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Nanoscale deposition of solid inks via thermal dip pen nanolithography

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We demonstrate that nanolithography can be performed using a heated atomic force microscope (AFM) cantilever tip to control the deposition of a solid organic "ink." The ink, octadecylphosphonic acid (OPA), has a melting temperature near 100 °C and can self-assemble on mica. Postdeposition analysis shows that deposition occurs only when the cantilever tip is heated above OPA's melting temperature, that the deposited structure does not spread significantly while cooling, and that a cool tip coated with OPA does not contaminate the substrate during subsequent imaging. Single lines were written with a width of 100 nm. This approach greatly expands the potential of dip pen nanolithography, allowing local control of deposition and deposition of materials typically immobile at room temperature, while avoiding potential problems arising from inadvertent deposition and postdeposition diffusion. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1785860]

Surface modification with scanning probe tips has become ubiquitous as a method for nanoscale patterning. One recent advance is dip pen nanolithography (DPN), wherein a chemically coated atomic force microscope (AFM) tip directs the deposition of the coating molecules (the "ink") from the tip to the contact area with the surface.[1] Molecules that have been successfully deposited include alkylthiols,[2,3] biomolecules,[4] silanes,[5] and sols.[6] The only apparent criterion for the ink molecules is sufficient mobility to transfer from the tip to the surface under ambient conditions.

Although the DPN process is robust, at least two limitations hinder its practical implementation. The first limitation is the inability to prevent deposition while the tip is in contact with the surface, because the tip constantly deposits molecules until depleted. Breaking the tip–surface contact does end writing but also leads to loss of registry between the tip and the surface. Furthermore, the tip still must contact the surface to perform metrology of the written structures. Thus, imaging of DPN-deposited features with an inked tip inherently causes contamination. The only method to avoid this contamination is to switch to an uncoated tip and attempt to relocate the deposited pattern, a complicated and time-consuming procedure. The second limitation is that there is little control over the deposition rate once a molecule has been coated onto the cantilever. Some studies have changed the rate of deposition and spreading through *global* control of the atmosphere or of the temperature;[7] however, *local* control has not been reported.

This letter presents the use of cantilevers with integrated resistive heaters to deposit an ink that is solid at room temperature, which we refer to as thermal DPN (tDPN). In tDPN, a heater cantilever is coated with a relatively high melting temperature material and the tip is brought into contact with a surface. When the cantilever is heated, the melted molecules flow from the tip onto the surface (Fig. 1). This approach allows the local deposition of molecules that are not mobile at room temperature and controls the rate at which they are deposited.

For the present study, an AFM cantilever produced for thermomechanical data storage by the IBM Zurich Research Lab was used, as is shown in Fig. 2. The silicon cantilevers were fabricated with a standard silicon-on-oxide cantilever fabrication process, and have a tip with a radius of curvature of ~100 nm.[8–10] The cantilever has a heating time in the range of 1–20 μs and a cooling time in the range of 1–50 μs.[11,12] The cantilever temperature can approach 700 °C in short pulses and, because the resistive heating element is also a temperature sensor, calibration of the cantilever temperature response is possible to within 1 °C.[8,10–12]

The cantilevers were coated with octadecylphosphonic acid (OPA), a versatile molecule that self-assembles into monolayers on mica,[13] metals such as stainless steel and aluminum,[14] and metal oxides such as TiO_2 and Al_2O_3.[15] It is especially suitable for tDPN since its melting temperature (T_m) is 99 °C,[16] well above room temperature but well within the thermal range of the heater cantilever. OPA was evapo-

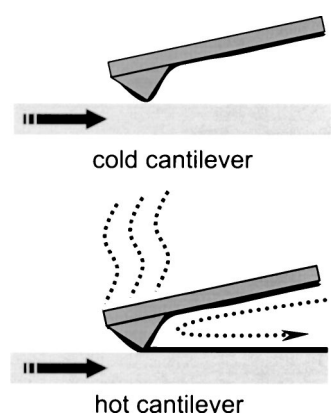

FIG. 1. Cartoon of tDPN concept. At low temperatures, the ink is frozen on the cantilever preventing transfer. At high temperatures, the ink melts and transfers from the tip to the substrate. Lines may be drawn as the substrate is moved relative to the tip.

