Influence of ZnO nanoparticles as electron transport material on the performance and stability of organic solar cells with sputtered Ag back electrodes

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Abstract. ZnO has been widely used as electron selective material in P3HT:PCBM organic solar cells with either conventional or inverted architecture in order to enhance the extraction of electrons and block the collection of holes at one electrode. In this work we investigate the influence of ZnO nanoparticles electron transport layer (ETL) on the performance and stability of P3HT:PCBM based organic solar cells with conventional architecture and magnetron sputtered back Ag contacts. Their stability in the dark and under real outdoor conditions was monitored by current-voltage measurements and impedance spectroscopy. The impedance spectra were taken as a function of applied bias under illumination in order to reveal more information about the degradation mechanisms taking place in the device.

1. Introduction

Organic solar cells have been widely investigated as a potential alternative to the inorganic photovoltaic devices due to their light weight and potential for fabrication on flexible substrates by cost-effective deposition processes [1]. Many varieties of polymer blends and different selective contacts have been employed in different device architectures in order to enhance their efficiencies and improve their stability. The most broadly investigated among polymer-fullerene bulk heterojunction blends remains the P3HT:PCBM polymer blend usually used in inverted architecture because of the stability issues with the conventional device architecture arising from the PEDOT:PSS hole transport layer and/or the Al back electrode [2].

In our contribution we have employed magnetron sputtered Ag electrodes on devices in conventional architecture glass/ITO/PEDOT:PSS/P3HT:PCBM/Ag and we have compared them to the same type of devices comprising a ZnO nanoparticles electron transport layer (ETL). Magnetron sputtering is usually not a preferable deposition method for the back electrode because it can damage the underlying layer but this method has the advantage over thermal evaporation of being scalable to large deposition areas.

Polymer solar cells are very prone to degradation induced from the environmental conditions as the polymers are inherently sensitive to water and oxygen ingress, which is identified as one of the main degradation mechanisms. In order to reveal the degradation mechanisms of organic solar cells,
extensive work has been conducted throughout the years [3-5] and in many studies accelerated degrading conditions without device encapsulation have been used. In our stability tests we used encapsulated devices to protect them from reactions with oxygen and water and we have investigated their behaviour after storage in the dark and in real outdoor conditions with a focus on the intrinsic interface degradation.

2. Experiment

2.1. Fabrication process
The organic solar cells were prepared on top of ITO pre-patterned glass substrates containing eight separate pixels, each of them having area 4 mm². The substrates were cleaned in deionized water, acetone and subsequently isopropanol for 10 minutes and were dried under nitrogen flow. The devices were then prepared by first spin-coating PEDOT:PSS and baking it at 120 °C for 15 minutes. The active layer was prepared in 1:1 weight ratio in 12 mg/ml chlorobenzene solution and was spin-coated in air. Then a layer of ZnO nanoparticles was spin-coated from solution on top of the active layer. The ZnO nanoparticle ink was purchased from Sigma-Aldrich and the size of the particles was 10 – 15 nanometers. The back Ag contacts were deposited by magnetron sputtering. The samples were encapsulated by a cover glass and UV-curable resin purchased from Ossila Ltd. Finally, all of the devices were subjected to post-deposition annealing treatment. The samples without ZnO ETL were annealed at 150°C for 10 minutes in ambient atmosphere, whereas for the devices with ZnO ETL an optimal annealing temperature of 120°C was found.

2.2. Device characterization
The J-V curves were measured with Keithley 2400 source meter under illumination and in the dark. A halogen lamp was used for the measurements under illumination providing standard illumination 100 mW/cm² and a Si photodiode was used as a reference for the sample illumination. The quantum efficiency measurements were performed by a computer controlled system including a Digikrom 240 monochromator, a lock-in amplifier, a chopper, a halogen lamp and a Si photodiode used as a reference. The impedance spectra were taken with a FFT impedance spectrometer in the time domain employing a multi-sine perturbation signal with amplitude of 25 mV. The spectra were characterized in the frequency range from 1 mHz to 100 kHz under standard illumination. EIS Spectrum Analyzer software was used for fitting the impedance spectra.

