (e.g., singlet oxygen) which then would act as oxidants for the polymer [7]. In the case of P3HT and Si-PCPDTBT, the triplet populations are reduced in the presence of fullerene

\* Corresponding author at: International Laser Centre, Ilkovicova 3, 841 04 Bratislava, Slovakia. Tel.: +421 2 654 21 575, +421 2 654 21 385.

E-mail address: [mamadou@ilc.sk](mailto:mamadou@ilc.sk) (M. Seck).

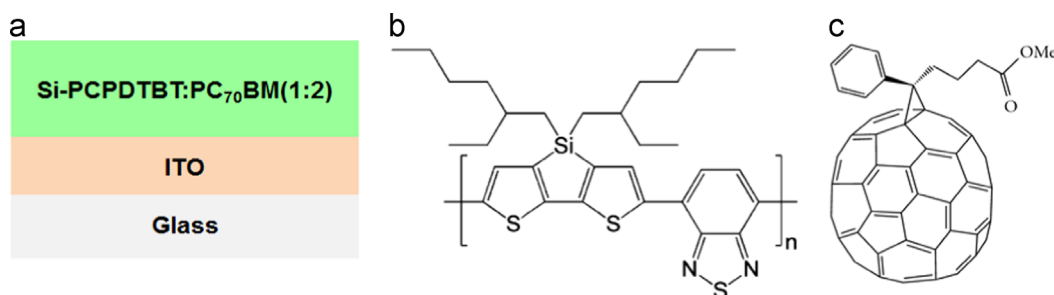


Fig. 1. The schematic cross-section of the investigated structures (a), chemical structure of the Si-PCPDTBT (b) and PC<sub>70</sub>BM (c) materials.

contributing therefore to a stabilization of the polymers. In organic solar cells, the diffusion of exciton (electron–hole pairs) created in the polymer (Si-PCPDTBT in our case) by light absorption is an important process. The dissociation of the exciton is normally achieved at the interface with the electron accepting material (PC<sub>70</sub>BM in our case). Thus, to quench as much exciton as possible in order to contribute to the photocurrent and therefore the device efficiency, the exciton diffusion length must be appropriate. The exciton diffusion length of the Si-PCPDTBT material was found to be approximately 10.5 nm comparing to that of the P3HT where it is 5.1 nm [8]. Even if all these advantageous properties favor Si-PCPDTBT as a donor material in BHJ OSCs, the stability of the polymer remains an important issue. The studies on the long-term stability and the degradation of solar cells have thus far been mainly focused on complete devices [9,10]. However, it is not always possible to distinguish between degradation of the active layer, the interface with the electrodes, or the contacts [11,12]. As an example, it has been showed that in devices with regular structure the corrosion of the low work function electrodes usually limits the lifetime [13]. In the publication of Seemann et al. they reported that in cells with inverted structure the degradation under photooxidation conditions affects mainly the active layer, consisting of a reversible part which is assigned to oxygen-induced doping and an irreversible part which is due to photooxidation [14]. The aim of this work is to understand how the Si-PCPDTBT:PC<sub>70</sub>BM BHJ blends' layers behave chemically and physically under different levels of photooxidation degradation resulting in term of UV absorbance loss of the polymer material (Si-PCPDTBT). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) was applied in order to study the changes of surface morphology of films after degradation. To investigate the materials composition of the layers, time of flight secondary ion mass spectrometry (ToF-SIMS), was used. Recent studies of the state of the art system P3HT:PC<sub>60</sub>PM using SIMS by the Krebs group [15,16] has shown that this method provides valuable information in this context.

Recently, Deschler et al. showed that under photooxidative conditions, an absorbance loss of the active layer by only 5% results in a dramatically fast decrease of the device performance. A loss of 90% of the power conversion efficiency, 30% of the fill factor and 88% of the current density have been found while the open circuit voltage remained not affected [17]. Authors also mentioned that a total absence of photovoltaic response in the cells have been observed after longer ageing periods corresponding to the 10% absorbance loss. In this context, since the layers used in our study have been degraded for long period (up to 80% absorbance loss), we focused on the characterization of the photoactive layer instead of the complete cell.

## 2. Experimental details

Si-PCPDTBT:PC<sub>70</sub>BM (1:2) blend layers (with nominal thicknesses around 300 nm) were deposited on ITO/glass substrate

(15 × 15 mm<sup>2</sup>) using the doctor blade method at Belectric OPV GmbH. Photooxidation degradation, under illumination (AM 1.5) with Xenon arc lamp at ambient air were performed resulting in term of UV absorbance loss of the polymer material. Scanning probe microscope (Solver P47H-PRO) was used for AFM measurement in semi-contact mode to characterize the surface properties on selected areas of 5 × 5 μm<sup>2</sup>. Inlens detector SEM LEO 1550 was also used to characterize the Si-PCPDTBT:PC<sub>70</sub>BM blend layers surface. The energy of the electron beam was 5 keV and different size areas, from nanometer (nm) to millimeter (mm) range were investigated. Ion ToF (SIMS IV) in dual beam mode was used to perform depth profiling. A liquid metal ion gun Bi<sup>+</sup> at 25 keV was used as analyzer gun and Cs<sup>+</sup> at 1 keV as sputtering gun with 300 μm × 300 μm size of the scanned area.

## 3. Results and discussion

SIMS depth profiles of the unexposed and differently photooxidized Si-PCPDTBT:PC<sub>70</sub>BM blend layers are shown in Fig. 2. The top left figure displays ion depth profiles recorded from a nondegraded active blend layer. The O<sup>-</sup> ion fragment intensity and those of the oxidized layer species demonstrate the presence of oxygen in the layer. The profiles appear rather flat over the film thickness in this manner suggesting homogeneous distribution of those species. Decrease of carbon and increase of InO<sup>-</sup> and even O<sup>-</sup> ion fragments indicate the position of the interface to the ITO substrate. Following the first photodegradation step (30% UV loss, see Fig. 2, top right) a significant increase of oxygen and of the NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sup>-</sup>, SO<sub>2</sub><sup>-</sup>, CO<sup>-</sup> ion fragment intensities becomes evident, which is caused by the oxygen diffusion and photooxidation of the active polymer material (Si-PCPDTBT:PC<sub>70</sub>BM). However, the oxygen ion and oxidized ion fragment intensities are not constant anymore with depth but decay from significantly enhanced intensities close to the film surface to intensities similar to those in the as prepared reference nondegraded active layer blend close to the buried interface to ITO. This is clear evidence for an inhomogeneous distribution of the oxidized species with an enhancement (only slightly less than an order of magnitude) near the surface. Photooxidation proceeds faster closer to the surface compared to the buried interface. At least part of the concentration gradient of the oxidized species with depth can be related to the expected exponential decrease of the light intensity, which is needed to drive the photooxidation of the light absorbing film, with depth distribution described by the Lambert–Beer absorption law. In addition, an even stronger intensity enhancement very close to the film surface may be recognized for the less oxidized ion species (SO<sup>-</sup>, NO<sup>-</sup>) compared to the higher oxidized ions (SO<sub>2</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>) ions. In contrast, the oxygen-free C<sub>3</sub><sup>-</sup> ion fragment exhibits about similar intensities for both samples and does not indicate inhomogeneity. Interestingly, the SiO ion fragment does not increase significantly in intensity after the first photodegradation step and indicates almost homogeneous SiO distribution.

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