Patterning techniques

A Nanofountain Probe with Sub-100 nm Molecular Writing Resolution**

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Controlled patterning of materials at the nanoscale is a preparatory but fundamental step in the development of nanostructures and nanodevices. Dip-pen nanolithography

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[**] This work was supported primarily by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0118025. We thank Prof. Chad Mirkin and his research group for many insightful discussions. The authors acknowledge the Microfabrication Applications Laboratory (MAL) of the University of Illinois at Chicago, the Materials Processing and Crystal Growth Facility (MPCGF) of Northwestern University, Northwestern University Atomic and Nanoscale Characterization Experimental Center (NUANCE), and the Electron Microscopy Center at Argonne National Laboratory, which is supported by the DOE Office of Science under contract no. W-31-109-Eng-38, for the fabrication and characterization facilities.

  DOI: 10.1002/smll.200500027

(DPN), a direct-write lithographic process, has achieved this objective and opened up many possibilities for nanoscale patterning.[1–7] In the DPN process, molecular inks coated on an atomic force microscope (AFM) tip are transferred to a substrate while the tip is held or laterally moved along a surface as programmed. Feature sizes less than 15 nm can be routinely patterned by molecular self-assembly of the ink on the substrate. However, the necessity of molecular-ink replenishment in the DPN technique leads to limited throughput and inevitable realignment during patterning processes, especially when complex or large-area patterns are to be generated. Hence, the concept of continuous feeding of molecular inks is a natural goal following the historical paradigm shift in the handwriting world: from quills to fountain pens. In this regard, several devices and technologies have been proposed. Micropipettes have been developed and referred to as fountain nanopens because of their capabilities to deliver liquid or gaseous materials,[8] proteins,[9] and photoresist[10] to surfaces. However, micropipettes cannot realize nanoscale patterning. The common problem of micropipette-based probes is that they suffer from ill-controlled aperture shapes and sizes, especially at the nanoscale. Moreover, the feature size of the patterns made by micropipettes is limited since it depends critically on the probe outer diameter, which typically leads to larger dimension of the patterns due to the formation of a liquid meniscus around the pipette tip during patterning. As a variation of this approach, a microfabricated aperture on an AFM tip was proposed, in which the aperture was constructed at the apex of a hollow pyramidal tip utilizing the back of the tip as a reservoir.[11] Like micropipette-based probes, the resolution of these AFM probes is determined by the outer diameter size. A while ago, we reported a novel microfluidic probe that was micromachined to have a microfluidic system integrated into AFM probes.[12–14] The concept was later adopted by Deladi et al. and a micromachined fountain pen for writing and etching was reported.[15] However, the size of patterned features obtained with such chips was about 1 μm. To our knowledge, none of the reported devices actually reached the stage of *true* nanoscale molecular writing, that is, sub-100 nm patterning. It is noted that for micropipette-based probes and apertured AFM probes, the ink in the liquid state at the lumen of the aperture floods the substrate when the tip is brought into contact with the surface due to surface tension. Also, in the case that the ink-dispensing aperture is located at the base of an AFM tip,[15] the liquid should flow out of the aperture and flood the tip to coat it, so that molecules can be readily transferred to a substrate when the tip is brought into contact. In either case, there is no good control of the amount of molecular ink to be transported to the substrate. This in turn results in feature sizes of about 1 μm.

In this work, we demonstrate a sub-100 nm patterning capability in fountain-pen mode, which was realized by implementing a volcano-like tip that has an annular aperture to control the position of the liquid–air interface at the aperture (Figure 1a and b). The novel microfluidic AFM probe, called the "Nanofountain Probe" (NFP), consists of a volcano tip, integrated microchannels, and an on-chip reservoir. When an ink solution is fed into the reservoir, it is driven by capillary action through the microchannel to the volcano tip to form a liquid–air interface around the volcano core. Surface micromachining techniques were used to fabricate the probes. The chip is designed and microfabricated to be mounted on commercial AFMs to exploit the scanner and optical deflection detection scheme of AFM instruments.

