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Guided Growth of Nanoscale Conducting Polymer Structures on Surface-Functionalized Nanopatterns

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Abstract: We describe an electrochemical method of directly growing conducting polymer nanostructures between metal electrodes with the geometry controlled by hydrophilic/hydrophobic patterns. The surface patterning can be achieved by a large number of lithographic methods such as AFM, electron-beam, elastomeric microprinting, and photolithography and is compatible with industrial semiconductor fabrication processes. Conducting polymer structures so formed have good alignment compared to bulk synthesis and are grown in place between electrodes. Polypyrrole field effect transistors have been produced using this method. Electrical measurements show conductivity strongly dependent on the presence of anionic dopant species during growth. Devices grown with a high concentration of dopant show metallic behavior, while those with less doping behave as p-type semiconductors.

Introduction

Conducting polymers (CPs) have been demonstrated to have very useful properties for electroluminescent devices,[1] field effect transistors,[2] and chemical sensors.[3] These electronic properties are tunable by modification of the chemical structure of the monomer units, allowing the broad knowledge of organic chemistry to be applied to band gap engineering. The impact of CPs in the field of electronics is expected to be great, due to this versatility, their mechanical flexibility, and their potential for extremely low-cost device fabrication.[4-6] Unlike inorganic semiconductor devices, CP devices do not have the expensive requirement of extreme environment control. Also, they have the potential to be used in inkjet printing for low-cost circuit fabrication, which is very attractive for the electronics industry. However, this also imposes the restriction that patterned polymers be solution- or melt-processable. As a class of compounds, however, many CPs tend to be insoluble, and intractable in general, in their conducting states. Functionalization of the polymer with moieties to increase solubility, such as in poly(3,4-ethylenedioxythiophene), is effective for achieving processability, but these substituents also alter the electronic properties, which is often undesirable.

Additionally, inkjet printing as a circuit patterning method offers poor performance compared to existing inorganic semiconductor patterning methods. A comparison of feature resolution in photolithography ($<$65 nm) and inkjet printing (20−50 μm) is particularly telling. More sophisticated inkjet printing methods allow field-effect transistors with much shorter channel lengths,[2,7] but to keep charging times short, low device volumes, and therefore high resolution in three dimensions, are required. Three-dimensional nanoscale CP structures have been obtained by several types of template polymerization[8-11] and scanning probe methods,[12-15] but all of these suffer from complicated mask fabrication, registration, and alignment processes, or they are not compatible with integrated circuit parallel fabrication techniques. Overly complex or low-throughput processes will fail to make full use of CP potential for low cost.

In this article, we present a method to pattern CP nanostructure devices using a grow-in-place vapor-phase procedure that guides growth of polymer by selective condensation on a chemically patterned substrate. While previous efforts have used hydrophilic patterning[16] and even selective condensation[17] to pattern a final CP structure, this is, to our knowledge, the first time such patterning has been used to directly grow devices in the submicrometer range.

