NANO LETTERS

2005
Vol. 5, No. 10
1867−1872

Multifunctional Probe Array for Nano Patterning and Imaging

Xuefeng Wang and Chang Liu*

Micro and Nanotechnology Laboratory, University of Illinois at Urbana-Champaign, 208 North Wright Street, Urbana, Illinois 61801

Received June 1, 2005; Revised Manuscript Received September 7, 2005

ABSTRACT

This letter reports the design, fabrication, and testing of a multifunctional scanning probe array for nanoscale imaging and patterning. The probe array consists of multiple cantilever probes, with each probe being able to perform a dedicated function such as scanning probe lithography (e.g., dip pen nanolithography and scanning probe contact printing) or scanning probe microscopy (e.g., atomic force microscopy and lateral force microscopy). The bending states of each probe can be controlled by using an integrated thermal electric actuator so that it is possible to engage any individual probe(s) independently for writing or imaging purposes. The multifunctional probe array is therefore capable of performing a rich variety of operations with minimal chemical crosstalk and high registration accuracy. It will eliminate the need for probe chip exchanges and increase the operational efficiency. The probe tips in a given array may be made of different materials. Further, the tip and cantilever may be made of different materials for a given probe. In this work, we focus on the development of a probe array consisting of dip pen nanolithography probes, scanning probe contact printing probes (of various tip sizes), and scanning probe microscopy probes.

In recent years, scanning probe microscopy (SPM) techniques have been used widely for nanolithography applications.[1−3] The scanning probe in an SPM instrument can be used to modify a substrate surface with nanoscale resolution through direct or indirect approaches.[4−6] Direct scanning probe lithography (SPL) methods, including dip pen nanolithography (DPN)[7−12] and scanning probe contact printing (SPCP),[13] allow the deposition of a variety of chemical and biological materials with high resolution and multilayer registration capability. DPN uses a sharp, chemically coated atomic force microscope (AFM) tip to transfer chemical molecules onto a solid surface. It has been used to generate patterns with sub-100-nm feature sizes. SPCP uses a cantilever probe with an elastomeric tip to print chemical patterns on a substrate surface. The tip is usually made of poly(dimethylsiloxane) (PDMS). The shape and size of the PDMS tip can be controlled by the design and fabrication processes. In SPCP, a chemical ink is first absorbed into the PDMS tip. Each contact by the tip to the substrate facilitates the local transfer of chemicals and creates a pixel print (analogous to microcontact printing[14,15]), whereas arbitrary patterns can be generated in a dot-matrix manner.

In existing practices of probe-based nanolithography, a single probe is often used for both writing and imaging. This creates risks of cross contamination during use. Although it is possible to switch the probes between writing and imaging runs, this practice proves inefficient in applications. For example, it is very time-consuming to register the writing and imaging probes with nanometer resolution.

For future nanotechnology applications, it is desirable to perform a rich variety of lithography and microscopy operations in sequential manners. A multifunctional probe array would be necessary to enable such operations.

We have developed a new multifunctional probe array device that allows scanning probe nanolithography to be conducted with minimal cross contamination, improved ease and efficiency of operation, and increased registration accuracy. As shown in Figure 1, the multifunctional array consists of multiple probes, each capable of performing a dedicated function. The distance between probe tips is predetermined in design and ensured in micromachining processes. Because the tip-to-tip distance is known, it is possible to spatially coordinate actions from multiple tips.

Each probe must be able to engage independently of others in order to utilize different functional probes simultaneously or sequentially. This calls for active probes, which can move their tips (attached at the distal ends of the cantilevers) up and down from a writing surface. The mechanical displacement capability can be achieved by integrating micromachined actuators with the probes. Commonly used actuation methods include thermal actuation, electrostatic actuation, and piezoelectric actuation.[16] Each actuation principle involves different actuator materials and fabrication steps.[17] The thermal actuation principle is used here because of its material simplicity, large actuation force, and low voltage operation. Each probe has a dedicated thermal actuator on

* Corresponding author. E-mail: changliu@uiuc.edu.

