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Morphological and micro-structural interface characterization in multilayer inverted polymer-fullerene bulk heterojunction solar cells

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ABSTRACT

Inverted polymer solar cells based on P3HT/PCBM bulk heterojunction were prepared on flexible polyethylene naphthalate (PEN) substrate. The effect of annealing of the PEN/ITO/ZnO multilayer and ZnO/P3HT:PCBM on the structural, morphological, photophysical and photovoltaic properties was investigated and scrutinized directly on the OPV devices using atom probe tomography (APT), scanning electron microscopy (SEM) and microfocus X-ray techniques. We carried out a 3D reconstruction of the interfaces of the multilayer containing PEN/ITO, ZnO/ITO and P3HT:PCBM/ZnO to address the interface micro-structure and its influence on the morphology of the photoactive film. The analyses show that the morphology of the interfaces is affected by the structure of each layer of the BHJ devices causing orientation of P3HT crystals with PCBM aggregates and ZnO, which in turn leads to a significant change of the charge transport across each layer and therefore photovoltaic performances.

1. Introduction

Flexible electronics holds a great promise for the development of future electronic devices [1,2]. However, there are technological barriers which have still to be overcome for spreading their integration. The progress of power conversion efficiency (PCE) record is stimulated by the synthesis of new donor and acceptor materials, implementation of new interfacial materials and also the analysis and control of each interface in the bulk hetero-junction (BHJ) structure [3]. The interfaces between organic polymers, metals and interfacial layers are often problematic since an interface with a barrier height of a few tens of mV can result in significant charge build-up and therefore significant loss of recombination and photovoltaic performance. In addition, the inevitable potential loss due to the shift of the energy level at the interface between the donor and the acceptor renders the electrode contacts critical factor to derive the net potential out of the BHJs. Therefore, the interface between the BHJ and both the anode and the cathode is of critical importance for charge transport and the extraction process, which determines device performance and long-term interfacial stability. Quantitative analysis of these interfaces is one of the keys to controlling the processing parameters, structure and performance of the final device. However, the interfacial analysis is challenging due to the complex chemistry of these interfaces. We note that nano-SIMS [4] is an interesting technique, which provides chemical details, whereas good-resolution imaging can be obtained in the energy-filtered transmission electron microscopy (EFTEM) [5]. However, laser-pulsed atom probe tomography (APT) combines sub-nanometer resolution with chemical sensitivity across the organic/inorganic interface. Furthermore, APT technique offers extensive capabilities for both 3D imaging and chemical composition measurements at the atomic scale. Contrary to EDS, TEM or STEM techniques which do not allow to characterize accurately light elements. Indeed, APT technique can detect and quantify all elements (even hydrogen) present in the analyzed material in the device structure with high sensitivity (about 50 ppm) with accurate 3D chemical constructions. Considerable efforts have been devoted to the analysis and elucidation of the problems caused by interfaces since the

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evolution of polymer solar cells, but it is only recently that it begins to evoke the morphology and the modification of the structure of each layer of the BHJ devices, and its impact on photovoltaic efficiency. Other studies were focused on the vertical phase morphology and its transport process and charge collection in the case of the BHJ is sandwiched between the two electrodes [6]. Indeed, the effect of the interface property on the morphology of the photoactive film has gained immense attention, mainly in the methods on controlling the vertical composition gradient D/A and the alignment of the energy at the BHJ/electrode/substrate interfaces. On the other hand, the use of flexible substrates is limited by the temperature window of annealing. Generally, two synthetic aromatic polyesters, polyethylene terephthalate (PET) and polyethylene naphthalate (PEN)] were previously used for flexible solar cells [3]. In addition, polyimides (PI) were often used as a polymer substrate, which has several advantages such as very high glass transition temperature (about 350 °C) and a competitive permeability compared to other substrates [6,7]. Unfortunately, PI is not transparent, which is important for solar cells. Sderstrm et al. [8] have textured the substrate by depositing a back reflector consisting of silver and zinc oxide in order to promote light scattering into the active layer. In addition, Ferekides et al. [9] have developed flexible foil substrates for CdTe thin film solar cells based on flexible stainless steel (SS) substrate. However, in order to reach high device efficiencies on flexible substrates, further studies on the appropriate processes and materials used in the inverted organic solar cells are needed [9,10]. Here, we use poly (ethylene-2,6-naphthalate) (PEN) as a substrate which cannot be heated above its glass transition temperature of 125 °C. However, its working temperature spans up to 155 °C [11] and PEN has a very strong resistance to many diluted acids and solvents. On the other hand, permeability and thermal stability (melting temperature of 256 °C) of this aromatic polyester reduce the thermal distortion at the interface and must therefore maintain the integrity of the ZnO (cathode interfacial layer)/ITO(electrode) multilayer and the performance of photovoltaic devices. A detailed study on the impact of the quality of PEN flexible substrate on the morphology of the layers deposited beyond its thermal stability window as well as the interfaces in the layers stack of inverted organic solar cell is necessary.