Shelf life stability tests were performed on devices which were kept in ambient environment under the standard testing protocol ISOS-D1 [6] by taking I-V and impedance spectroscopy measurements in regular time intervals for the period of 10 months. The samples were also tested for degradation in real outdoor conditions by exposure to sunlight irradiation for 5 hours per day around midday. This experiment was carried out in July and August 2020 by exposing the samples on the rooftop of the laboratory on sunny days with measured temperatures of the sample holder ranging between 35 and 45°C. During exposure they were kept under open circuit conditions. Their J-V characteristics were taken after every 5 hours of exposure.

3. Results and discussion

3.1. Performance and shelf lifetime
The initial performance of as-deposited devices with sputtered silver electrodes is very poor as we have shown in our previous work [7], but it improves drastically after annealing at temperatures up to 150°C. All of the devices with sputtered Ag contact directly on top of the active layer presented an S-shaped curve that gradually improved with increasing annealing temperature but was still present at 150°C. The S-shape of an I-V curve is usually related to the formation of extraction barrier for carriers at one of the interfaces with the selective contacts. The insertion of ETL resulted in better fill factor and higher open circuit voltage. Figure 1 shows the performance of the two types of devices under
investigation after post-deposition annealing compared to their performance after more than 7000 hours storage in the dark ambient environment. The devices demonstrate good stability with no significant losses in their main I-V parameters. Although the cells with ZnO ETL show superior performance to devices without ETL, both types of solar cells were able to retain their initial parameters when stored in ambient environment suggesting that they had adequate encapsulation and stable electrodes.

Figure 1. I-V characteristics of (a) solar cell without ETL and (b) with ZnO ETL before and after storage in the dark.

3.2. Outdoor degradation study

3.2.1. Current-Voltage measurements. The stability of the organic solar cells was analyzed under real outdoor conditions for 140 hours. Figure 2 shows the change in the I-V characteristics and the evolution of its main parameters with time.

Figure 2. (a) Evolution of the main I-V parameters with time of the exposure to outdoor conditions; (b) J-V characteristics of fresh and aged devices.

It can be seen that both devices experience significant degradation for such a short period and the cells that did not include an ETL degraded at much faster rate with an initial “burn-in” period after the first five hours exposure to sunlight irradiation. In previous works with much more controlled environment of the fabrication process and testing conditions this burn-in period was estimated to last for a much longer time for P3HT:PCBM based solar cells [8]. Here we observe a sharp initial decline in the fill factor and to a smaller extent in Voc and Isc causing the efficiency to drop immediately below 80% of
its initial value. The second phase of the degradation is much slower. As is known light irradiation along with the elevated temperature, enhance simultaneously all the degradation processes in the devices. The decay in the fill factor in encapsulated devices is usually a symptom of interface electrical degradation that causes an increase in the parasitic resistances of the device. The device with ZnO ETL also experiences a decline in the fill factor but it doesn’t turn into S-shape in the course of aging. The normalized data of the external quantum efficiency spectra of both types of solar cells was analyzed before and after the degradation process and no spectral change was observed during the degradation process.

3.2.2. Impedance spectroscopy

Impedance spectroscopy analysis was performed to investigate in detail the change in the resistive and capacitive components of the devices in the course of aging. Figure 3 (a) and (b) shows the Nyquist diagrams in the impedance complex plane for the solar cell without an ETL, obtained before exposure to outdoor conditions at different applied bias under illumination. At low voltages up to 300 mV, a single depressed semicircle was observed and these spectra were fitted using the simple equivalent circuit shown in the inset of figure 3 (a). The parallel resistance in this case decreased with the applied voltage which is in consistency with results of other groups obtained for optimized organic solar cells [9]. A constant phase element (CPE) was used for modelling a non-ideal capacitor in order to account for the distribution of the relaxation times which is thought to be a result of inhomogeneities of the active layer, porosity etc. The CPE element is usually characterized by its impedance as defined in [10], and an equivalent capacitance that can be derived from the average time constant and the resistance parallel to the CPE element [10].

