Performance and stability of two types of bulk heterojunction polymer solar cells with sputtered back contacts

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Abstract. Two types of polymer solar cells with active layers of P3HT:PCBM and PCDTBT:PCBM in a standard configuration were deposited by spin-coating the polymer layers and sputtering the Ag back contacts. After encapsulation, they were subjected to post-deposition annealing and were studied by measuring their current-voltage characteristics and quantum efficiency spectra. Their stability was examined by exposing them to solar radiation in open-circuit conditions for several hours every day for a total of 80 hours. Their characteristics were measured regularly throughout this period. The performance of the two types of cells are compared and discussed.

1. Introduction
Polymer-based solar cells have been the subject of intensive research in recent years. The most thoroughly studied bulk heterojunction (BHJ) system has been P3HT:PCBM. It is comparatively stable under ambient conditions. The usual architecture of polymer solar cells includes ITO and PEDOT:PSS as a transparent front contact and an anode, as well as evaporated Al as a back contact. In our previous studies, sputtered contacts of both Al and Ag were employed [1]. It was observed that post-production annealing could improve their performance considerably. Another advantage of the sputtered Ag contacts that was observed was the fact that samples with such contacts did not degrade with storage time in the dark as much as those with evaporated Ag and Al ones.

The polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) was introduced mainly due to its lower HOMO and the potential to obtain higher open-circuit voltages [2]. In this study, we combined it in a BHJ with PCBM and used sputtered Ag back contacts and post-deposition annealing. This system was compared to the one with a P3HT:PCBM active layer with regard to their performance through current-voltage measurements, quantum efficiency spectra and stability studies under solar irradiation.

2. Experimental
The samples studied were deposited on glass substrates covered with structured ITO from Ossila Ltd. The glass plates were cleaned using warm water, acetone and isopropanol and treated with UV-ozone.

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before spin-coating PEDOT:PSS from a water solution, followed by annealing at 130 °C in an Ar ambient on a hot plate for 30 min. This was followed by the deposition of the active layer. For the P3HT:PCBM samples, a 1:1 weight ratio of the two constituents in 12 mg/ml chlorobenzene solution was employed. For the PCDTBT:PCBM samples, the weight ratio was 1:4 in a 20 mg/ml solution of dichlorobenzene. All spin-coating depositions were carried out in air. After deposition, the samples were kept in solvent vapor for 30 min in order to achieve a better active layer structure. The Ag back contacts were deposited by magnetron sputtering. The samples thus obtained, representing a matrix of six solar cells each with an area of 4.5 mm², were encapsulated using a cover glass and a light-cured resin from Ossila Ltd.

The encapsulated samples were subjected to post-deposition annealing on a hot plate in ambient atmosphere. The current-voltage characteristics were measured using a fully automated computerized system employing a halogen lamp for illumination. The quantum efficiency spectra were taken by a computer-controlled equipment including a halogen lamp, a Digikrom 240 monochromator, a chopper, a lock-in amplifier and a calibrated Hamamatsu Si photodiode used as a reference.

The stability experiments were implemented by exposing the samples to sunlight for five hours every day under open-circuit conditions during the month of August in Sofia and measuring their current-voltage characteristics before and after each exposure. Seven cells of each kind were studied. The whole experiment lasted for 80 hours. The temperature of the samples during the irradiation experiments was 42 °C.

3. Results and discussion

Figure 1 shows typical current-voltage characteristics of the solar cells with a P3HT:PCBM active layer before and after post-deposition annealing, as well as after degradation in the sun for 80 hours. The post-deposition annealing for this type of samples was performed at 150 °C. It has been shown in previous studies [1] that this is the optimal temperature for this kind of active layers.

