SUPPORTING INFORMATION

Band Bending in Conjugated Polymer Films: Role of Morphology and Implications for Bulk Charge Transport Characteristics

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1. **Preparation of spin-casted and matrix-assisted pulsed laser evaporation (MAPLE)-deposited samples**

All substrates were cleaned by ultrasonication in an Alconox® detergent solution, DI water, acetone, hot Hellmanex® solutions and 2-propanol for 5 minutes each, followed by UV-ozone treatment for 20 minutes. Kelvin probe force microscopy (KPFM) and current extracted by linearly increasing voltage (CELIV) measurements were performed on polymer films on indium tin oxide (ITO)/glass substrates coated with a layer of poly(3,4-ethylenediosythiophene): polystyrene sulfonate (PEDOT:PSS).

Poly(3-hexylthiophene) (P3HT) (Reike Metal, ~95% regioregularity, M_w = 50,000 g/mol) solutions were prepared by dissolving the polymer in 1,2-dicholorobenzene (DCB). Solutions were allowed to mix overnight before being filtered with 0.45 µm polytetrafluoroethylene (PTFE) filter. To make the spin-casted films, filtered solutions were spun onto prepared substrates at 600 rpm for 2 minutes.

MAPLE deposition was performed with a system purchased from PVD products with a Er:YAG laser (Quantel) of 2.94 µm wavelength. An emulsion-based approach[1] was utilized in which the P3HT was dissolved in DCB and then mixed with benzyl alcohol and deionized water that contained 0.0005 wt % sodium dodecyl sulfate surfactant at a ratio of 1:0.3:3. To create an emulsion, the mixture was ultrasonicated until visibly homogeneous. The emulsion was then placed in a cooled (-170 °C) target cup, and upon freezing, the chamber was pumped to a high vacuum condition ($< 2 \times 10^{-5}$ Torr). ITO/PEDOT substrates were placed 5.5 cm above the target cup, and both the target cup and the substrates were kept at constant rotation during deposition. The laser fluence was maintained at ~1.3 J/cm^2 at a repetition rate of 5 Hz as it rastered across

the frozen emulsion surface. The deposition time was varied to achieve varying thicknesses of P3HT films. Thicknesses of the samples were confirmed with spectroscopic ellipsometry.

2. Work function measurement by Kelvin probe force microscopy (KPFM)

KPFM measurements were performed using Pt-coated Si probes made by Nanosensors (stiffness ~0.5-1 N/m, resonant frequency ~75 kHz) on an Asylum Research MFP3D atomic force microscope. Most measurements were made in air with 10-30% humidity. KPFM acts as a double-pass, intermittent contact technique. First, the sharp metallic tip raster-scans across the surface of interest, measuring the topography. During the first pass, the cantilever is driven at its first harmonic resonance frequency, and the amplitude of this mechanical oscillation is used as the feedback signal. In the second pass, which follows the same path as the first pass, an AC bias at the first harmonic resonance frequency of the cantilever is applied to the tip that generates oscillating electrical forces between the tip and sample. The mechanical oscillations of the cantilever are set to zero and the tip is lifted to a set height ("lift height"). This distance is between 10-20 nanometers, which captures the electrostatic interactions but remains far removed from short-range VDW forces. A lock-in amplifier is employed to extract the electrical force component with the first harmonic frequency and apply a DC bias until this oscillation is nullified. These oscillations are continually nullified as the tip follows the second pass, providing a local map of the surface potential.

Shown theoretically, an AC bias, applied to the tip during the second pass, leads to an electrostatic force between the tip and sample that is given by:

$$F_{el} = -\frac{1}{2}\Delta V^2 \frac{\partial C(z)}{\partial z},$$ (1)

where z is normal to the sample surface, ΔV is the voltage difference between the tip and the contact potential difference and dC/dz is the capacitive gradient between the tip and sample. The voltage difference can be written as:

$$\Delta V = V_{tip} - V_{CPD} = (V_{DC} - V_{CPD}) + V_{AC}\sin(\omega t)$$, (2)

where $V_{DC} + V_{AC}\sin(\omega t)$ is the voltage applied to the tip and V_{CPD} is the contact potential difference voltage. By plugging equation (2) into (1), the electrostatic force is given by:

$$F_{el} = -\frac{1}{2}\frac{\partial C(z)}{\partial z}[(V_{DC} - V_{CPD}) + V_{AC}\sin(\omega t)]^2$$. (3)

This electrostatic force can be separated into three components – one static, one dependent on the first harmonic (ω) and one dependent on the second harmonic (2ω). The component dependent on the first harmonic, sought with KPFM, is given by:

$$F_{\omega} = -\frac{\partial C(z)}{\partial z}(V_{DC} - V_{CPD})V_{AC}\sin(\omega t)$$ (4)

Equation (4) shows, if the DC bias is applied to match that of the CPD, $F_{\omega} = 0$ and electrical oscillations of the tip will be nullified. In this way, the applied DC bias is equal to that of the CPD and this value can be acquired across the surface of the sample. The V_{CPD}, as first seen in equation (2), is defined as:

$$V_{CPD} = \frac{\varphi_{tip} - \varphi_{sample}}{-e},$$

(5)

where φ_{tip} and φ_{sample} are the work functions of the tip and sample, respectively, and $-e$ is the elementary charge. As equation (5) shows, the work function of the tip must be known to find the absolute work function of sample. This is accomplished through the use of highly ordered pyrolytic graphite (HOPG), which has a well-defined work function of 4.6 eV.

3. **Out-of-plane mobility measurements by current extracted by linearly increasing voltage (CELIV)**

The out-of-plane carrier mobility measurement was conducted on samples of ca. 100 nm thickness. The triangle voltage for the CELIV measurement was created by a BK Precision 4075 function generator and the responded current was amplified using a FEMTO amplifier before being recorded by a Tektronix digital oscilloscope. All of the mobility measurements were carried out in a vacuum cryostat (Janis Inc.) at specific temperatures controlled by a temperature monitor (LakeShore Cryotronics). In a CELIV measurement, there are two major contributions to the responded current: the displacement current $j(0)$ due to the geometric capacitance of the sample and the drift current $\Delta j = j - j(0)$ resulting from the extraction and flow of free charge carriers within the film. The hole mobility μ in a CELIV measurement is calculated using the following relation[2]

$$\mu = \frac{2h^2}{3At_{max}^2 (1 + 0.36\frac{\Delta j}{j(0)})}$$

Here, h is the film thickness, A is the voltage ramping rate and t_{max} is the time at which the current reaches the maximum value. The electric field dependence measurement at each temperature was performed by changing the ramping rate, A (electric field, $E = At_{max}/h$).

REFERENCES

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