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Direct Writing of a Conducting Polymer with Molecular-Level Control of Physical Dimensions and Orientation

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Achieving the highest performance in organic electronic devices requires nanometer-scale control of the organic film structure.[1,2] For instance, field-effect mobilities in organic field-effect transistors depend strongly on the molecular ordering both within the organic film and with respect to the substrate. Although small organic molecules can be reliably deposited with nanoscale thickness control,[3] the fabrication of polymer nanostructures remains a significant challenge due to the large number of conformational degrees of freedom found in polymers. Conventional polymer deposition methods, such as spin-coating and vapor deposition, cannot control the polymer nanostructures, hampering improvements of polymer-based electronic devices. Herein we report a new technique for polymer deposition, thermal dip-pen nanolithography (tDPN),[4] that can write molecularly ordered polymer nanostructures with exquisite control of both physical dimensions and orientation. Using tDPN, we deposited poly(3-dodecylthiophene) (PDDT) nanostructures on silicon oxide surfaces with lateral dimensions below 80 nm and monolayer-by-monolayer thickness control from a single molecular monolayer (~2.6 nm) to tens of monolayers.

In tDPN, a custom-made atomic force microscope (AFM) cantilever with an integrated tip heater is precoated with an "ink" that is solid at room temperature. The ink is then precisely deposited onto a substrate surface when the tip temperature is set close to the ink's melting temperature. The tDPN tip may be reproducibly heated within milliseconds up to 1000 °C,[5] well above the melting temperature of PDDT ($T_m = 120$ °C[6,7]). PDDT (Scheme 1a) belongs to a class of conducting polymers, poly(3-alkylthiophene)s (P3ATs), that show great promise as active elements in organic electronics.[2,8] These polymers are chemically stable, soluble in common solvents, and easily processible.[8] Most importantly, they have shown some of the highest field-effect mobilities among conducting polymers (as high as 0.1 $cm^2\ V^{-1}\ s^{-1}$).[1,9] Note that, to achieve such high mobilities, a high degree of molecular order is required in the film and at the interface between the film and the gate oxide (SiO_2).[1]

Figure 1a demonstrates that a PDDT monolayer covering several square micrometers with relatively few defects can be easily deposited on room-temperature SiO_2 by raster-scanning a PDDT-coated tip heated to 134 °C, above PDDT's T_m but less than its degradation temperature of 175 °C.[10] (See Supporting Information for details on tip preparation.) Moreover, a subsequent scan over the first layer forms a second monolayer without disturbing the first one. A narrow third monolayer was also formed. The uniformity of the layers is manifested in the average height profile (Figure 1a). An analysis of the roughness (not shown) reveals that the roughness of the first two monolayers was comparable to (or less) than that of the substrate ($r_{rms} = 0.22$ nm), suggesting a high degree of uniformity and order with the film.

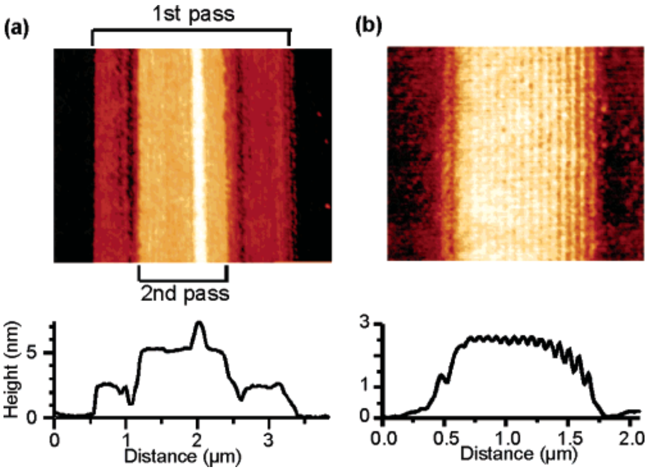
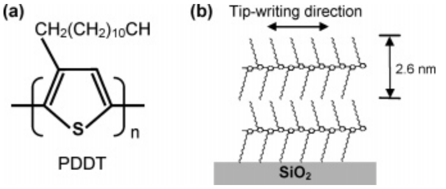


Figure 1. Tapping-mode AFM images of PDDT films deposited on SiO_2. The PDDT-coated tip was raster scanned from the top right to the bottom left at 5 μm/s with 47 nm per line while it was heated at (a) 134 and (b) 117 °C. In (a), the outer square resulted from the first pass, which deposited a single monolayer. After 50 s, the second pass deposited a second monolayer without disturbing the first. Below is the average height for each of the scan lines. In (b) is shown the alignment of polymer strands parallel to the tip-writing (fast scan) direction. Below is the average height for each of the scan lines.

Scheme 1. (a) PDDT and (b) First and Second Monolayers of PDDT on SiO_2



The thicknesses of the first three monolayers in Figure 1a are 2.4, 2.7, and 2.2 nm, respectively. These thicknesses correspond closely to the PDDT interlayer spacing of 2.6 nm found in X-ray diffraction studies[6] of P3AT films. In these studies, the P3AT films were composed of submicrometer-size crystalline domains embedded in an amorphous matrix, with each crystalline domain having a lamella structure with $\pi-\pi$ interchain stacking stabilizing two-dimensional sheets. On the basis of the thickness of the discrete layers, we conclude that our PDDT structures are composed of molecularly ordered, bulk-like lamella with the alkyl groups oriented perpendicular to the substrate (Scheme 1b). Note that this is the preferred orientation of the polymer to achieve a high field-effect mobility.[1] Although there have been several recent reports of scanning probe deposition of conducting polymers,[11−15] to our knowledge, our results are the first demonstration of nanoscale deposition of *molecularly ordered* polymer nanostructures with controlled thicknesses.

