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Direct-Writing of Polymer Nanostructures: Poly(thiophene) Nanowires on Semiconducting and Insulating Surfaces

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The emerging field of nanotechnology offers possibilities for studying fundamental chemical and physical principles at nanometer size scales, while also providing research avenues to new platform technologies such as nanodevices and nanosensors.[1−3] One current challenge in the nanotechnology area is the fabrication and interconnection of nanodevices on semiconducting surfaces such as a silicon wafer. Conducting polymers are one potential class of materials for this application. Conducting polymers[4−6] are already of widespread interest for applications ranging from electronic devices to mechanical actuators.[7−9] Current photolithography, microcontact printing, template synthesis, and scanning electrochemical microlithography techniques afford conducting polymer microstructures, but these techniques possess significant limitations for patterning structures of $<$100 nm dimensions.[10−13] The capability to direct-write and pattern polymeric materials with interesting electronic and electrooptical properties at the nanoscale creates a number of opportunities since a large variety of monomers/polymers are available. Herein, we use Electrochemical Dip-Pen Nanolithography (E-DPN) to fabricate polythiophene nanostructures on semiconducting and insulating surfaces in the sub-100 nm regime.

Electrochemical Dip-Pen Nanolithography is a new AFM lithography technique.[14] E-DPN, like other DPN techniques, relies on spontaneous condensation to facilitate transport of material from the AFM tip to the surface.[14−18] A chemical/physical process, such as covalent bonding or an electrochemical reaction, then immobilizes the material on the surface. Since the reaction occurs at the AFM tip, material deposition localizes on the patterns traced by the tip. Using DPN techniques, nanostructures composed of organic,[15,18] semiconducting,[14] or metallic materials[14,17] are easily obtained of controlled and well-defined nanometer shape and size. In this report, we electrochemically polymerized 3,4-ethylenedioxythiophene (EDOT) at the AFM tip/substrate interface to create poly-EDOT nanowires. Poly-EDOT is a well-known conducting polymer possessing interesting electrical and electrooptic properties, and of interest for antistatic, electrostatic, and conducting coatings as well as for light emitting diodes.[19,20]

In a typical experiment on a Nanoscope IIIa AFM (Digital Instruments), a highly doped tapping mode AFM tip (Silicon-MDT, dopant concentration 10^{17} atoms/cm^3) is first coated with monomer by immersion in a solution of 1:1 v/v EDOT/$CHCl_3$ and dried. A clean, silicon (111) wafer with native oxide is used as the substrate. To pattern nanostructures, a negative bias voltage is applied between the AFM tip and the surface, the setpoint voltage is reduced to 15% of the original value to reduce the tip-surface separation, and the tip is translated across the surface in a preprogrammed pattern. The applied voltage electrochemically polymerizes the monomer, resulting in tip-defined deposition of poly-EDOT on the substrate (Figure 1). The polymerization mechanism is shown in Scheme 1.

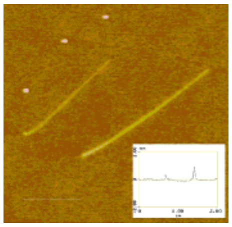
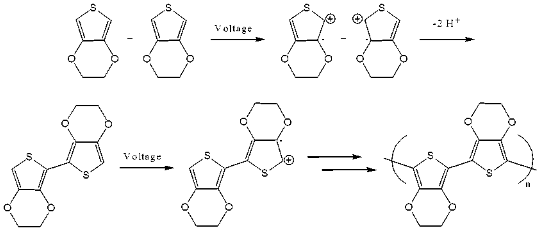


Figure 1. Two polymer lines written at 10 (left) and 1 nm/s (right). The humidity was 28% and the voltage was −12 V. Polymer line width: 50 nm scale bar: 1 μm. Inset: Cross-section of the two lines.

Scheme 1. Oxidative Polymerization Mechanism of Poly-EDOT



Polymeric nanostructure morphology is dependent on the humidity, applied voltage, and translation speed of the tip. The applied voltage depends on the thickness of the oxide layer on top of the Si wafer; patterning on native oxide requires between −9 and −15 V, but higher voltages are required for thicker oxides. Higher voltages afford thicker and broader structures than lower voltages. No deposition of nanostructures occurs without an applied voltage. Slower translation speeds yield thicker features than those fabricated at higher translation speeds. Figure 1 shows two lines fabricated at different translation speeds illustrating that structure dimensions are controlled via the translation speed and the voltage. As shown in the Figure 1 inset, the line patterned at slower translation speed is higher than the line drawn at faster speed. These results are consistent with time and voltage dependent oxidative polymerization of the EDOT monomer to produce poly-EDOT nanostructures.

