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Nanoscale mapping by electron energy-loss spectroscopy reveals evolution of organic solar cell contact selectivity

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ABSTRACT

Organic photovoltaic (OPV) devices are on the verge of commercialization being long-term stability a key challenge. Morphology evolution during lifetime has been suggested to be one of the main pathways accounting for performance degradation. There is however a lack of certainty on how specifically the morphology evolution relates to individual electrical parameters on operating devices. In this work a case study is created based on a thermodynamically unstable organic active layer which is monitored over a period of one year under non-accelerated degradation conditions. The morphology evolution is revealed by compositional analysis of ultrathin cross-sections using nanoscale imaging in scanning transmission electron microscopy (STEM) coupled with electron energy-loss spectroscopy (EELS). Additionally, devices are electrically monitored in real-time using the non-destructive electrical techniques capacitance–voltage (*C*–*V*) and Impedance Spectroscopy (IS). By comparison of imaging and electrical techniques the relationship between nanoscale morphology and individual electrical parameters of device operation can be conclusively discerned. It is ultimately observed how the change in the cathode contact properties occurring after the migration of fullerene molecules explains the improvement in the overall device performance.

1. Introduction

Organic photovoltaics (OPVs) devices have witnessed an impressive improvement in power conversion efficiencies (PCE) now reaching 10% for single layer bulk heterojunction (BHJ) solar cells [1]. However, device stability remains one of the key challenges for their commercialization. There are many factors affecting the device stability with moisture, heat and light regarded as the main stress factors [2]. Solution-processed OPVs are usually based on BHJ films of semiconducting polymers blended with a soluble fullerene derivative that form an interpenetrated bicontinuous network [3]. The organic layer harvests sun light and generates charges via charge transfer from the polymer (donor) to the fullerene (acceptor) that are collected at selective electrodes [3]. Performance of OPVs is strongly dependent on the donor/acceptor morphology [4] and variations of the

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internal arrangement of donor and acceptor molecules is considered to be the main source of efficiency decrease limiting their potential commercialization [5].

Numerous studies have focused on the importance of the bulk morphology properties of the organic layer [6,7]. The use of additives [8], solvent annealing [9] and thermal treatments [10] can enhance the crystallinity and would increase the device efficiency. Enhanced crystallinity of the polymer phase have been correlated with high mobility [11] and improved device performance [12]. Importantly, intimately mixed donor/acceptor domains are required to provide optimum surface area to enable efficient charge separation [13]. However, the ability of PCBM molecules to diffuse through the blend film is often regarded as the primary cause of thermally induced degradation of solar cell performance [14]. The link between morphology modification and performance has usually been discussed in terms of the bulk properties of the active layer [15], but very little attention has been paid to the evolving properties of the active layer/outer contact interfaces. For example, molecular orientation of the polymer in intimate contact with the extracting electrode could be limiting the collection ability [16]. Indeed, morphology of the active layer in BHJ solar cells is frequently the result of a meta-stable configuration and several vertical segregation profiles can be formed [17]. Thermodynamically stable morphology blends can be obtained by using high transition temperature (T_g) polymers [18] or by cross-linking the organic phase [19]. In general terms one of the issues that still require intensive work is the understanding of specific mechanisms behind active layer/outer contact interface chemical and morphological evolution and its relationship to device performance.

Several morphology characterization techniques are currently available for organic photovoltaic devices and the reader is referred to two recent reviews [20,21]. For example, advanced techniques such as Grazing Incidence X-ray Diffraction (GXID) [22] or Electron Microscopy [13,23] provide access to the structure and length scales of the donor:acceptor domains. Alternatively, depth profile concentration of donor:acceptor blends can be analyzed by using Dynamic Secondary Ion Mass Spectroscopy (SIMS) [24], Variable-Angle Spectroscopic Ellipsometry (VASE) [17], Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) [25], etc. On the other hand, advanced electrical techniques are also available which allow understanding individual electrical processes taking place in an operating device. Techniques include Transient Absorption Spectroscopy (TAS) [26], Transient Photovoltage (TPV) [26], Capacitance–Voltage (C–V) [27] or Impedance Spectroscopy (IS) [28]. Interestingly electrical characterization offers the possibility to measure devices using non-destructive methods that enable real-time monitoring.

In this work a case study is created based on a thermodynamically unstable organic layer. The morphology evolution is correlated with the individual electrical processes taking place in the device, and revealed by compositional analysis of ultrathin cross-sections using spatially resolved electron energy-loss spectroscopy (EELS) in the analytical scanning transmission electron microscope (STEM). Additionally, devices are electrically monitored in real-time using the non-destructive electrical techniques C–V and IS. By comparison of imaging and electrical techniques the relationship between morphology and photovoltaic parameter evolution in operating devices is conclusively established. It is ultimately observed how the change in the cathode contact properties occurring after the fullerene molecules migration explains the improvement in the overall device performance. The formation of a PCBM-rich layer contacting the ZnO electron-selective layer at the cathode causes both the increase in electron selectivity and establishes a good electrical connection between ZnO and the inner active layer fullerene molecules.

2. Results

2.1. Materials and solar cells fabrication

The method to produce the solar cells is based on standard processing conditions used in the literature [29,30]; full details can be found as Supporting Information and a brief description is provided here. Devices were prepared in the inverted configuration ITO/ZnO/P3HT:PCBM/MoO_3/Ag. Pre-cleaned patterned ITO was coated with commercially available ZnO nanoparticles to provide film thickness of about 50 nm. Substrates were heated at 100 °C for 5 min followed by a further treatment in the glovebox at 130 °C for 10 min. Spin coated P3HT:PCBM films (~100 nm) were thermally treated at 130 °C for 10 min. Device fabrication was completed by thermal evaporation of MoO_3 (10 nm) and Ag (100 nm). Ten independent devices (4 pixels each) were encapsulated with epoxy and a glass slide for electrical characterization. Devices were kept in the glovebox in the dark at all times excluding the time required for electrical characterization (<15 min). Some un-encapsulated devices were kept in the glovebox for the whole period of the test to characterize the final state of the device using STEM measurements.

2.2. Film and device characterization

Cross-sections of devices were prepared by focused-ion-beam milling using a Helios NanoLab DualBeam (FEI) to a thickness of ~45 nm [31]. For morphological studies of the cells cast from $CHCl_3$ and to prevent degradation or morphological changes due to storage of the ultrathin cross-sections, STEM investigations were conducted on the same day of FIB preparation. These were done with a Titan QU-Ant-EM microscope (FEI), operated at 120 kV and equipped with a GIF Quantum energy filter (Gatan). STEM dark-field imaging was used for visualization of the integrity of organic and inorganic layers. The pixel size for these images is 0.8 nm, which is sufficient to show the structure the ZnO layer. Afterwards hyperspectral STEM–SI data sets were acquired across all functional layers at a spatial resolution of 1.3 nm. Electron energy-loss spectra contain contributions from elastic and inelastic scattering up to 90 eV energy-loss, using a dispersion of 0.05 eV/pixel. The applied electron dose for dark-field and hyperspectral images was in total ~300 e/A^2, which was shown to damage the electronic structure of the functional, organic materials but not the bulk plasmon