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(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539−541.
(2) Stutzmann, N.; Friend, R. H.; Sirringhaus, H. *Science* **2003**, *299*, 1881−1884.
(3) Dong, S. J.; Sun, Z. H.; Lu, Z. L. *J. Chem. Soc., Chem. Commun.* **1988**, 993−995.
(4) de Gans, B.-J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203−213.
(5) Forrest, S. R. *Nature* **2004**, *428*, 911−918.
(6) Cheng, K.; Yang, M.-H.; Chiu, W. W. W.; Huang, C.-Y.; Chang, J.; Ying, T.-F.; Yang, Y. *Macromol. Rapid Commun.* **2005**, *26*, 247−264.
(7) Sele, C. W.; von Werne, T.; Friend, R. H.; Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 997−1001.
(8) Ramanathan, K.; Bangar, M. A.; Yun, M.; Chen, W.; Mulchandani, A.; Myung, N. V. *Nano Lett.* **2004**, *4*, 1237−1239.
(9) Nickels, P.; Dittmer, W. U.; Beyer, S.; Kotthaus, J. P.; Simmel, F. C. *Nanotechnology* **2004**, *15*, 1524−1529.
(10) Ma, Y. F.; Zhang, J. M.; Zhang, G. J.; He, H. X. *J. Am. Chem. Soc.* **2004**, *126*, 7097−7101.
(11) Peng, C. Y.; Kalkan, A. K.; Fonash, S. J.; Gu, B.; Sen, A. *Nano Lett.* **2005**, *5*, 439−444.
(12) Maynor, B. W.; Filocamo, S. F.; Grinstaff, M. W.; Liu, J. *J. Am. Chem. Soc.* **2002**, *124*, 522−523.
(13) Jang, S. Y.; Marquez, M.; Sotzing, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 9476−9477.
(14) Jegadesan, S.; Advincula, R. C.; Valiyaveettil, S. *Adv. Mater.* **2005**, *17*, 1282−1285.
(15) Lim, J.-H.; Mirkin, C. A. *Adv. Mater.* **2002**, *14*, 1474−1477.
(16) Wang, J. Z.; Zheng, Z. H.; Li, H. W.; Huck, W. T. S.; Sirringhaus, H. *Nat. Mater.* **2004**, *3*, 171−176.
(17) Natarajan, S.; Kim, S. H. *Langmuir* **2005**, *21*, 7052−7056.

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Dendritic polymer structures were electrochemically grown between micropatterned electrodes from a monomer vapor.[18] The growth was shown to require a critical value of relative humidity during growth, suggesting that a condensed layer of water on the surface of the sample is needed for polymerization. The accepted mechanism for polymerization of heterocycles such as pyrrole and thiophene involves elimination of protons, and electrochemical studies have found that the presence of some amount of protic solvent is helpful for growth of high-quality polymer.[19] Solvent condensation on a surface is dependent on the affinity of the surface for that solvent, which in turn is dependent on the surface functionalization. At ambient temperatures and humidities, a small amount of water will be absorbed on a hydrophilic region of a substrate, but not on the adjacent hydrophobic regions. Many systems and techniques for patterning the hydrophobic/hydrophilic structures on a surface exist,[20,21] including techniques that are compatible with well-developed methods in the semiconductor industry. Thus, the creation of CP nanostructures using the reported method can use both ultrahigh-resolution techniques such as e-beam or AFM lithography ($<$10 nm feature size) and highly parallel methods such as photolithography (wafer-scale patterning in a single step).

Experimental Section

Sample Preparation. All experiments were carried out on highly doped silicon wafers with a 1000-nm thermally grown oxide layer (Silicon Inc., Boise, ID). Gold electrodes were thermally evaporated to a thickness of 40 nm, with a 5-nm adhesion-promoting layer of chromium, and were patterned by a standard photolithography/lift-off procedure using Shipley 1813 photoresist. Surface affinity patterning was performed on a hexamethyldisilazane (HMDS) self-assembled monolayer (SAM) applied in the vapor phase. After application of the HMDS SAM, samples were washed with chloroform or 2-propanol and sonicated for 5 min. Hydrophilic patterns were formed in the SAM by an AFM "nanoshaving" procedure described earlier[12] using a Digital Instruments MultiMode AFM connected to a Nanoscope IIIa controller. The electrode gaps to be modified were first imaged with a force setpoint as close to zero as could be obtained (within 100 nN uncertainty for the cantilevers used). When the appropriate scanning range was located, the force setpoint was increased by about 2.5 μN and scan speed was reduced to 6 μm/s. When newer, sharper tips were used, significantly less force was needed for modification. For narrow features ($<$150 nm), the slow scan axis was disabled, and scanning stopped after 10 passes. For less confined ($>$500 nm), lower resistance devices, as would be used for electrical characterization, the slow scan axis remained enabled, and the modified area was scanned three times. Successful affinity modification was verified by friction-mode imaging of the sample using the same tip (Figure 1). Friction contrast was assumed to be due to selective removal of the hydrophobic HMDS layer, as opposed to locally increased surface roughness.

