Shelf life and outdoor degradation studies of organic bulk heterojunction solar cells

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Abstract. We studied the degradation of different types of bulk heterojunction devices, in which the materials comprising the active layer and/or the materials used for the back electrode are varied. The devices are deposited on ITO covered glass and have the structure PEDOT:PSS/BHJ/Me, where PEDOT:PSS is the hole transport layer, BHJ (bulk heterojunction) is the active layer comprising a polymer donor (e.g. PTB7, PCDTBT) and a fullerene derivative acceptor (e.g. PC60BM, PC70BM) deposited by spin coating, Me is the metal back contact, which is either Ag or Al deposited by magnetron sputtering or thermal evaporation. The device performance was monitored after storage in the dark at ambient conditions by following the evolution of the \(J-V\) curve over time. Results of real conditions outdoor degradation studies are also presented. The stability of the different solar cell structures studied is compared.

1. Introduction

Organic solar cells (OSCs) have been intensively studied as a low-cost alternative to the solar cells based on inorganic semiconductors. The goal of power conversion efficiency of above 10 \% has been achieved by successful device optimization of bulk heterojunction solar cells [1]. However, device lifetime continues to be a key limitation for their commercial application. Long-term stability of OSCs is currently one of the major topics for this technology and combinations of various donor and acceptor materials are being studied in order to obtain more stable devices.

A considerable body of work has been published in recent years describing the stability and degradation behavior of the most stable but relatively low-efficient poly(3-hexylthiophene) P3HT:fullerene-based organic solar cells [2]. On the other hand, low band-gap polymers are researched as promising materials that are able to achieve higher efficiencies than the P3HT:fullerene system, but few reports have appeared dealing with their stability upon exposure to real outdoor conditions.

Here we report on the shelf life and outdoor degradation of devices based on thieno[3,4-b]thiophene-\textit{alt} -benzodithiophene (PTB7) and the fullerene derivatives [6,6]-phenyl C71-butyric acid

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methyl ester (PC70BM) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC60BM). Devices based on PTB7 in combination with PC70BM have achieved efficiency over 7%, but the blend was found to suffer from poor stability [3]. Pristine PTB7 is very susceptible to photooxidation and further research and modifications of the polymer are needed to prevent this degradation.

A promising material which has been shown to have high degree of photochemical stability is the donor-acceptor copolymer poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] PCDTBT [6]. The most studied device structure based on this polymer is glass/ITO/PEDOT:PSS/PCDTBT:PC70BM/Al. It is known that thermal annealing is not desirable for this structure, in contrast to the devices based on the crystalline P3HT polymer [5]. We explored the stability under outdoor sun irradiation and in the dark of annealed PCDTBT:PC70BM devices with thermally evaporated Al cathodes and compared their performance over time to identical unannealed devices. We have also compared these results to the behavior of similar devices with magnetron-sputtered Ag back contacts.

2. Experimental
The solar cells were prepared on glass/ITO substrates. Prior to the HTL deposition, the substrates were cleaned with distilled water, acetone and isopropanol followed by UV ozone treatment. PEDOT:PSS was spin-coated from water solution and annealed for 10 minutes at 130°C in Ar. The PCDTBT:PC_{70}BM BHJ was deposited by spin-coating from dichlorobenzene solution with concentration 10 mg/ml (1:4 weight ratio) in ambient conditions. For the cells with the sputtered Ag contacts, a concentration of 30 mg/ml was used. The PCDTBT polymer and the substrates were purchased from Ossila Ltd. The PTB7:PC60BM and PTB7:PC70BM blends were prepared in a 1:1.5 weight ratio in 25-mg/ml solution of dichlorobenzene and spin-coated in air. The PTB7 polymer used for the experiment was synthesized in the Institute of Polymers of the Bulgarian Academy of Sciences. After spin-coating, the samples were annealed in Ar for 15 minutes at 50°C. Finally, an aluminium layer was thermally evaporated on top of the active layer for back contact. For some of the PCDTBT:PC70BM solar cells, Ag contacts were deposited by magnetron sputtering. The samples thus prepared represent a matrix of six independent cells of area 6 mm² each. The devices were encapsulated using a cover glass on top of the back metal contact glued by epoxy UV-curable resin from Ossila Ltd. After the encapsulation, the devices comprising PTB7:PC70BM (PC60BM) active layers were annealed in air for 10 minutes at 120°C. Some of the PCDTBT:PC70BM solar cells were annealed for 10 minutes at 110°C, while others were left as deposited.

The J-V characteristics were acquired in periods of ten to twenty days in order to determine the lifetime in the dark of the devices stored in ambient environment. The J-V measurements were conducted using a fully-automated computerized system including a halogen lamp as an illumination source adjusted to deliver 100 mW/cm².

The experiment for outdoor degradation study was performed by exposing the samples under open circuit conditions every day on the rooftop of the laboratory for five hours around midday (between 10 a.m. and 3 p.m.) in July and August 2017. Five cells of each kind were studied for this experiment. Their performance was recorded before and after each exposure. The temperature range during irradiation was from 35°C to 45°C.