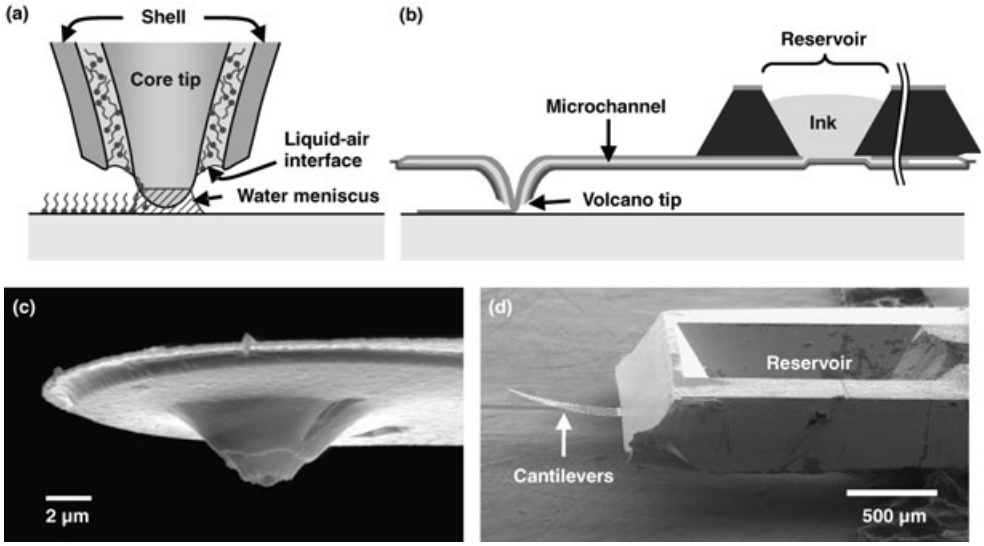

Figure 1. a) Writing mechanism of the NFP device. A molecular ink fed from the reservoir forms a liquid–air interface at the annular aperture of the volcano tip. Molecules are transferred by diffusion from the interface to a substrate and a water meniscus is formed by capillary condensation; b) ink from the reservoir is delivered to the dispensing tip via capillary force; c, d) scanning electron micrographs of a volcano dispensing tip (c) and an on-chip reservoir (d).

To microfabricate the nanofountain probe, we used standard surface micromachining procedures. The procedure started with formation of tips by undercut etching of a silicon substrate with precursor oxide caps, followed by removal of the caps and oxidation sharpening. The tips served later as molds for the formation of the dispensing volcano probes. The fabrication continued with the definition of microchannels. For this purpose, a $Si_3N_4/SiO_2/Si_3N_4$ trilayer was deposited on the silicon substrate and patterned to define the shape of a cantilever, which was aligned onto the aforementioned tips. Subsequently, the oxide layer of the patterned trilayer was etched starting from the side walls, to form an undercut. A selective "bird's beak" oxidation step created a microchannel in the not-yet-released cantilever by lifting the edge of the lower nitride film until it touched the

upper nitride layer. A supplementary silicon nitride or gold film was conformally deposited to ensure sealing and patterned along the cantilever with a 2 μm margin. Through the steps of microchannel formation, the trilayer and sealing layer were conformally coating the tip prepared at the beginning. A thick photoresist (≈4 μm) was spin-coated on the substrate in such a way that the end part of the tips protruded above the photoresist surface. Reactive ion etching was utilized to etch the protruding part of the tip until the silicon oxide sacrificial layer was reached. Wet etching of the sacrificial oxide layer created a volcano-shaped silicon nitride tip. Through this etch, the tip was connected to the microchannel. In order to release the cantilevers, a mask was applied onto the backside of the substrate to define an etch window and an on-chip reservoir. Bulk etching of the substrate from the back released the chip with the cantilever and simultaneously completed the on-chip reservoir. The resulting chip is shown in Figure 1c and d. Details of the microfabrication steps, selection of materials, and various processes are reported elsewhere.[14,16]

To test the functionality of the integrated fluidic system, the ink delivery to the tip from the on-chip reservoir via the microchannels was investigated. For this purpose, the on-chip reservoir was fed with deionized water containing a fluorescent dye (dextran, Texas Red, Molecular Probes, Inc.). A micropipette was used to place a droplet of the solution onto the reservoir without applying any pressure. The chip was mounted under a fluorescence microscope and the cantilevers were imaged. Since the microchannel-embedding cantilevers are semitransparent, optical images could be obtained showing that the channels are completely filled with the solution (Figure 2). Using the same scheme but with