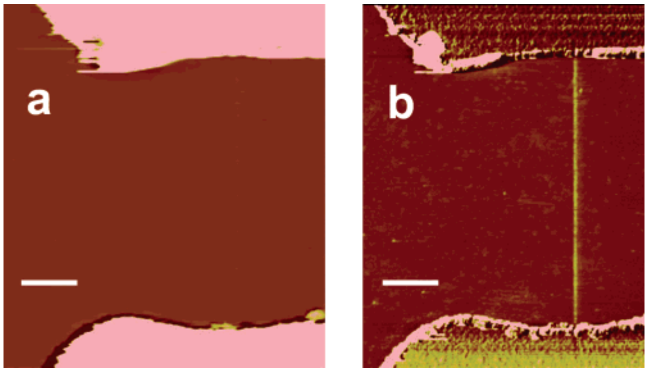

Figure 1. Contact mode AFM height (a) and friction (b) images of a typical gap between gold electrodes after hydrophilic patterning of a thin line. Scale bars are 1 μm.

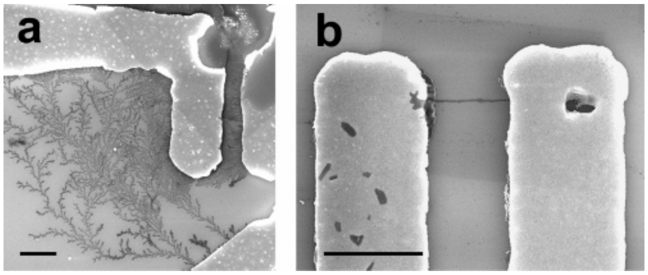

Figure 2. SEM micrographs of polypyrrole fibers grown from monomer vapor on (a) a bare silica surface and (b) a hydrophilically nanopatterned surface. The gold electrodes are visible in both images. Scale bars are both 5 μm.

Polymer Growth. Samples were wire bonded to a surface-mounting board with gold wire using a Kulicke & Soffa wire bonder. The boards were then inserted into an electrical socket in a home-built chamber in which a small vial of pyrrole monomer had been placed and through which water or dopant vapors could be pumped. Voltage was applied to the appropriate electrodes with a Keithley 2400 sourcemeter controlled by LabView software. Applied voltages were varied between 5.0 and 20.0 V. Relative humidity was monitored, when the presence of hostile dopant vapors did not prevent it, with a Honeywell HIH 3610 humidity sensor, also monitored through a sourcemeter and LabView. Resistance of the circuit was simultaneously monitored. Time of growth varied from 0.5 to 12 h. After growth had been stopped, the sample was checked for the presence of polymer structures by tapping-mode AFM.

Electrical Characterization. Gate voltage dependencies of the polymer structures were measured by scratching away the insulating oxide layer on a corner of the substrate and contacting the exposed silicon with one probe of a probe station. The current across the polymer channel for a fixed source−drain voltage was monitored by a sourcemeter and plotted against the voltage applied to the silicon back gate.

Results and Discussion

Polymer Growth. Polymer growth across an electrode gap on bare silica was widespread and not confined to the smallest electrode gap. In control experiments, HMDS functionalization of the silica surfaces prevented polymer growth even after more than 12 h of applied bias. Hydrophilic surface patterning was successful in confining polymer growth to a small predefined area (Figure 2). The size of the polymer structures matched the size of the modified area on which they were grown. Polymer structures were fibrillar, with individual chains 10−30-nm thick, as measured by AFM. The fibril density increased with growth time, but very thin films (no more than 20-nm thick) were almost always grown. It was found that anionic dopants, introduced intentionally or present as impurities, were necessary to grow conductive structures. Structures grown with only surface impurities exhibited low conductivities and poor reproducibility. Thus, a controlled method to provide dopant species was needed.

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(18) Su, M.; Fu, L.; Wu, N. Q.; Aslam, M.; Dravid, V. P. *Appl. Phys. Lett.* **2004**, *84*, 828−830.
(19) Machida, S.; Miyata, S.; Techagumpuch, A. *Synth. Met.* **1989**, *31*, 311−318.
(20) Critchley, K.; Jeyadevan, J. P.; Fukushima, H.; Ishida, M.; Shimoda, T.; Bushby, R. J.; Evans, S. D. *Langmuir* **2005**, *21*, 4554−4561.
(21) Sugimura, H.; Ushiyama, K.; Hozumi, A.; Takai, O. *Langmuir* **2000**, *16*, 885−888.