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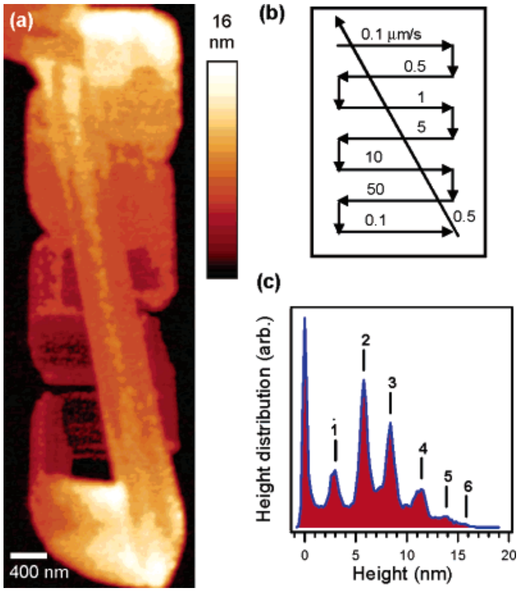

Figure 2. (a) Tapping-mode AFM image of a PDDT film deposited on SiO_2 at 134 °C. (b) The writing pattern with the respective v_{tip} (μm/s). The v_{tip} for vertical lines was 1 μm/s. (c) Height distributions of the PDDT nanostructures. The numbers represent the number of monolayers.

Depositing a single monolayer allowed us to investigate further the two-dimensional structure of PDDT self-assembly (Figure 1b). During this raster deposition, the tip temperature, 117 °C, was slightly below the PDDT melting temperature, but higher than its glass transition temperature, ~50 °C (and hot enough to initiate writing). These conditions create aligned polymer bundles 73 ± 4 nm wide, equivalent to the width of ~190 PDDT strands. The bundles are much narrower than the average length of a PDDT strand (~500 nm), suggesting that the deposited polymer strands are aligned parallel to the fast-scan direction (Scheme 1b), possibly aided by mechanical combing[16] by the tip. Additional evidence of anisotropic alignment during single-pass deposition (with less combing) can be found in the Supporting Information. Anisotropic alignment of polymer strands can significantly improve electronic or optoelectronic devices. A recent study by Hoofman et al.[17] showed that the one-dimensional intrachain charge carrier mobility of an isolated conducting polymer is more than 3 orders of magnitude higher than that in bulk. Scanning tunneling microscopy analysis, currently underway, should further elucidate the structure and electronic properties of these highly ordered structures.

The thickness and morphology of the written structures are dependent on the writing speed and tip temperature. To study their dependence on the writing speed, a serpentine pattern was written at various writing speeds v_{tip}, ranging from 0.1 to 50 μm/s, while the tip temperature remained constant. A representative AFM image of a pattern written on a SiO_2 substrate at 134 °C is displayed in Figure 2a, with the corresponding height histogram shown in Figure 2c. Notice that the polymer is deposited in *discrete layers* (a total of six are observed in this pattern), similar to those observed during epitaxial film growth, with an average layer thickness of 2.6 ± 0.24 nm. At this tip temperature, multilayered structures are deposited at the lowest v_{tip} (0.1 μm/s), a single layer is formed from 5 to 10 μm/s, and a discontinuous pattern of single-layer islands is deposited at 50 μm/s.

To study the effect of the tip temperature on the thickness and morphology, the pattern writing was repeated for tip temperatures slightly below and above that required for melting the bulk polymer (118 and 150 °C, respectively). At 118 °C, three monolayers are deposited at the slowest speeds, with average thickness 2.8 ± 0.23 nm/monolayer; at 150 °C, up to 14 layers are formed with an average thickness of 2.5 ± 0.32 nm/monolayer (Supporting Information). Multilayer structures can be built up by multiple depositions, as evidenced by the additional layers discretely deposited on the diagonal return path.

Controlling the temperature of the tip provides tDPN unique advantages over conventional DPN.[18,19] The higher deposition rate available allows tDPN to write polymer structures faster than conventional DPN. For example, to obtain a uniform film over a designated area, conventional DPN often requires multiple raster scans over the area.[18] Conventional DPN lines of conducting polymers suffered from discontinuity even at $v_{tip} < 0.5$ μm/s.[14] In contrast, tDPN can deposit a uniform PDDT monolayer in a single sweep at >10 μm/s. Increasing the polymer temperature during deposition may also accelerate the polymer ordering process. Finally, the low vapor pressure of the polymer inks used in tDPN should allow the deposition of polymer nanostructures in ultrahigh vacuum.

In summary, we demonstrate that polymer nanostructures can be directly written by tDPN with unprecedented control. The thickness can be controlled monolayer-by-monolayer, with each monolayer being aligned along the deposition direction and with respect to the surface. Line widths <80 nm are also readily achieved (Supporting Information). The ability to write molecularly ordered polymer nanostructures offers opportunities not only to reliably investigate the intrinsic limit of charge transport in polymer nanostructures but also to integrate polymer-based components directly into conventionally fabricated devices. Finally, the capability of tDPN to control physical dimensions and molecular ordering may hold for other types of macromolecules.

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Supporting Information Available: Experimental procedures; anisotropic orientation of PDDT; height distributions of PDDT patterns at 118 and 150 °C; and a PDDT pattern with line width <80 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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