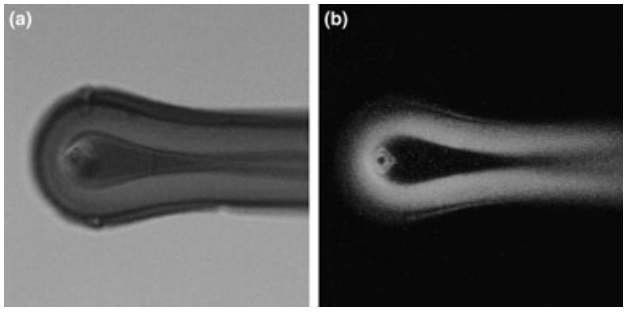

Figure 2. Flow test with a solution of fluorescence dye in deionized water: a) Transmission optical micrograph with empty channels; b) transmission fluorescence optical micrograph—the bright color stems from the fluorescence emission of the dye.

transmission optical microscopy, we examined the filling with commonly used inks: saturated solutions of 1-octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHA) in acetonitrile, ethanol, or methanol. All the combinations succeeded in reaching the volcano tips by filling the microchannels.

Connectivity between the channel and dispensing tip was also evaluated through scanning electron microscopy (SEM) imaging of the tip after the fed ink had dried completely. It was observed that feeding the molecular ink left behind precipitated molecular clusters in the volcano aperture (Figure 3). Experiments for improving the aspect ratio and sharpness of the probes were also performed by growing nanowires through e-beam-assisted W deposition. The deposition of the W nanowire was accomplished when the

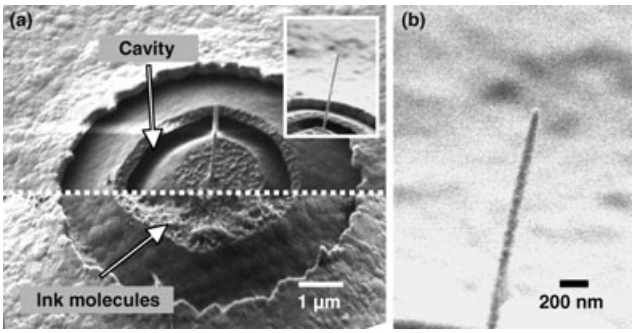

Figure 3. a) Empty volcano cavity prior to ink supply (above the line); volcano filled with molecules after ink supply (below the line). The two images are combined for the purpose of comparison. The inset shows a nanowire grown at the center of the volcano by the e-beam-enhanced deposition of W; b) an image of a W nanowire with MHA molecules coating its surface.

electron beam was focused at one spot on the tip and a W precursor gas was injected in the SEM chamber (Zeiss 1540XB Crossbeam). For these experiments, configurations with poor volcano-shaped tip geometry were chosen, usually obtained close to the edges of the wafers. SEM observations after ink feeding revealed that transport of molecular inks along the W nanowire is in fact achieved (Figure 3). Molecular precipitation was observed along with an increase in nanowire surface roughness.

The imaging capability of the NFP was evaluated by mounting an NFP device into a Dimension 3100 Digital Instruments AFM operated by deflection sensing in contact-mode. Tip-surface contact forces in all imaging experiments ranged from 1 to 3 nN. Imaging of a $40 \times 40\ \mu m^2$ area was performed on a calibration target containing an array of $10 \times 10\ \mu m^2$ squares of 80 nm in height. The images showed good agreement with those obtained with commercially available tips.[16] Since the NFP is designed as a rectangular-shaped beam, the sensitivity in lateral-force imaging (friction-force measurement) was better than with commercial tips (the level of signal in the AFM instrument was ≈10 times higher than for Si_3N_4 Veeco contact-mode probes), which is advantageous in imaging self-assembled monolayer patterns. This imaging capability is important because it implies not only the ability to examine immediately the deposited patterns, but also a means to realign probes for writing with multiple materials.