10.1021/nl051016w CCC: $30.25
Published on Web 09/24/2005

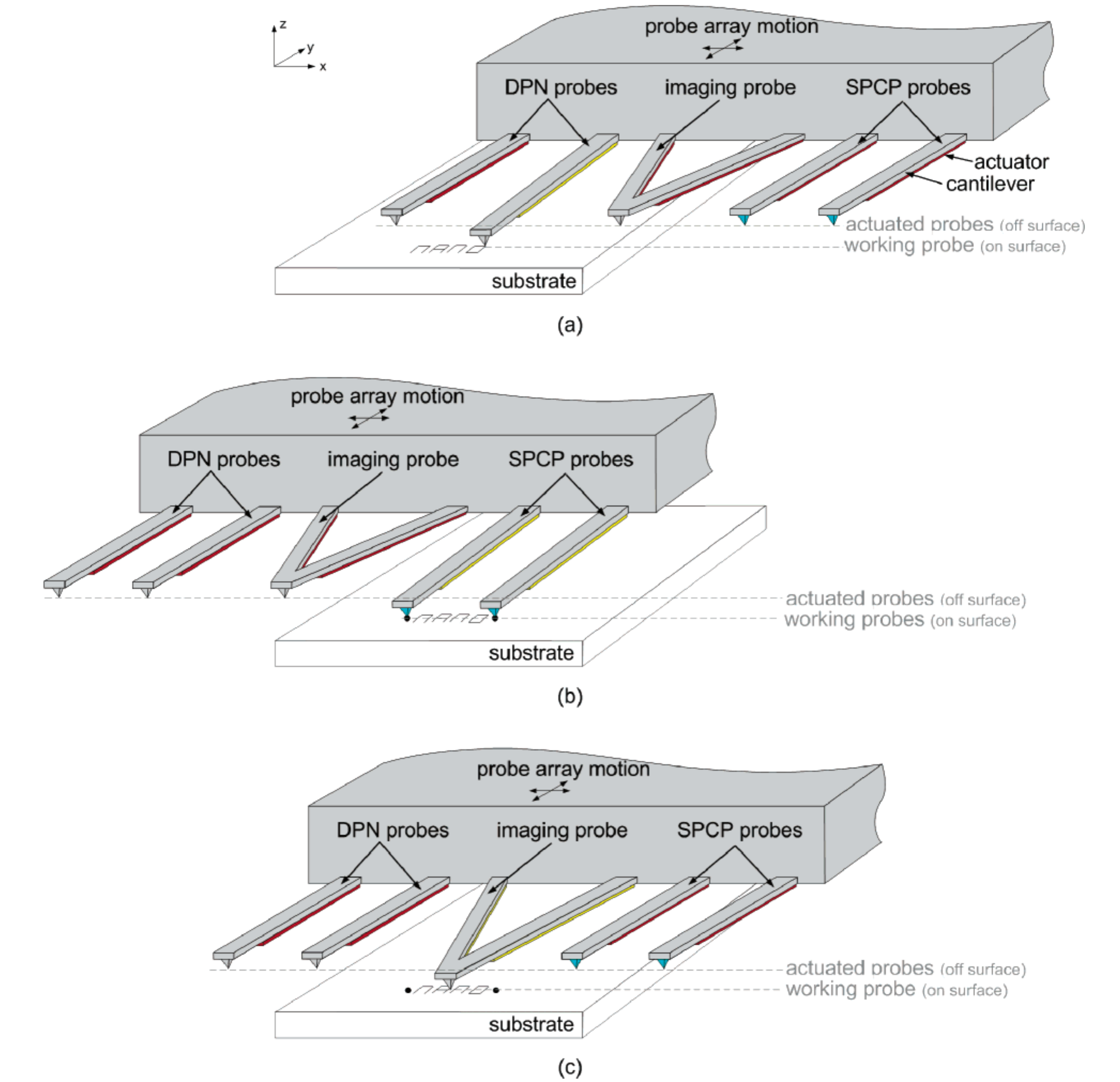


Figure 1. Schematic diagrams showing sequential operations of lithography and microscopy using an active multifunctional probe array consisting of different functional probes. (a) A DPN probe is used for nanopatterning, while other probes in the array are actuated to lift away from the substrate surface. (b) The SPCP probes are used to generate submicrometer or microscale dot patterns. The relative displacement between the probes and the writing surface can be achieved by moving either the probe array (shown here) or the writing substrate (not shown). (c) An imaging probe is used to image the patterned features.

its cantilever. When actuated, the cantilever is bent by the differential thermal expansion of two compositional layers.

In this work, we focus on the development of a probe array consisting of DPN probes, SPCP probes (of various tip sizes), and microscopy imaging probes. In the future, probes of other functions (e.g., conductive probes) or made of other materials (e.g., metals and polymers)[18] can be integrated in this array to expand its functionality.

The development of an active multifunctional probe array for DPN, SPCP, and microscopy involves careful selection of the probe and actuator materials and optimization of the fabrication processes. Challenges emerge when tips, cantilevers, and actuators of different materials must be integrated side by side. Although probes for DPN, SPCP, and imaging have been made separately in the past, conventional methods for making scanning probes need to be modified in order to achieve overall compatibility for an integrated multifunctional probe array. For example, DPN patterning usually uses silicon nitride (Si_3N_4) tips. Fabrication of these tips requires an elevated process temperature for Si_3N_4 deposition. (The temperature for plasma-enhanced chemical vapor deposition (PECVD) of Si_3N_4 is 300 °C.) SPCP probes, however, require PDMS materials for tips. The PDMS tip can be fabricated through a mold-and-transfer process.[13] But the