Since polymerization occurs at a negative voltage, oxidation of the underlying silicon surface may compete with polymerization. To confirm that the deposited nanostructures are composed of poly-EDOT rather than locally oxidized silicon, a number of experiments were performed. First, the polymer nanostructures are resistant to HF etching, whereas HF removes SiO_2 features. The polymer nanostructures can be removed by ultrasonication in nonaqueous solvents such as $CHCl_3$, unlike SiO_2 features. In addition, the deposited nanostructures act as nucleation sites for gold nanoparticle formation. Specifically, in situ reduction of $HAuCl_4$ in the presence of an oxidized Si wafer surface containing a poly-EDOT nanostructure affords a higher density of Au nanoparticles on the poly-EDOT nanostructure than on the SiO_2 surface (see Supporting Information). As expected, thiophene has a higher propensity for binding gold than oxidized silicon, and has been previously used

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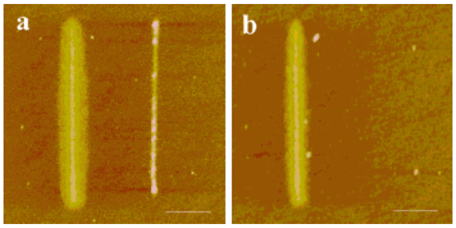

Figure 2. SiO_2 (left-hand line) and polymer (right-hand line) features (a) before and (b) after chemical oxidation with 2:1 H_2SO_4:H_2O_2. The polymer line was fabricated at 10 nm/s, 48% humidity, −12 V. Polymer line width: 30 nm; scale bar: 250 nm.

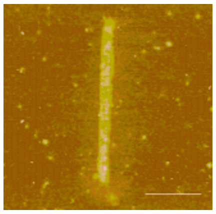

Figure 3. Polymer line patterned on 500 nm thermally grown SiO_2. The line was written at 10 nm/s, 47% humidity, −130 V. Polymer line width: 200 nm; scale bar: 1 μm.

to aid gold nanoparticle formation.[21] Finally, the nanostructures created by E-DPN of EDOT are not resistant to strong chemical oxidation. Figure 2a shows a SiO_2 line created by surface anodization and a line created by E-DPN of EDOT. After treatment with a 2:1 H_2SO_4:H_2O_2 solution (Figure 2b), the line created by E-DPN of EDOT is removed by chemical oxidation but the SiO_2 line remains unchanged, confirming that the two lines are chemically different. *(Note: the H_2SO_4:H_2O_2 solution reacts violently with organic compounds. Caution should be used when handling this solution)* These results are consistent with E-DPN deposition of poly-EDOT. Moreover, this E-DPN technique provides a method for depositing polymer and oxidizing the Si surface simultaneously (see Supporting Information). This opens the possibility of a one-step nanoelectronic device fabrication; the underlying oxide layer serves as a gate oxide while the deposited polymer is the semiconducting/conducting layer. Because constant-voltage conditions are used to deposit the polymer, the amount of surface oxidation and polymer deposition also depends strongly on the tip morphology and the local deposition conditions.

Interestingly, polymer deposition also occurs on insulating surfaces where bulk polymerization will not occur. Figure 3 shows a line written on a Si wafer with a 500 nm thermal oxide. The voltage applied during E-DPN was −130 V. We have not fully established the polymer nanostructure formation mechanism, but our working hypothesis is that deposition may arise from an electric-field-induced polymerization of EDOT at the AFM tip. It is well-known that the electric field at a biased AFM tip is large, since the tip is very sharp (radius of curvature ~5−10 nm). Deposition occurs at the anodic silicon oxide surface, in agreement with previous bulk experiments.[19,20] This is confirmed by the observation that when the polarity of the bias voltage is reversed, no polymer deposition is observed. The identity of the reduced species at the tip is unclear. Further experimental and theoretical efforts are currently underway to determine the mechanism for the polymer deposition.

Patterning poly-EDOT on insulating surfaces provides a means to use this polymer in components for electronic nanodevices such as transistors, diodes, or sensors. Though E-DPN is a serial process and may not be useful for high-throughput applications, it is useful for laboratory-scale nanofabrication. Traditionally, devices are fabricated with expensive equipment (photolithography, E-beam lithography) using multistep procedures (wafer processing, alignment, etc.), but E-DPN is a single-step, easy, and flexible technique for fabricating single devices. Presently, we are combining this E-DPN technique with conventional photolithography and E-beam lithography to test the electrical and electrooptical properties of the deposited polymeric nanostructures as well as to fabricate functional devices.

In summary, well-defined poly-EDOT nanostructures of less than 100 nm dimensions are created on semiconducting and insulating surfaces with E-PDN. The morphology of these polymeric nanowires is controlled by humidity, applied voltage, and tip translation speed. This technique is intrinsically site-specific and may be used for laboratory scale fabrication of complicated structures using multiple “inks”. Importantly, with E-DPN the current repertoire of building blocks expands to now include monomers used to prepare polymers with tailored electronic and electrooptic properties. In conjunction with other micro- and nanofabrication strategies, E-DPN is likely to facilitate the design and development of novel devices for the electronics, defense, pharmaceutical, and biotechnological industries.

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Supporting Information Available: Figures showing the selective adsorption of nanoparticles on the polymer nanostructures and oxidation of Si surface underneath the polymer nanostrutcures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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