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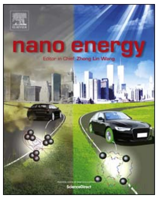

Full paper

Energy band alignment in *operando* inverted structure P3HT:PCBM organic solar cells

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ABSTRACT

Inverted structure thin-film organic solar cells (OSCs) are becoming increasingly important as they deliver higher power conversion efficiency and demonstrate better long-term stability than conventional devices. However, the energy band alignment and the built-in field across the device, which are crucial in understanding the device operation, is yet to be directly characterized. Here we present a direct visualization of the energy level alignment in *operando* inverted structure poly(3-hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) OSCs using cross-sectional scanning Kelvin probe microscopy. The raw data of measured energy level alignment appear to be inconsistent with each other, and sometimes can even be contradictory to the device polarity observed in current density-voltage measurements. It is identified to be caused by the tip/cantilever induced convolution effect, which may severely mask abrupt energy level offsets at the thin electrode interlayers. A numerical deconvolution method is devised to quantitatively recover the energy level alignment across the device, and reveals the non-uniform electric field distribution in photoactive layer.

1. Introduction

Inverted structure organic solar cells (OSCs), with holes extracted from the top electrode and electrons from the bottom electrode, have the reverse polarity from conventional structure OSCs. In spite of the relatively short history of development, inverted structure devices are becoming increasingly important due to their high power conversion efficiency (PCE), good long-term device stability and the adaptability to tandem device structures [1–5]. The energy band depth profile of inverted structure devices has its unique features compared to that of conventional structure devices. The thin electrode interlayers in the inverted devices are expected to introduce abrupt energy level offsets in the depth profile. Substantial research efforts have been made to analyze energy levels at the active layer/interlayer interface, and the results demonstrated that interfacial doping/dipole is one of the most important factors that lead to non-uniform electric field distribution and determine the charge carrier transport [6–10]. However, characterizations of the energy band depth profile across the entire inverted structure devices are still rarely seen in literature. One such effort actually reported an energy band depth profile whose direction of the built-in field was opposite to the device polarity measured from *J-V* curves [11]. These conflicting results require direct measurements for clarification.

Cross-sectional SKPM is a powerful tool in measuring vacuum level (VL) depth profile in thin-film devices [11–15]. We have previously used this technique to visualize the energy level alignment in *operando* conventional structure OSCs [16]. It was discovered that the finite tip size and the cantilever beam crosstalk result in a convolution effect, which causes an apparent smoothing and averaging in measured surface energy depth profiles [17–19].

Here we further present an improved *in-operando* cross-sectional SKPM study on inverted structure poly(3-hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) OSCs (Fig. 1) to reveal the true energy band alignment and built-in field distribution. It is observed that the same tip/cantilever convolution effect is highly significant in inverted structure device measurements, to a degree that under certain conditions that the abrupt energy level offsets introduced by interlayers could be completely masked and the measured VL profile

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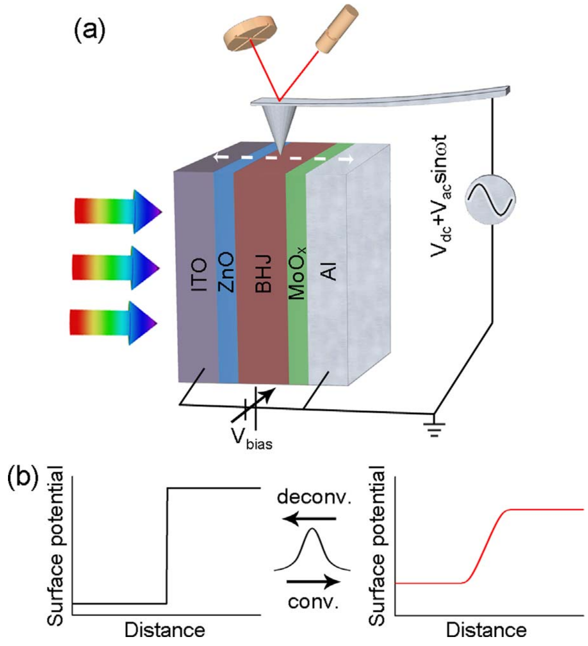

Fig. 1. (a) Schematic illustration of SKPM measurements of the vacuum level depth profile of *operando* cross-sectional devices. (b) The SKPM measured profiles are the convolution of the true profile and the tip transfer function. The true profile can be recovered via numerical deconvolution.

may appear to be contradictory to the device polarity. To resolve this issue, a deconvolution process including a calibration on a molecular beam epitaxy (MBE) grown GaInP/GaAs reference sample and a numerical deconvolution calculation is devised to negate the tip and cantilever induced convolution effects in SKPM. The true energy band alignment in inverted OSCs has thus been recovered for the first time. The results confirm that the work function of the interlayers and interfacial effects are critically important in determining the energy level alignment and leading to a non-uniform electric field across the active layer in inverted structure OSCs.