![Figure 3](image)

**Figure 3.** Nyquist plots of a device without ZnO ETL before exposure to sunlight irradiation (a) at low applied voltages up to 300 mV resulting in a single semicircle and fitted with a simple R||CPE circuit shown in the inset; (b) at high applied voltages where an additional feature appears in the low frequency region.

An unusual increase in the parallel resistance was observed in the impedance spectra of fresh devices without ZnO for applied voltage approaching Voc and an additional feature resembling a tail of the main semicircle appeared at very low frequencies (figure 3 (b)). These spectra were best modeled with the equivalent circuit with two CPE elements shown in the inset of figure 3 (b). This model consists of two parallel R||CPE circuits to account for the low frequency feature. The parallel resistance R1 for voltages above 400 mV increased even more with degradation time and the tail of the large semicircle became more pronounced (figure 4 (a)). As the inflection point of the S-shaped I-V curve shifted to lower voltages with degradation time, the onset of the low frequency feature of the impedance spectra also moved to lower voltages and they could no longer be fitted with model A (figure 4 (b)). Although the feature at low frequencies appeared to the Nyquist spectra at voltages below 400 mV (figure 4 (b)), R1 decreased in spectra between 0 and 300 mV for aged devices.
The main parameters were extracted from the fits and an example of their evolution with time is presented in figure 5 for 515 mV applied DC voltage which was the initial Voc of the device. There was a larger uncertainty associated with the CPE2 parameters obtained from the fits but the values were sufficient for qualitative observation of the trend. We observe that Rs in both models which is usually related to a part in the series resistance remains nearly constant and does not change with time. CPE1 has a capacitive character ($n \sim 1$) with equivalent capacitance of about 10 nF and does not change significantly with time and it might represent the geometrical capacitance of the sample. A characteristic effect is that CPE2 has large equivalent capacitance but there is a decreasing tendency of the coefficient $n$ with values between 0.6 and 0.5. Such a low value of $n$ might be due to a significant presence of interfacial inhomogeneities which may cause diffusion and limit the current at voltages around Voc. Interestingly, we did not observe the feature at low frequency in the measured dark impedance spectra which implies that it may be related to a formation of an extraction barrier to the photogenerated carriers.

![Figure 4](image.png)

**Figure 4.** (a) Nyquist diagram (device without ZnO ETL) of impedance spectra above 400 mV after 110 hours exposure to outdoor conditions; (b) Impedance spectrum at 300 mV before and after outdoor exposure showing that the low frequency arc moved to lower voltages with device degradation.

![Figure 5](image.png)

**Figure 5.** The dependence of the resistive and capacitive components of the solar cell without ETL, obtained from fitting with equivalent circuit B with degradation time for 515 mV applied DC voltage.

The impedance spectra of the solar cells with ZnO ETL presented a single semicircle for all the applied DC voltages up to 100 kHz in the complex impedance plane and were fitted with single $R||CPE$ circuit. The trend observed with the variation of the impedance parameters with applied bias was consistent with previous studies explaining the behaviour of optimized organic solar cells (figure 6) [9]. Figure 6 shows the variation of the fitting parameters with degradation time up to 95
hours of exposure. At short circuit conditions, a decrease in $R_p$ is observed with time which is in agreement with the drop in the shunt resistance estimated from the I-V curves, while there were no significant changes in the device $V_{oc}$ for this period and the parallel resistance at 550 mV remains nearly constant.

Figure 6. Dependence of the ac parameters of the solar cell with ZnO ETL on degradation time at (a) short circuit conditions and (b) applied voltage of 550 mV near the $V_{oc}$.

4. Conclusions
We have studied the influence of ZnO nanoparticles as electron transport material on the performance and stability of P3HT:PCBM solar cells with conventional architecture and magnetron sputtered Ag contacts. The insertion of spin-coated ZnO nanoparticles ETL between the active layer and the sputtered Ag electrode in conventional device architecture can considerably increase the performance of these types of devices and improve their stability under real outdoor conditions. ZnO ETL layer effectively prevents the active layer from plasma damage during the sputtering deposition of the silver electrode and in this way it allows sputtering to become alternative method for the deposition of the back electrode of organic solar cells.

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