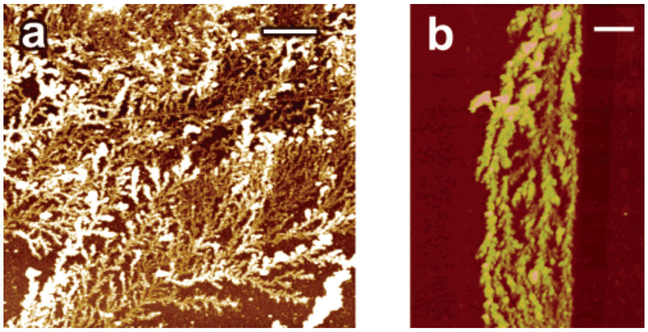

Figure 3. Tapping-mode AFM images of polypyrrole fibers as grown on (a) an unmodified silica surface and (b) a hydrophilic rectangle scraped from an HMDS SAM. While the unrestrained sample has some short-range order owing to chain rigidity and a common branching angle of 60°, long-range order is essentially absent. The confined sample shows good alignment with the direction of electrical transport in the device. Scale bars in (a) and (b) are 2000 and 500 nm, respectively.

HCl is mobile in the vapor phase and dissociates in water to give Cl^- ions, which have been shown to dope polypyrrole.[22] We therefore repeated the growth procedure in the presence of 6 M HCl. Polypyrrole structures grown in this way displayed much higher growth rates, more ordered structures, and conductivities more than 3 orders of magnitude higher than those of comparable samples doped only by impurities. Growth progress was monitored through measurement of electric resistance across the electrodes. Resistance dropped steadily in most cases but suddenly for some highly doped samples. A steady decrease suggests a slow increase in the diameter of poorly conducting, very thin polymer fibers, while a sudden drop suggests a thicker fiber has just bridged the electrode gap.

The restriction of polymer growth to a confined area also affected the orientation and order of the chains. Polymer grown on a bare silica surface was dendritic and showed very little long-range order. In contrast, fibers grown in a confined region of hydrophilic surface functionalization were relatively well ordered and parallel (Figure 3). Because conducting polymers are quasi one-dimensional conductors,[23] a high degree of alignment greatly improves electrical transport.[24,25]

In addition to simple rectangular and straight line structures, the direct growth method also provides the capability to grow more complex nanostructures. The versatility of the patterning method is demonstrated by the structure shown in Figure 4a. A thin line with two 90° turns was patterned, and polypyrrole was able to grow continuously along it. This ability suggests that complex circuits can be created using this method. It was also found that synthesis of structures could be halted before the growth bridged the gap (Figure 4b), then restarted with a later growth step. This suggests that, using different polymer precursors with different electronic structures for two growth steps, heterojunction devices can be created.

Electronic Measurements. For electronic transport in conducting polymers, charge carrier availability and carrier delocalization are both required. Charge carriers are introduced to the polymer structures by oxidation of monomer units within the polymer chain. Typically, this oxidation proceeds up to a maximum percent doping, where a fraction of the total number of monomer units has been oxidized. When this maximum is reached, the polymer will conduct as a metal and will display no gate dependence. However, at doping levels with low carrier concentrations, an external electric field can introduce charge carriers and control polymer conductivity. Thus, the growth method can be used to create both metallic and semiconducting structures. In the case of lightly doped polypyrrole, the electric-field sensitivity is that of a p-type semiconductor. Gate dependencies seen in the samples doped only by impurities, however, were weak. This is due to the relatively poor charge delocalization of the samples grown at low doping levels. Conductivities for these samples were usually in the range of 0.0001 S/cm, even after post-growth doping. Semiconducting samples of higher quality were produced from highly doped samples grown in the presence of HCl, with maximum conductivities around 0.1 S/cm. These samples were then electrochemically reduced, and the Cl^- dopants were removed, reducing the available charge for transport, while retaining the carrier delocalization properties. After this, the samples gave well-defined gate curves, as shown in Figure 5.