2. Experimental section

2.1. Device fabrication and characterization

The inverted structure OSCs with a stacking of ITO/ZnO/P3HT:PCBM/MoO$_x$/Al were fabricated by sequentially cleaning pre-patterned ITO glass substrates (15 Ωsq^{-1}) using ultrasonication for 10 min in a detergent, deionized water, ethanol, acetone and isopropyl alcohol, followed by treatment with oxygen plasma for 10 min. Then, ZnO nanocrystal solution synthesized according to our previous reports was spin-coated onto ITO substrates and annealed at 150 °C for 20 min [20]. The P3HT (1-Material Inc.): PCBM (American Dye Source Inc.) blend (36 mg/ml, 1:0.8 w/w) was dissolved in 1,2-dichlorobenzene and stirred at 60 °C for 14 h in a glove box. The blend active layer was prepared by spin-coating at 600 r.p.m. for 60 s, and annealed at 130 °C for 10 min. A 20-nm or 80-nm MoO$_x$ layer and 100-nm Al layer were subsequently evaporated under a pressure of 4×10^{-4} Pa through a shadow mask to define the active area of the device (0.12 cm^2) and to form a top anode.

The *J–V* characteristics of the devices were recorded using a Keithley 2635 A source meter (Keithley Instruments Inc., Cleveland, OH, USA) under one sun, AM 1.5 G irradiation (100 mW cm^{-2}) from a solar simulator (Newport 67005, Newport, Irvine, CA, USA). The illumination intensity was calibrated using a reference cell (Oriel 91150V). The light-soaking effect was checked by applying a UV filter, which was not significant here [21,22]. External quantum efficiency (EQE) spectra were measured by a Merlin (Model No. 70104) Digital Lock-in Radiometry System using a 300-W xenon lamp and a 74125 Oriel Cornerstone 260 1/4m monochromator with order-sorting filters (Newport). The light intensity at different wavelengths was modulated through an aperture and calibrated using a 70714 UV-enhanced Si photodiode (Newport). All of the measurements were performed under ambient atmosphere at room temperature.

2.2. MBE reference sample

GaInP (Ga:In 0.51:0.49 for lattice match)/GaAs heterojunction on p^{++} GaAs wafer was grown by a Veeco GEN20A dual-chamber all solid-state MBE equipped with valved phosphorous and arsenic cracking cells. The typical growth rate of GaAs and GaInP was 1 µm/h, and the growth temperatures of the GaAs and GaInP were 580 °C and 510 °C respectively. Be was used as p-type doping source and doping concentration was 2.2×10^{18} cm^{-3} in GaAs and 8.0×10^{17} cm^{-3} in GaInP. The group-III mole fraction (In and Ga in this case) was calibrated by a combination of beam flux gauge and X-ray diffraction (XRD) measurements to satisfy lattice match.

2.3. Device cross-section preparation and characterization

The device cross-section was fabricated using an Ilion$^+$ 693 System (Gatan Inc.). A freshly mechanically cleaved device was mounted into the vacuum chamber (6.4×10^{-5} Torr) and cooled using liquid nitrogen. Then, the device was milled by argon ions using a beam voltage of 5 keV and a beam current of 10 µA for ~ 2 h. Five cross-section samples were prepared for thin interlayer and thick interlayer devices respectively, the error bars of PCE before and after cross section preparation, and after SKPM measurement are listed in Table S1. Stability of typical cross-sectioned devices was tested under continuous light illumination in the glove box.

The morphology of the device cross section was characterized using FEI Quanta 400 FEG SEM (FEI Corp., Hillsboro, OR, USA). The SKPM surface potential (SP) profile measurements of device cross-sections were carried out using a Park XE-120 AFM (Park Systems Corp., Suwon, Korea) using Cr/Au-coated conducting tips (NSC18, Mikromasch, Tallinn, Estonia) with a resonance frequency of ~ 80 kHz and a spring constant of ~ 2 N m^{-1}. Amplitude modulation (AM) mode SKPM [23,24] was carried out in a nitrogen gas filled glove box. During the first pass, standard AC mode imaging (typical tip oscillation amplitude 20 nm) was performed to acquire the topography and phase signal of the sample; in the second pass, the tip was lifted up by a certain height (typically 10 nm) and scanned on the basis of the topography line obtained from the first pass. An AC voltage (3 V in amplitude and 10 kHz in frequency) was applied to actuate the cantilever, and the DC voltage applied to the tip that nullifies the tip-sample interaction was collected as the SP signal. The VL profile can be obtained by multiplying the measured SP profile with the absolute electron charge (at least 10 scan lines are included for averaging) [25,26]. Fig. 1a shows the configuration of device-wiring during cross-section characterization. The Al electrode was grounded. The ITO electrode was connected with the Al electrode in short-circuit; open-circuit conditions were simulated by disconnecting the wire between the two electrodes. A full-spectrum optical fiber was used to transmit AM 1.5G solar simulator light to illuminate the device from the ITO glass side. Bias voltage was applied via a tunable voltage source between the electrodes.

2.4. Numerical convolution and deconvolution simulation

Numerical simulations were performed using Wolfram Mathematica 10 with home-written codes. The SKPM measurements were simulated as a convolution of the true SP profiles and the tip transfer functions with noise. Tip transfer functions were obtained by adjusting the σ and A parameters to make the simulated (i.e. convoluted) profile of a