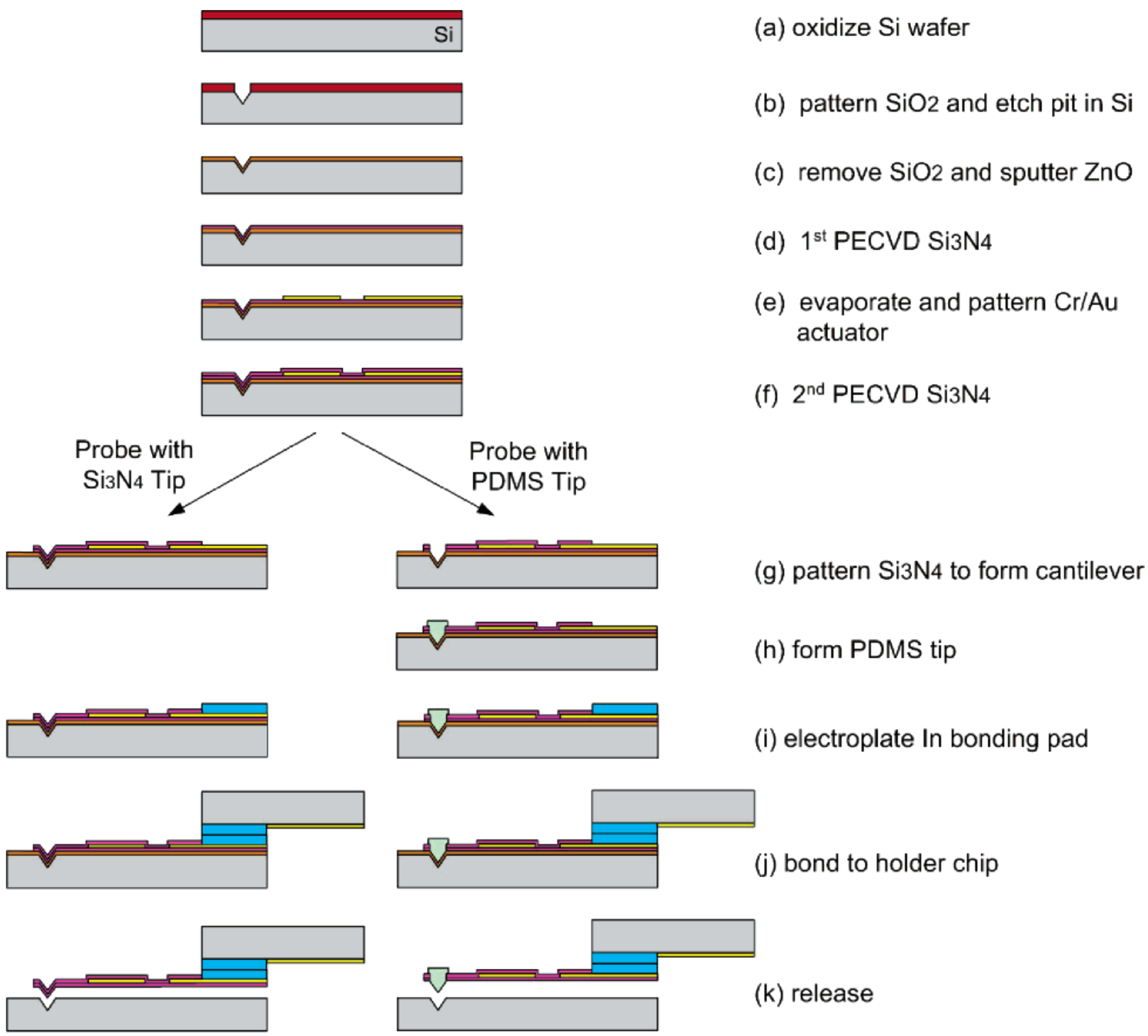


Figure 2. Schematic diagram of the probe array fabrication process consisting of two types of probes.

temperature of the chip may not exceed 200 °C after the PDMS is cured to maintain the chemical and physical properties of the PDMS material.

The fabrication process of a multifunctional probe array consisting of Si_3N_4 and PDMS tips is shown in Figure 2. A general mold-and-transfer technique[18] was determined to be the preferred fabrication method. This technique allows multiple tip materials to be incorporated in one array, ensures the sharpness of the tips, and satisfies temperature/chemical compatibility requirements. In this case, the tips are made of Si_3N_4 and silicone elastomer PDMS, whereas the cantilevers are made of Si_3N_4. The mold-and-transfer technique can be extended to accommodate other materials for the tips and cantilevers.[18]

In our process, a {100} single-crystal silicon (Si) wafer is first oxidized (Figure 2a). The silicon dioxide (SiO_2) layer is patterned, and small square windows of various sizes are opened in the oxide. The SiO_2 layer is used as a mask. The patterned wafer is then immerged into preferential Si etchant ethylenediamine pyrocatechol (EDP) solution at 95 °C. The EDP etching of Si is anisotropic and crystal-orientation-dependent. After timed etch, cavities are formed in Si substrate bounded by {111} planes (Figure 2b). Depending on the etching time and sizes of openings in the SiO_2 layer, the cavities may end in a sharp point or exhibit flat bottoms ({100} crystal plane). These cavities are used as masters to mold probe tips in the subsequent processes.

After the cavities are formed in the Si wafer, the SiO_2 mask layer is removed by using buffered hydrofluoric acid. A thin layer of zinc oxide (ZnO) is sputtered on the entire wafer (Figure 2c). Because ZnO is etched readily by most acids with fast etch rates,[19] it serves as a sacrificial layer for device release. A thin Si_3N_4 layer (0.2 μm thick) is deposited on top of the ZnO layer (Figure 2d). Metal thin films are evaporated and patterned to form resistive actuator elements (Figure 2e). Another Si_3N_4 layer (0.8 μm thick) is deposited and patterned to form probe cantilevers (Figure 2f). The two Si_3N_4 layers sandwich the metal actuator in between to prevent detachment of the metal film from Si_3N_4. Thermal

