Direct Deposition of Electronic Materials with Thermal DPN

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Abstract

In recent years there has been a significant effort to improve or augment lithographic techniques for electronic device fabrication. Although improvements in ultimate resolution have been a central goal, other goals have also been pursued that may be important avenues to advance device fabrication. These alternate objectives include reduction of toxic by-products ("green chemistry"), integration of disparate materials into a single structure (e.g., organic and inorganic), and production or prototyping of low numbers of integrated circuits at relatively low unit cost. Progress towards all these goals is found in a new lithographic technique, thermal Dip Pen Nanolithography (tDPN). In tDPN (Figure 1), an atomic force microscope (AFM) cantilever is custom fabricated to include a heater directly above the tip. The tip is then coated with an "ink" that is solid at room temperature but that can be melted by the integrated heater. When the ink is melted, it flows onto the surface and solidifies, thereby allowing arbitrary patterns to be written.

Introduction

The first reports of the directed deposition of molecules using AFM cantilevers were by Jaschke and Butt[1] who followed the aggregation of ODT (octadecanethiol) deposited by a scanning probe tip onto a mica surface. This probe-directed deposition was later reproduced by the Mirkin group at Northwestern University where the technique was greatly refined, the range of inks expanded, and the term "Dip Pen Nanolithography" coined. Subsequent development in that and many other groups has lead to a highly versatile technique, capable of patterning with ~10 nm resolution and with a wide range of materials that may be deposited.[2] These materials deposited now range from biological (e.g., DNA, antibodies, and proteins) to organic (e.g., thiols and silanes) to inorganic (e.g., sols and metal salts). Finally, an instrument optimized for DPN using 10 cantilevers is now commercially available (NScriptor; Nanoink, Inc.).

Despite these many advances, several desirable features were lacking in standard DPN. First, the deposition protocol requires that the ink be fluid at room temperature to allow transfer from the tip to the surface. This means, however, that the ink will *always* flow while the tip is in contact; therefore, there is no easy means of starting and stopping deposition. Lifting the tip away from the surface has been the only means of stopping deposition, but this brought with it loss of tip-surface registry and the potential for erratic transfer of ink as the tip was removed from the substrate. Secondly, although it is possible to change the deposition rate by changing the global environment (the temperature or humidity of the air), standard DPN has no rapid, local means of varying the deposition rate. This would be a critical if, for instance, one were using an array of tips coated with several different inks to pattern a surface. Finally, many potentially useful materials can not be deposited without the presence of a solvent to maintain fluidity, or are simply impossible to deposit because of they are solid under ambient conditions.

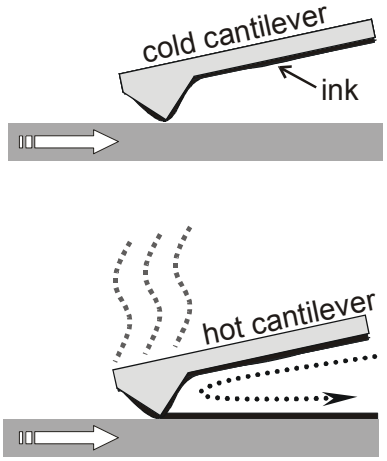

Figure 1. Scheme of Thermal Dip Pen Nanolithography. When the cantilever is cool, the ink if frozen on the tip and does not flow. When the cantilever is heated, the ink flows from the tip onto the surface. Moving the tip allows arbitrary patterns to be written.

Many of these shortcomings may be overcome if local heating is used to control the fluidity of the ink—the essential improvement of tDPN over standard DPN. In tDPN, a resistive heater integrated into an AFM cantilever controls the fluidity of molecules, the "ink," previously deposited on the AFM tip. Because the ink is chosen to be solid at room temperature, no deposition occurs when the unheated AFM tip contacts the surface. When the AFM tip is then heated to a temperature equal to or greater than the ink's melting temperature (T_m), the ink flows from the tip to the surface. The deposition rate can be controlled and deposition turned on and off by adjusting the tip temperature and the writing speed. This control is clearly illustrated in Figure 2, where deposition of octadecylphosphonic acid (OPA, $T_m \approx 98°C$) onto mica is attempted at four different temperatures. When the temperature of the cantilever is below T_m, no deposition is observed. At OPA's T_m moderate deposition is seen, and well above T_m robust deposition is seen, with the expected height (2.5 nm) of a well-formed monolayer. Confirmation that the molecule was deposited as expected came from a friction force image of the area (not shown), which showed a decrease in friction over the deposited monolayer. It is well-known that methyl terminated SAMs like OPA will reduce friction on materials such a mica.