Conductivities of the polymer structures created in this study were lower than those reported for bulk synthesis methods. This problem could probably be solved by fine-tuning the growth conditions such as temperature, monomer and dopant concentration, or electrochemical potential. These growth conditions have

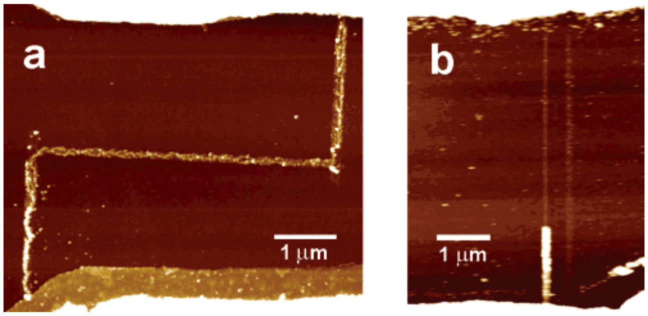

Figure 4. Polypyrrole growth can be guided to create complex patterns (a) and structures that do not cross the gap completely (b). (b) The scraped line is visible as well as the polymer. Both images are tapping-mode AFM.

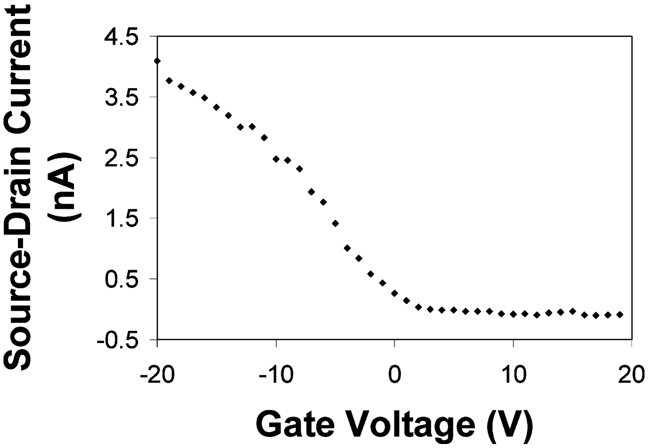

Figure 5. Gate-voltage dependence of source−drain current is shown for a polypyrrole device grown in the presence of 6 M HCl on a 1-μm gate oxide layer. Source−drain voltage is 10 V. The device tested was 5-μm long and 680-nm wide in cross section, with an average vertical thickness of 15 nm at the narrowest region.

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(22) Warren, L. F.; Anderson, D. P. *J. Electrochem. Soc.* **1987**, *134*, 101−105.

(23) Prigodin, V. N.; Samukhin, A. N.; Epstein, A. J. *Synth. Met.* **2004**, *141*, 155−164.

(24) Sato, K.; Yamaura, M.; Hagiwara, T.; Murata, K.; Tokumoto, M. *Synth. Met.* **1991**, *40*, 35−48.

(25) Hagiwara, T.; Hirasaka, M.; Sato, K.; Yamaura, M. *Synth. Met.* **1990**, *36*, 241−252.

been shown to have a large effect on the conductivity and mobility of the polymer,[22] and thus significant improvement of the performance of grown structures can be expected.

Conclusion

We have demonstrated a versatile method for patterning polypyrrole with high resolution, complex geometry, control over electrical properties, and superior orientation compared to other synthesis methods. Because the growth is confined to a surface pattern, semiconductor devices with relatively high performance can theoretically be made. If the guided growth process can be generalized to parallel surface patterning methods such as photolithography, the low-cost potential of CP devices can be retained. Further, the polymer fibers are grown in alignment with the direction of electrical transport, something that is impossible for all CP device fabrication methods other than electrochemical growth. Future experiments exerting more control over the electrochemical environment of the polymerization reaction are expected to yield devices with better structure and delocalization, improving properties in both the metallic and semiconductor modes. If this is realized, guided growth can have great potential for fabrication of CP electronics.

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Supporting Information Available: High-resolution images of the polypyrrole structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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