3. Results and discussion
3.1. Degradation behavior of devices stored in ambient environment
Figure 1 shows the J-V characteristics of two typical glass/ITO/PEDOT:PSS/PCDTBT:PC70BM/Al devices. One of them was subjected to post-fabrication annealing in air at 110°C; the other was not annealed. Both devices were stored in the dark and characterized again after two weeks. The open-circuit voltage (Voc) of the annealed sample decreased by nearly 100 mV after the annealing, while the short-circuit current (Jsc) remained almost unchanged. The decline in the performance of PCDTBT-based BHJs after annealing has been observed and studied in [5]. In a previous work [6], we studied PCDTBT:PC70BM bulk heterojunction solar cells with magnetron-sputtered Ag contacts and
observed a slight improvement in the J-V curves after annealing at 120 °C. In figure 2, the normalized quantum efficiency (QE) spectra measured before and after annealing at 110 °C are compared. The shape of the curve has not changed after thermal annealing; this provides evidence that the thermal degradation in this case was not related to morphological changes or oxidation in the active layer of the device, which would have resulted in a change of the shape of the spectral response.

After 15 days storage in the dark, a sharp drop in the Voc of the unannealed sample was observed, which reached the Voc of the annealed device. We speculate that this behavior might be related to chemical changes at the interface between the active layer blend and the cathode.

Figure 1. J-V characteristics of glass/PEDOT:PSS/PCDTBT:PC70BM/Al annealed and unannealed devices after 15 days of storage in the dark.

Figure 2. Normalized quantum efficiency of PCDTBT:PC70BM solar cells of freshly prepared device and after annealing at 110 °C.

Figure 3. Evolution of the parameters obtained from J-V curves for three solar cells with PCDTBT:PC70BM active layers, stored in the dark.

Figure 4. Evolution of the parameters obtained from J-V curves for solar cells with PTB7:PC70BM (PC60BM) active layers, stored in the dark.
The performance of the solar cells studied was measured frequently for 120 days in order to observe their behavior when stored in ambient environment. The evolution of the main parameters obtained from the J-V measurements and normalized to their initial value is shown in figure 3. For the unannealed device, after an initial sharp drop during the first fifteen days, the Voc stabilizes and for the next measurements decreases very slowly. The annealed device, in contrast, does not show such drastic drop in Voc during the first fifteen days, but it declines gradually and seems to saturate after about 60 days. For both devices, there is a slight decrease in the initial Jsc; afterwards it remains unchanged. The fill factor (FF) decreases linearly with time which could be an indication of increasing series resistance. The parameters of a third structure with silver sputtered back contact are also plotted for comparison (filled symbols). As the graph illustrates, this device is more stable than the devices with thermally evaporated aluminium electrodes, which is in agreement with our previous work [6], although it should be noted that this device had initially a higher series resistance.

The devices with active layers PTB7:PC70BM and PTB7:PC60BM showed improvement in their J-V characteristics after thermal annealing at 120 °C with an increase in their FF. The devices were stored in ambient environment and were monitored frequently for 160 days. The different lengths in the aging periods for the various devices arise from the different time of their fabrication. The evolution of the main parameters is presented in figure 4. It is evident, that the FF of the sample with the PC70BM acceptor degrades faster than FF of the sample having PC60BM in the active layer. The FF of both devices decreases by about 30 % for 160 days. Also a decline is observed in the Jsc, while the Voc remains unchanged.

3.2. Outdoor degradation
Five representative samples for the structures discussed in the previous section were selected and their behavior was monitored upon daily exposure to sun irradiation. Figure 5 and figure 6 show the time evolution of the device parameters for cells with PCDTBT:PC70BM and PTB7:PC70BM(PC60BM) active layers, respectively. Only results from the inner cells of the 6-pixel matrix were selected and presented in this work because during the experiment we found that the edge cells degraded very fast as a result of insufficient edge encapsulation. As seen in the figures, the devices having PTB7:PC70BM(PC60BM) active layers experience more abrupt burn-in degradation in the first five hours of exposure than the PCDTBT:PC70BM-based devices. By the
end of the experiment, after 200 hours of exposure to outdoor conditions, all of the devices studied with thermally evaporated Al back contacts decreased their performance significantly. Both PTB7:PC70BM- and PTB7:PC60BM-based solar cell experienced severe degradation after the first five hours of exposure to sun irradiation. Their short-circuit current dropped by 45% and 35%, respectively, which is almost double the amount of current drop in PCDTBT:PC70BM-based structures.

The PCDTBT:PC70BM-based solar cell with silver sputtered cathode showed the most stable behavior in comparison to the other two similar samples. The annealed and unannealed devices showed similar behavior in the first 20 hours of exposure to outdoor conditions which suggests that the initial stage of the burn-in process does not depend on the post-deposition annealing.

4. Conclusions
We studied and compared the shelf life and outdoor degradation of two types of organic bulk heterojunction solar cells that were spin-coated in air. The PCDTBT:PC70BM samples experience a significant decrease in the open-circuit voltage after the first two weeks of storage in the dark, which we attribute to possible chemical changes at the active layer/electrode interface that seem to be accelerated by thermal annealing. PCDTBT:PC70BM samples with silver sputtered contacts show superior resistance to outdoor weathering compared to the samples with thermally evaporated aluminium back contacts. Samples with aluminium back contacts experience longer lifetime upon sunlight exposure when they are not subjected to post-deposition thermal treatment.

The solar cells based on PTB7:PC60BM degrade faster than the cells using the PC70BM acceptor. Both types of devices degrade very fast upon exposure to sunlight irradiation.

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