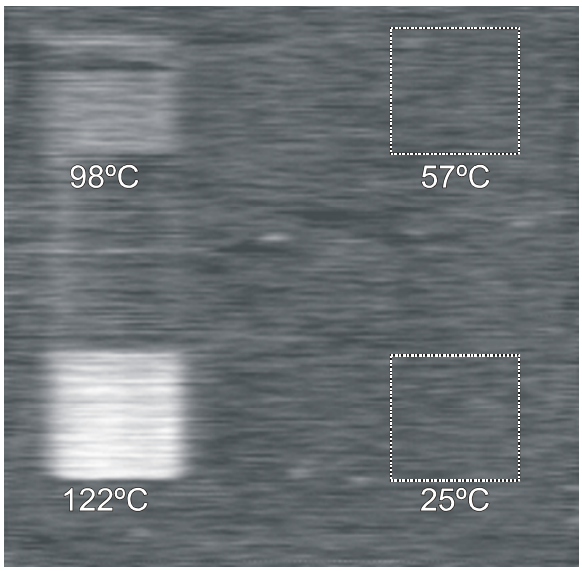

Figure 2. An AFM height image (2.5 µm across) of a surface scanned with a heated AFM cantilever tip for 256 s in each of four 500 nm squares on a 1 µm grid. The cantilever tip temperature during each of the scans is shown. No deposited material is observed from the two low-temperature scans. When the tip is near OPA's $T_m \approx 98°C$, light deposition is observed. Robust deposition occurred when the cantilever temperature was 122°C.

tDPN is especially well-suited to the deposition of polymers. First, unlike conventional DPN, tDPN does not require the presence of water[3] and so the choice of ink is not limited to water-soluble polymers.[4] Secondly, because the polymer is deposited above its melting point, well-formed monolayers are created. Finally, because the polymer freezes after contact with the surface, it is possible to overwrite previously written layers with new layers to build up three dimensional structures or, if multiple polymers were to be used, heterostructures. The polymers deposited so far with tDPN include mylar, MEH-PPV (poly[2-methoxy-5-2'-ethylhexyl) oxy-1,4-phenylvinylene]), and PDDT (poly(3-dodecylthiophene)).

Figure 3 illustrates the controlled deposition of PDDT—a semiconducting polymer of interest in organic electronics—onto a SiO_2-coated Si substrate. The coated tip was carefully heated and rastered over a rectangular area to deposit a single monolayer of the polymer. A second pass using the same parameters deposited a second monolayer without disturbing the first. The stepwise nature of the deposition is clearly illustrated when the line scans are averaged to produce an average cross-section (Fig. 3B).

Moreover, if a height histogram is performed on the same data, the thickness of each layer is seen to be 2.5 nm. This thickness compares favorably to the thickness as determined by x-ray diffraction of PDDT monolayers in the preferred high electron mobility orientation.[5] We infer from this thickness that the PDDT can be additively patterned one molecular layer at a time with high crystallinity. Moreover, lines of polymer can also be written and the thickness controlled by varying the tip temperature and speed. The current resolution limits for the linewidth is 75 nm, most likely limited by the relatively high radius of curvature (~100 nm) of the custom fabricated cantilevers. As this radius of curvature decreases, it is expected that narrower patterns will be possible. To the best of our knowledge, such extensive control over deposition (i.e., nanoscale linewidths and molecular layer control) is not achievable by any other additive patterning method.