![Figure 1. J-V characteristics of a solar cell with a P3HT:PCBM active layer – as-deposited, after annealing and after 80 hours degradation in the sun.](image)

Figure 2 illustrates the current-voltage characteristics of a typical solar cell with a PCDTBT:PCBM active layer, again, as-deposited, after annealing and after degradation under the same conditions as above. The annealing this time was performed at 60 °C, 90 °C and 120 °C (the characteristic after annealing at the highest of these temperatures is only shown in the figure). Although there is data in the literature that PCDTBT should not be annealed at temperatures higher than 90°C [3], our data showed an improvement of the cell parameters after annealing at 120 °C.

![Figure 2. J-V characteristics of a solar cell with a PCDTBT:PCBM active layer – as-deposited, after annealing and after 80 hours degradation in the sun.](image)
When comparing the two figures, the following differences are noticeable. The characteristics of the cells with a P3HT:PCBM active layer, which we will denote as A-cells (as opposed to B-cells for the ones with a PCDTBT:PCBM active layer), are very poor in the as-deposited state, but improve significantly after post-deposition annealing. On the other hand, the as-deposited B-cells show better characteristics, but do not improve as much after annealing. The B-cells have a greater open-circuit voltage ($U_{oc}$), which is to be expected bearing in mind the literature data [2]. However, their short-circuit current density ($J_{sc}$) is smaller and they have a much higher series resistance, which leads to a lower fill factor as well.

Figure 3 and figure 4 display the normalized quantum efficiency spectra of the two types of solar cells before and after degradation. Both types of solar cells do not show any effective absorption of photons with wavelengths longer than 700 nm, which is a shortcoming of these active layers as they do not utilize an important part of the solar spectrum. As shown in our previous work [4], degradation under concentrated UV radiation leads to a change in the shape of the quantum efficiency spectrum of P3HT:PCBM solar cells. We interpreted this as evidence for deterioration of the interchain order in the active layer after UV irradiation. Keeping the cells under real conditions in the sun, however, does not lead to such effects in the quantum efficiency spectrum, as seen in figure 3. As evident from figure 4, annealing and degradation in the sun do not lead to a noticeable change in the shape of the quantum efficiency of solar cells with a PCDTBT:PCBM active layer.

Figure 5 presents the evolution of the solar cell parameters, fill factor ($FF$), short-circuit current ($I_{sc}$), open-circuit voltage ($U_{oc}$) normalized to their initial values, of two different A-cells. Analogous data for the B-cells is presented in figure 6. When comparing the degradation of the solar cell parameters, a number of peculiarities can be observed. As a whole, the B-cells have degraded to a greater extent at the end of the experiment. However, all their parameters undergo a sharp initial drop in the first few hours of solar irradiation, after which the degradation is very slow, especially for one of the samples. In the case of the A-cells, the degradation is more gradual throughout the experiment. A similar behavior has been observed for these two types of active layers in reference [5], where the samples had evaporated Al back contacts instead and the degradation experiments were carried out indoors using a solar simulator. In our experiments, the initial sharp drop is larger, takes place for a shorter time and is observed for $J_{sc}$ as well.
Figure 5. Evolution of the $J-V$ parameters with the time of solar irradiation of two different samples with a P3HT:PCBM active layer.

Figure 6. Evolution of the $J-V$ parameters with the time of solar irradiation of two different samples with a PCDTBT:PCBM active layer.

4. Conclusions
It is shown that polymer solar cells with two different active layers, namely, P3HT:PCBM and PCDTBT:PCBM, prepared in air and having sputtered Ag back contacts demonstrate the following differences: The P3HT:PCBM solar cells show a higher $J_{sc}$ and fill factor ($FF$), while the PCDTBT:PCBM ones have a higher $U_{oc}$, but their series resistance is very high. The PCDTBT:PCBM cells do not improve as much as the P3HT:PCBM ones after annealing. Some of these issues are thought to be related to the sputtered back contacts, which will be the subject of further studies.

The degradation experiments under real conditions show a sharp drop in the characteristics of the PCDTBT:PCBM solar cells in the first hours of irradiation, after which their parameters stabilize, while those of the P3HT:PCBM samples keep on falling slowly and steadily. If the initial drop is taken into account, the PCDTBT:PCBM cells degrade to a greater extent.

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