Writing experiments were subsequently performed to demonstrate the capabilities of the NFP device. Patterns with line widths as small as 40 nm have been successfully written using "normal" volcano tips (without a W nanowire). In these experiments, the ink—a solution of MHA in ethanol at a concentration of 1 mM—was supplied via the on-chip reservoir to the dispensing tip by capillary action. After the tip was brought into contact with a gold substrate,

the molecules were transported to the substrate, creating the desired pattern as the tip was laterally moved along a preprogrammed path (Figure 4). The pattern was obtained with a sweeping rate of 0.05 $\mu m\,s^{-1}$ at room temperature and a relative humidity of 60%. The effect of humidity on

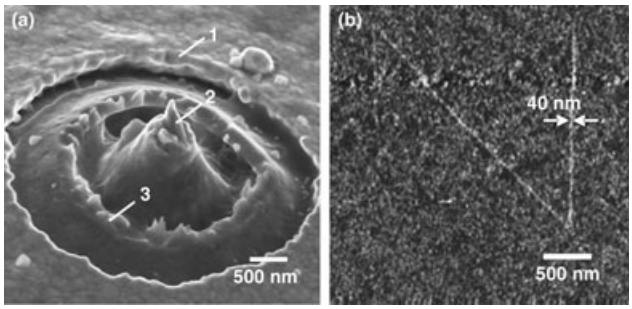

Figure 4. a) Scanning electron micrograph of a volcano tip used for the writing experiment: 1) Au sealing layer, 2) writing tip, 3) top nitride layer (volcano shell); b) Lateral force image of MHA deposited onto a gold substrate by the volcano tip. Both writing and imaging were performed by the same tip.

the feature size is currently under investigation and quantification. It should be mentioned that the writing process was as repeatable as the DPN writing mode.

Taking into consideration that the microfabricated tip radius is about 3 times the patterned line width, the resolution is somewhat surprising. We attribute this feature to the tip roughness, resulting from the reactive ion etching step during its microfabrication, which leads to a much smaller contact area than that which would occur if the tip were perfectly smooth. We are currently investigating this feature in more detail together with the writing with W nanowires. The results will be reported in a later publication.

The same NFP was used many times to generate lines and the smallest feature width was 40 nm, with most line widths less than 100 nm. Sub-100 nm feature sizes were typically obtained with most tips that did not present microfabrication defects. It was also possible to improve tip sharpness by the aforementioned nanowire growth by means of e-beam-enhanced deposition. The size of features written by such tips was in the same range as those obtained with monolithic tips.

It should be highlighted that it was possible to use the same probe with multiple ink feeds of the same solution over a period of a day without cleaning. Consistent and reproducible feature sizes were obtained. It had been expected that the channels would be clogged easily with molecules if a saturated solution were to be used, even with one dose of MHA solution in ethanol. Because of that, a solution of low concentration (1 mM) was employed. Upon feeding such a solution to the probe, the filling state of the microchannels was inspected using a transmission optical microscope. It was observed that there was always fluid filling the channels with sparsely existing air bubbles, typically smaller than half of the channel width. For periods longer than a day, the probes were successfully cleaned by immersion in ethanol or piranha solution (H_2SO_4/H_2O_2 3:1 (v/v)), which was previously used to clean AFM tips in DPN experiments.[17,18] However, the fountain probes were kept immersed longer than regular AFM tips (usually overnight), to provide enough time for molecules coated inside the channels to diffuse out.

In summary, sub-100 nm molecular patterning has been achieved in fountain-pen writing mode with an AFM probe integrated with a volcano tip, microchannels, and a reservoir. The volcano tip has experimentally shown controlled transport of ink to avoid molecular flooding of substrates, ensuring high-resolution patterning. Standard microfabrication techniques were used, which allow the fabrication of massively parallel fountain probe arrays and integration of multiple reservoirs for sub-100 nm patterning over large areas with multiple inks. The devices have application in the fields of nanolithography, combinatorial nanochemistry, biosensors, nanodevices, and beyond.

Keywords:
atomic force microscopy · microfabrication · molecular writing · nanolithography · patterning

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Received: January 24, 2005
Published online on April 5, 2005