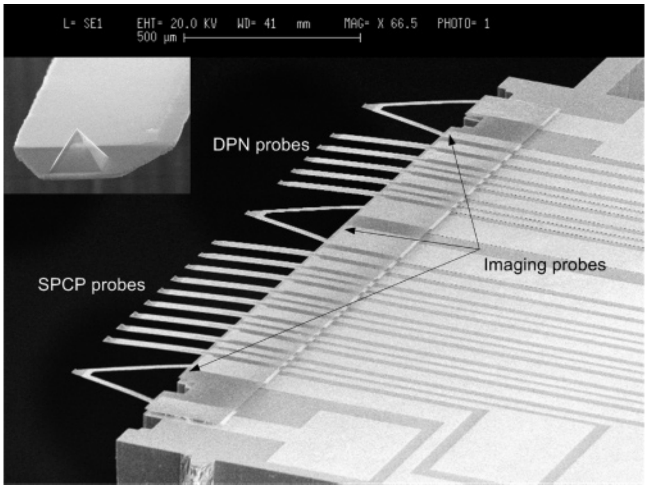


Figure 3. SEM micrograph of a multifunctional probe array. This array consists of five DPN probes (Si_3N_4 tip), nine SPCP probes (PDMS tip) and three imaging probes (Si_3N_4 tip). The inset shows a Si_3N_4 tip with a curvature radius of 100 nm. The distance between adjacent rectangular cantilever probes is 100 μm. The distance between adjacent V-shaped and rectangular probes is 250 μm.

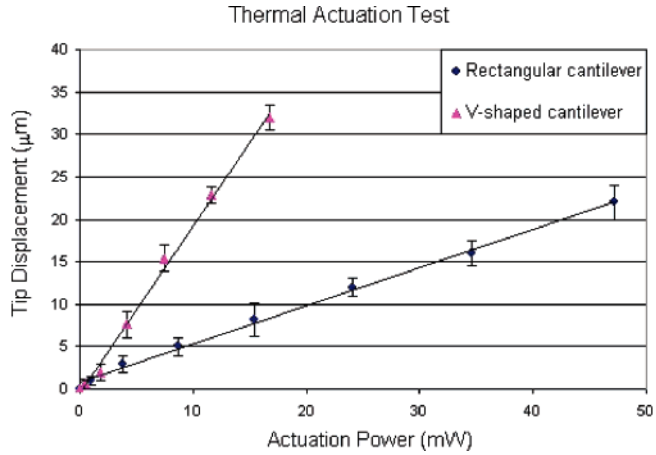


Figure 4. Measured thermal displacement of the probe tip at different actuation powers.

actuation action is achieved by the differential thermal expansion of the metal and the Si_3N_4 layers.

The Si_3N_4 film deposited in the cavities in the Si substrate also forms the Si_3N_4 tips for DPN and microscopy probes. For probes with PDMS tips, windows in Si_3N_4 are opened at the distal ends of the cantilevers until the underlying Si substrate is exposed (Figure 2g). A liquid-form PDMS precursor is applied on the wafer. Excessive PDMS over the front surface is removed using a rubber blade, leaving only PDMS in the cavities for tip molding[20] (Figure 2h). The chip is then baked in a 90 °C convection oven for 30 min to cure the PDMS.