In this paper, we use atom probe tomography (APT), scanning electron microscope (SEM) and microfocus X-ray scattering techniques to analyze the interfaces directly in the OPV device and to obtain a 3D reconstruction of each of the interfaces in a multilayer containing PEN/ITO, ZnO/ITO and P3HT:PCBM/ZnO. In fact, the multilayer PEN-substrate /ITO/ZnO was annealed at a relatively low temperature limited by the polymer thermal stability. Its chemical and thermal stability as well as its crystalline structure was analyzed as a function of annealing temperature (160 and 180 °C). To this end, we study and explore the crystalline order in poly(3-hexylthiophene) (P3HT) that has a direct impact on the performance of the OPV device. The performance of the polymer supported solar cells is compared with the one on the rigid substrates (glass) which have been heat treated in the same way. Finally, additional photoluminescence (PL) analysis is used to explore the photophysical properties at the both interfaces (ZnO/P3HT and ZnO/P3HT:PCBM) and the charge transport across active/electron selective layers. This study shows that the thermal activation and expansion through the PEN substrate caused structural and electronic modification of the interfaces in PEN/ITO/ZnO and ZnO/P3HT:PCBM multilayers and therefore the performance of organic photovoltaic devices.

2. Experimental

2.1. Material and device elaboration

The fabrication process of the organic solar cells (OSC) is detailed hereafter. PEN / ITO (Indium tin oxide) substrates (20 × 20 mm^2, ≤ 15 Ω/sq.) (PECF-IP-Peccel Technologies, Inc.) were first cleaned in an ultrasonic bath with detergent, acetone and isopropyl alcohol and deionized water (DI water). UV ozone cleaning was further performed for 30 min. The ZnO target (from Neyco Co.) utilized for sputtering had a 99.999% purity. ZnO films were deposited on PEN/ITO substrates by RF magnetron sputtering under different deposition conditions such as working pressure, substrate temperature and deposition power [11,12]. The deposition was carried out in Ar atmosphere at a pressure of $10{\cdot}10^{-3}$ mbar and a constant RF power of 100 W. The substrate temperature was around 40 °C. The ZnO thickness was about 54 nm. After ZnO deposition, one PEN/ITO/ZnO stack (as-prepared sample) was annealed in a quartz tube under a continuous oxygen flow for 1 h, at different temperatures, between 160 and 180 °C. One as-prepared sample was not annealed and served as a reference. The rest of the stack (P3HT:PCBM/MoO_x/Ag) was deposited in identical conditions for all samples. The photoactive layer was deposited on ZnO using spin-coating technique from a P3HT: PCBM poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester(PCBM) solution (1:1 wt ratio in dichlorobenzene) to form a 120 nm-thick layer. The P3HT (98.5% regioregular from Sigma Aldrich GmbH) and the PCBM ($PC_{61}BM$ from Nano-C) were used as received without further purification. The PEN/ITO/ZnO/ P3HT:PCBM stacks were then annealed at 140 °C for 15 min under nitrogen atmosphere (in glove box). Finally, MoO_x (99.99% from Sigma-Aldrich GmbH) and silver (Ag) were deposited sequentially through a shadow mask by thermal evaporation in vacuum at $2{\cdot}10^{-6}$ Torr. The structure of the cells developed in this study is shown schematically in Fig. 1. The thickness of MoO_x and Ag are found to be around 5 and 120 nm, respectively. Device active area was about 9 mm^2. For comparison the OSC devices were also prepared using rigid substrate and following the same procedure, based ITO-coated glass substrates from Przisions Glass & Optik GmbH, Germany (CEC20S, ≤ 20 Ω/sq., 20 × 20 mm^2).

2.2. Device characterization

X-ray diffraction (XRD) was performed using a Rigaku SmartLab diffractometer (200 mA, 45 kV) equipped with a Ge (220) × 2 monochromator and using $CuK_\alpha 1$ incident radiation (λ = 0.154056 nm). Symmetric ω - 2θ scans were done on the OSC devices.

Synchrotron-based micro-focus X-ray diffraction (SR-μXRD) measurements were carried out at the ID13 beamline of the ESRF. The monochromatic X-ray beam with the wavelength of 1.0 Å was focused

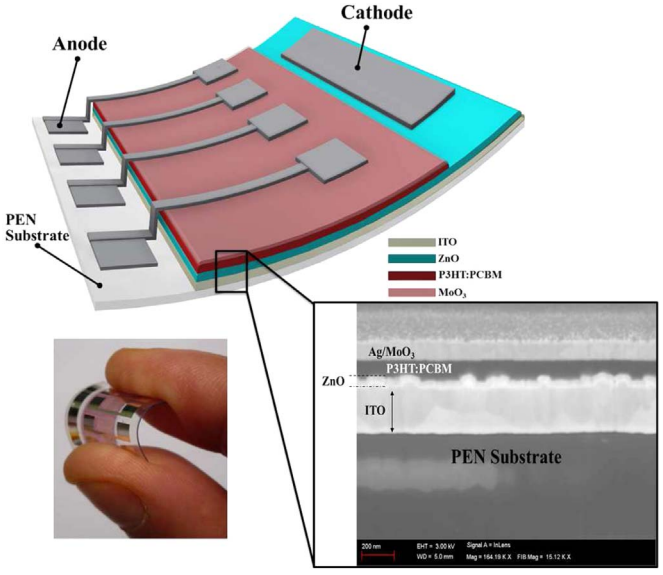

Fig. 1. Schematic illustration of inverted organic solar cell (OSC) with cross-section scanning electron microscope (SEM) image for non-annealed stack (PEN/ITO/ZnO/P3HT:PCBM/MoO_x/Ag).