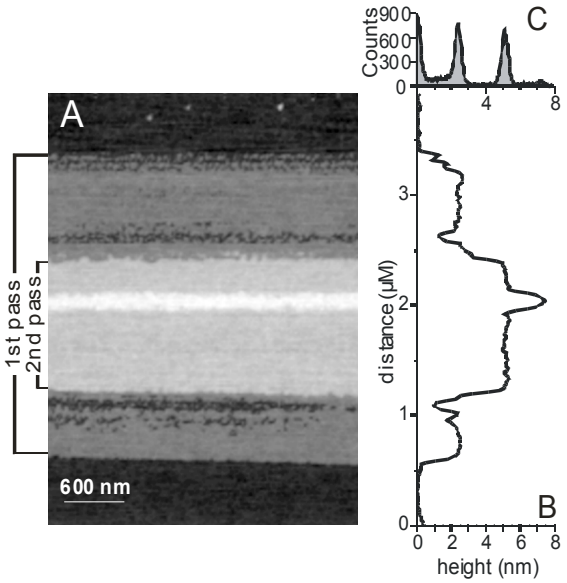

Figure 3. (A) Tapping-mode AFM image of a PDDT film deposited on SiO_2. The PDDT pre-coated tip was rastered at 5 µm/s with 47 nm per line while heated above PDDT's T_m. The outer pattern resulted from the first pass, which deposited a single monolayer. After 50 s, a second (rectangular) scan deposited a second monolayer without disturbing the first. (B) The average height profile. Discrete height changes are apparent for each layer. (C) Height histogram of the film with peaks at 0, 2.4, 5.1, and 7.3 nm.

The extensive thermal range of the cantilevers allows many more inks to be used than in standard DPN. The cantilever temperature can approach 700°C in short pulses and may be heated to 550ºC in steady state. Our exploration of high melting point inks has recently led to the deposition of indium metal. tDPN was used to directly write indium metal lines <80 nm wide onto glass and silicon substrates (Figure 4). In general, it is a recurring challenge to deposit *continuous* conducting nanometer-scale wires. We are able to test the continuity by directly writing the In nanowire across a sub-micron gap between gold electrodes. Ohmic contact was achieved, although the conductance was indicative of indium oxide (which is also a conductor). Auger Electron Spectroscopy (not shown) confirmed the composition as indium oxide, as expected for an In nanowire deposited under ambient conditions.

Although the capabilities demonstrated to date will be useful in laboratory settings to create and explore nanoscale structures, full realization of this technique will require fabrication in parallel. Arrays of 4,096 individually controlled thermal cantilevers have already been fabricated by IBM for use in the "Millipede" memory storage system.[6] Thermal cantilevers may be designed to give heating times in the range of 1–20 µs and cooling times in the range of 1–50 µs.[7] Thus, rapid and highly parallel patterning of surfaces should be possible. Given tDPN's ability to deposit insulators (OPA), semiconductors (PDDT), and conductors (In

metal), it should be possible to write electronic circuits directly. Moreover, because the molecules in tDPN can be solid at room temperature, it should be possible to build up multi-layer, multi-component patterns to create true three-dimensional nano-structures.

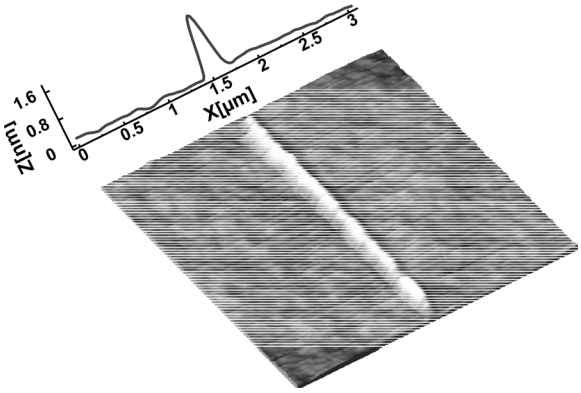

Figure 4. Indium metal deposited with and imaged with a single thermal cantilever. The line is 1.7 nm high and 3 μm long.

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Author Biography

Dr. Paul Sheehan received his Ph.D. from Harvard University for work on the mechanics of carbon nanotubes and on the nanotribology of solid lubricants. After a National Research Council postdoctoral fellowship at the Naval Research Laboratory (NRL) studying the use of magnetoelectronics for DNA sensing, he was hired as a Research Chemist by NRL's Surface Nanoscience and Sensor Technology Section. His current research interests include scaling laws at the nanoscale and the development of new methods of nanopatterning.