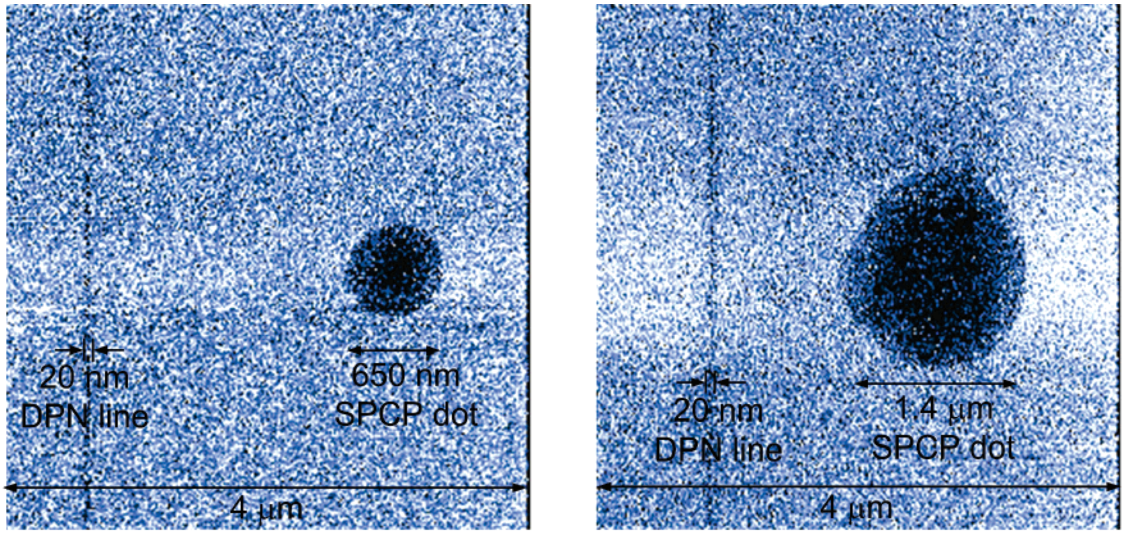
A holder chip is fabricated separately with conductive wires on it. Indium (In) solder bumps are electroplated on both the probe and the holder chips (Figure 2i). The bonding sites provide both electrical connection and mechanical anchoring. Indium is selected as the bonding material because of its low melting temperature (156.6 °C). This is important because the presence of cured PDMS tips forbids any process temperature above 200 °C. The two chips are first aligned and temporarily bonded together on a contact aligner. The assembly is bounded permanently in a nitrogen environment by reflowing the indium bumps at a temperature close to its melting point (Figure 2j). The final device is released by dissolving the ZnO sacrificial layer (Figure 2k).

A completed probe chip is shown in Figure 3. The device has 17 tips with varying tip sizes and different materials. Among these probes, there are five rectangular DPN probes with Si_3N_4 tips of 100-nm curvature radius, nine rectangular SPCP probes with PDMS tips of three different sizes (300-nm round tip, 1-μm flat top, and 5-μm flat top), and 3 V-shaped imaging probes with Si_3N_4 tips of 100-nm curvature radius. The blunt PDMS tips allow coarse features to be generated more rapidly. Multiple tips of the same material and size in an array are designed to offer redundancy or to carry different chemical inks. The rectangular and V-shaped cantilevers represent two typical probe designs used in scanning probe microscopy and lithography. The device shown in Figure 3 has a 100-μm spacing between adjacent rectangular cantilever probes and a 250-μm spacing between adjacent rectangular and V-shaped probes. The tip-to-tip distance can be reduced further to a sub-100-μm scale for higher density or compatibility with a specific SPM instrument.

The thermal actuation performance of the actuators has been tested by measuring the vertical displacement of the probe tips at various current input levels. Figure 4 shows that the tip displacement increases linearly with increasing actuation power for both rectangular and V-shaped probes. The V-shaped probe has a larger thermal displacement than the rectangular probe at the same actuation power because of its thinner resistive heater design and thus higher induced temperature on the probe. The thermal displacement enables the probe tip to be raised up from the writing surface against surface adhesion forces to suspend the lithography process.[21]

Micro and nanolithography tests using this probe array have been conducted on a Thermomicroscopes AutoProbe M5 AFM machine using 1-octadecanethiol (ODT) as the ink. The ink molecules are coated on the probe tips using the contact inking method.[13] A gold-coated Si chip is used as the writing surface. It is mounted on a calibrated high-precision XY stage, which provides in-plane motions with nanoscale resolution. The tip-to-tip distances of the probes on the same chip are measured using a scanning electron microscope. The probe array is mounted on the AFM scanning head and brought into contact with the writing surface. In the lithography process, the XY stage is used to displace the writing surface by a distance corresponding to the tip and the desired pattern spacings for achieving pattern registration.