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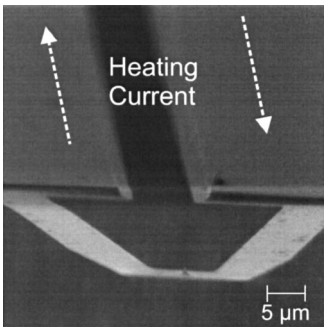

FIG. 2. SEM image of the heated cantilever device. The cantilever tip has a radius of curvature of approximately 100 nm.

rated onto the AFM cantilever and tip by first heating a scintillation vial containing 60 mg of OPA on a hot plate set at 110 °C. The cap of the scintillation vial was then replaced for 30 min with a tip holder maintained at ~35 °C. From ellipsometry (not shown), it is known that this procedure deposits the mass equivalent of two complete monolayers of OPA.

OPA patterns deposited via tDPN are presented in Fig. 3, which shows a mica region where the deposition of four squares was attempted. A coated tip was rastered over each

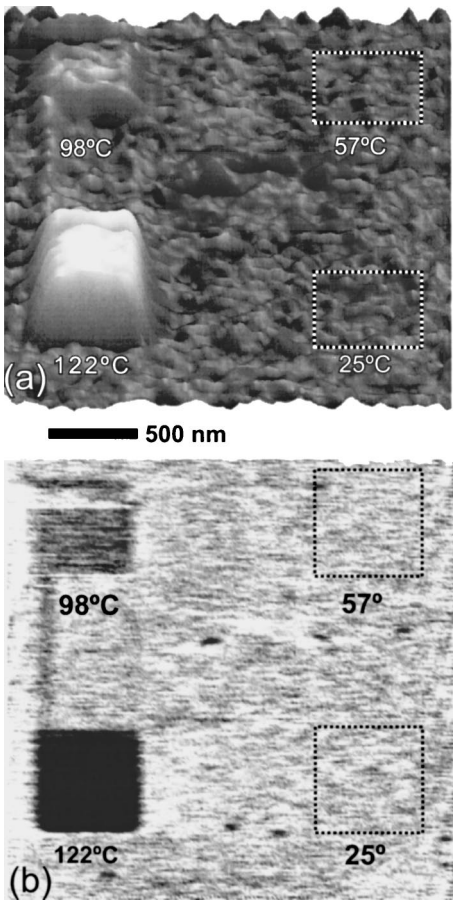

FIG. 3. (a) A topographic image (2.5 μm across) of a surface scanned with a heated AFM cantilever tip for 256 s in each of four 500 nm squares on a 1 μm grid. The cantilever tip temperature is shown for each of the four scans. No deposited material is observed from the two low-temperature scans. The scan at 98 °C, about OPA's T_m, resulted in light deposition. Robust deposition occurred during the final scan when the cantilever temperature was 122 °C. (b) Friction image of the same area showing no deposition in the first two squares followed by increasing deposition in the second two. Darker areas indicate lower friction, as expected for OPA on mica.

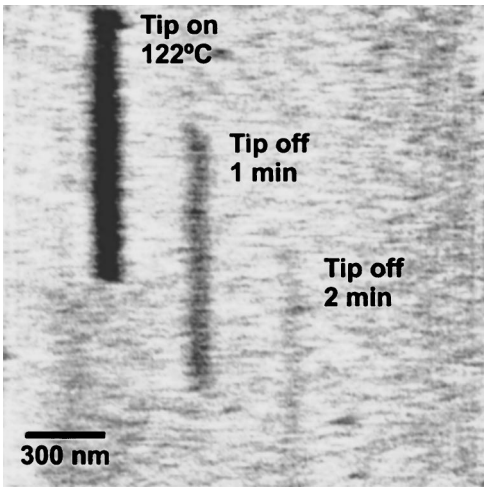

FIG. 4. Friction image of a mica surface scanned with a coated AFM cantilever tip for 60 s in each of three lines. The cantilever was heated for the first line (upper left) and then allowed to cool during the second two. OPA continued to transfer from the tip onto the surface after the cantilever heater had been turned off.