We demonstrate the multitude of functions that can be achieved by the probe array using different pens. As shown in Figure 5, a nanoscale line pattern is first created using a DPN probe. Then the writing surface is moved so that an SPCP probe hovers above the nanoscale features just created and prints a new dot pattern nearby. The amount of lateral displacement of the writing surface is determined by the



(a) (b)

Figure 5. Lateral force microscopy (LFM) images of ODT patterns generated on a gold-coated Si surface by different probes in the same array. (a) A 20-nm-wide line generated by a Si_3N_4 DPN tip and a 650-nm-diameter dot generated by a PDMS SPCP tip with 300-nm curvature radius; (b) A 20-nm-wide line generated by a DPN tip and a 1.4-μm-diameter dot generated by a SPCP tip with a 1×1 μm^2 flat top. The writing speed for the line patterns is 0.1 μm/s and the tip−substrate contact time for the dot patterns is 1 m in both tests. The size of the images is 4×4 μm^2.

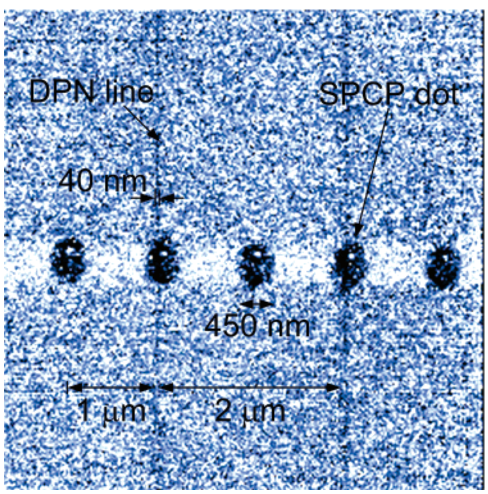


Figure 6. LFM image of aligned dot and line patterns. The size of the image is 5×5 μm^2.

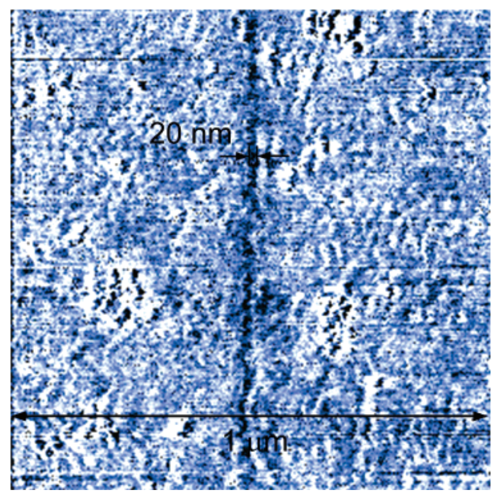


Figure 7. LFM image of a 20-nm-wide ODT line generated by a DPN probe and imaged by a microscopy probe in the same array. The image size is 1×1 μm^2.

distance between the two lithography probes and the desired spacing between the patterns. The Si_3N_4 DPN tips can readily generate sub-50-nm features, whereas the blunt PDMS SPCP tips can create patterns of submicrometer or micrometer scale. Patterns with sizes differing by two orders of magnitude can be readily created side-by-side using DPN and SPCP probes in the same array.

Because the tip-to-tip distance is known, accurate registration between patterns generated by different probes can be achieved easily. Figure 6 shows good registration of lines drawn by a DPN tip and dots printed by an SPCP tip. The lines are generated first using a Si_3N_4 DPN probe. Then the writing surface is moved for a predetermined distance corresponding to the distance between the two tips, and the PDMS SPCP tip is used to print dots on the lines. The dots are 450 nm in diameter with 1-μm spacing and the lines are 40-nm wide with 2-μm spacing. The alignment error between lines and dots is about 50 nm.