500 nm square four times at 2 Hz and 128 lines per scan, or for a total scan time of 256 s. For each square, the temperature of the cantilever was increased, finally exceeding OPA's melting temperature. When the cantilever was held below OPA's T_m, either at 25 °C or 57 °C, no patterned squares were observed. Raising the cantilever temperature to 98 °C, near OPA's T_m, resulted in light deposition. The average height of this area was 1.1 nm, which is slightly less than one-half the height of a full monolayer. Robust deposition was finally seen when the cantilever temperature was raised to 122 °C, creating a square pattern with a height of 2.5 nm, indicative of a full monolayer, as shown in Fig. 3(a). The corresponding friction image, shown in Fig. 3(b), confirms OPA deposition. The binding of OPA to mica exposes a methyl terminal group which would reduce friction relative to the bare mica surface. No change in friction was observed for the lower cantilever temperatures. The light deposition at 98 °C reduces friction slightly, as expected, and the full monolayer deposited at 122 °C reduces friction much further.

Although deposition started instantaneously upon heating, deposition continued for a time after the heating current was stopped. Figure 4 shows three lines written via tDPN where the tip sequentially traced three vertical lines for 1 min apiece. The cantilever was heated only for the first, upper left, line. Thus, deposition continued for roughly 2 min after the cantilever heating was stopped. Although such a delay does not pose a problem for laboratory usage, it could potentially limit high-throughput commercial applications. In contrast to this delay, modification of ultrathin polymer layers on a silicon surface was shown to be highly localized near the tip and fully complete in the range of 1–10 μs.[8,10–12] The present system differs from that system in that it includes the coated ink and a mica substrate with a much lower thermal conductivity than Si.[17] The present experiments do not indicate whether the ink remains hot on the tip or whether the substrate is significantly heated by the tip; although, a simple scaling of the cooling time constants yields ~10 μs for the cantilever, ~100 ns for the tip, ~10 ns for the ink, and ~10 s for the heated region of the substrate. Thus, it is likely that residual heat in the substrate prolonged the writing and that deposition would cease

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quickly on substrates with greater thermal conductivity, such as Si or a metal. Careful selection of the substrate material and engineering of the write speeds could reduce the tDPN write time into the 100 kHz range demonstrated in the data storage application.[10,12]

Two features of Fig. 4 reveal the potential for significantly improving this lithography method. First, the linewidth (full width at half maximum of cross section) in this unoptimized system is only 98 nm across, which is comparable to the radius of curvature of the tip used, ~100 nm [from a scanning electron microscope (SEM)]. Heated cantilevers with tips sharper than 20 nm have been fabricated,[9,18] and these cantilevers have made marks in a polymer as small as 23 nm.[10] Advances in tip construction should therefore allow a decrease in linewidth by an order of magnitude. Second, although the ink is presumably cooler with each subsequent line, there is no appreciable change in linewidth. The independence of linewidth on temperature suggests that the width is mainly determined by the sharpness of the tip, not diffusion of the OPA molecules following deposition. This aspect of tDPN is in contrast to conventional DPN, where increasing the global temperature increases both the deposition rate and the subsequent spreading of the pattern caused by surface diffusion. Global heating thereby leads to larger patterns presumably having larger halos of contamination. Thus, local control over heating will allow fast deposition rates *and* sharp features. Careful engineering of the cantilever, tip, and substrate should allow tDPN to write features as small as 10 nm.

The thermal deposition process described is a significant refinement of DPN. tDPN allows deposition to be turned on or off and allows the deposition rate to be controlled locally. It does so while retaining the ability to pattern sharp features at the nanoscale. Second, tDPN should provide instant metrology without the risk of contamination. Although more extensive tests will be required, none of the hallmarks of contamination were observed, such as halos[3] around deposited features or "fill-in" patterns following repeated imaging with coated tips.

The development of tDPN opens several opportunities for DPN-based nanofabrication. Large arrays of heater cantilevers have been fabricated that can write more than 10^6 pixels/s,[9,10,18,19] and thus reasonable write times could be achieved over wafer-scale areas. Thermal control should in principle allow deposition of a wide variety of solid inks that were previously inaccessible to DPN. For instance, metals of appropriate melting temperatures could be patterned with this technique, creating a nanometer scale "soldering iron." Finally, because the molecules in tDPN can be solid at room temperature, it should be possible to build up multilayer multicomponent patterns to create true three-dimensional nanostructures.

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