With the lithography and imaging probes in the same array, the patterning results generated by the DPN or SPCP probes can be imaged immediately for inspection. Figure 7 shows the LFM image of a 20-nm-wide line generated by a DPN probe and imaged by an imaging probe from the same probe array. No evidence of cross contamination is found.

In conclusion, this letter reports development of an active multifunctional probe array for nanoscale direct chemical pattern generation and imaging. The probe array consists of 17 probes for 3 categories of operations: dip pen nanolithography, scanning probe contact printing, and pattern imaging. With this probe array, patterns of nano- through microscale can be generated with good registration and imaged immediately without the risk of cross contamination and the inconvenience of changing probe chips.

Acknowledgment. This work was supported by the DARPA Advanced Lithography Program and the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF award no. EEC-0118025. We wish to thank Professor Chad Mirkin and Dr. Seung-Wok Chuang at Northwestern University (Evanston, IL), Dr. David Bullen at the University of Illinois, and Dr. Ray Eby of NanoInk Corporation for helpful discussions.

References

(1) Quate, C. F. *Surf. Sci.* **1997**, *386*, 259.
(2) Nyffenegger, R. M.; Penner, R. M. *Chem. Rev.* **1997**, *97*, 1195.
(3) Kramer, S.; Fuierer, R. R.; Gorman, C. B. *Chem. Rev.* **2003**, *103*, 4367.
(4) Eigler, D. M.; Schweizer, E. K. *Nature* **1990**, *344*, 524.
(5) Schoer, J. K.; Zamborini, F. P.; Crooks, R. M. *J. Phys. Chem.* **1996**, *100*, 11086.
(6) Wegscheider, S.; Kirsch, A.; Mlynek, J.; Krausch, G. *Thin Solid Films* **1995**, *264*, 264.
(7) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
(8) Hong, S.; Zhu, J.; Mirkin, C. A. *Science* **1999**, *286*, 523.
(9) Maynor, B. W.; Li, Y.; Liu, J. *Langmuir* **2001**, *17*, 2575.
(10) Li, Y.; Maynor, B. W.; Liu, J. *J. Am. Chem. Soc.* **2001**, *123*, 2105.
(11) Ginger, D. S.; Zhang, H.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 30.
(12) Zhang, H.; Elghanian, R.; Amro, N. A.; Disawal, S.; Eby, R. *Nano Lett.* **2004**, *4*, 1649.
(13) Wang, X.; Ryu, K. S.; Bullen, D. A.; Zou, J.; Zhang, H.; Mirkin, C. A.; Liu, C. *Langmuir* **2003**, *19*, 8951.
(14) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.
(15) Whitesides, G. M.; Ostuni, E.; Takayama, S.; Jiang, X.; Ingber, D. E. *Annu. Rev. Biomed. Eng.* **2001**, *3*, 335.
(16) Kovacs, G. T. A. *Micromachined Transducers Sourcebook*; McGraw-Hill: New York, 1998.
(17) Wang, X.; Bullen, D. A.; Zou, J.; Liu, C.; Mirkin, C. A. *J. Vac. Sci. Technol. B* **2004**, *22*, 2563.
(18) Zou, J.; Wang, X.; Bullen, D. A.; Ryu, K. S.; Liu, C.; Mirkin, C. A. *J. Micromech. Microeng.* **2004**, *14*, 204.
(19) Gardeniers, J. G. E.; Rittersma, Z. M.; Burger, G. J. *J. Appl. Phys.* **1998**, *83*, 7844.
(20) Ryu, K. S.; Wang, X.; Shaikh, K.; Liu, C. *J. Microelectromech. Syst.* **2004**, *13*, 568.
(21) Bullen, D.; Wang, X.; Zou, J.; Chung, S.-W.; Mirkin, C. A.; Liu, C. *J. Microelectromech. Syst.* **2004**, *13*, 594.

NL051016W