MASSIVELY PARALLEL MULTI-TIP NANOSCALE WRITER WITH FLUIDIC CAPABILITIES – FOUNTAIN PEN NANOLITHOGRAPHY (FPN)

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ABSTRACT

Arrays of atomic force microscope (AFM) probes were developed for applications of dip-pen nanolithography (DPN), which is capable of surface patterning with functionalized bio-molecules and can be used to construct biological and chemical sensors. Microchannels were embedded in AFM probes to transport ink or bio-molecules from reservoirs to substrates, realizing continuous writing at the nanoscale. This so-called "fountain-pen nanolithography" (FPN) device was developed using surface and bulk micromachining. A volcano tip, which is a completely novel design for microfluidics, was built at the end of the AFM probe as a dispensing mechanism. Numerical simulations were performed to evaluate flow characteristics and the optimal materials for the volcano-tip probes. The results determined the selection of appropriate materials and the design of microfabrication steps. Multi-layer films and thermal oxidation were used to integrate volcano tips and microchannels into AFM probes. The proposed FPN devices will likely expand the capabilities of surface functionalization and manipulation at the nanoscale in a massively parallel way.

1. INTRODUCTION

Nanopatterning capability is indispensable to fabricate and investigate the nanoworld. Dip-pen nanolithography (DPN) provided an affordable direct writing process, capable of a few tens of nanometers resolution, using atomic force microscopy (AFM) tips [1]. In DPN, molecules are delivered to a surface through a water meniscus. DPN with multiple inks [2] and multiple commercial tips [3] was employed to expand its capability in terms of patterning of multi-species and patterning speed. One disadvantage of DPN in the current stage is that the writing species need to be replenished periodically, requiring the AFM probe to be dismounted, which interrupts the writing process. Several studies reported upon methods that can be utilized to overcome the ink supply drawbacks in conventional DPN. Quartz microprobes, produced by pulling capillary micropipettes, were introduced as an alternative to conventional microfabricated cantilevers [4-6]. Moreover, a pulled micropipette with a small aperture (300 nm diameter) was used to continuously deliver photoresist to a substrate enabling chemical reaction and repair of nanoscale structures [7]. A drawback of these micropipettes is the difficulty in arraying, which is essential to overcome another disadvantage of the conventional DPN, the low speed writing, inherent to the AFM motion. As an effort to

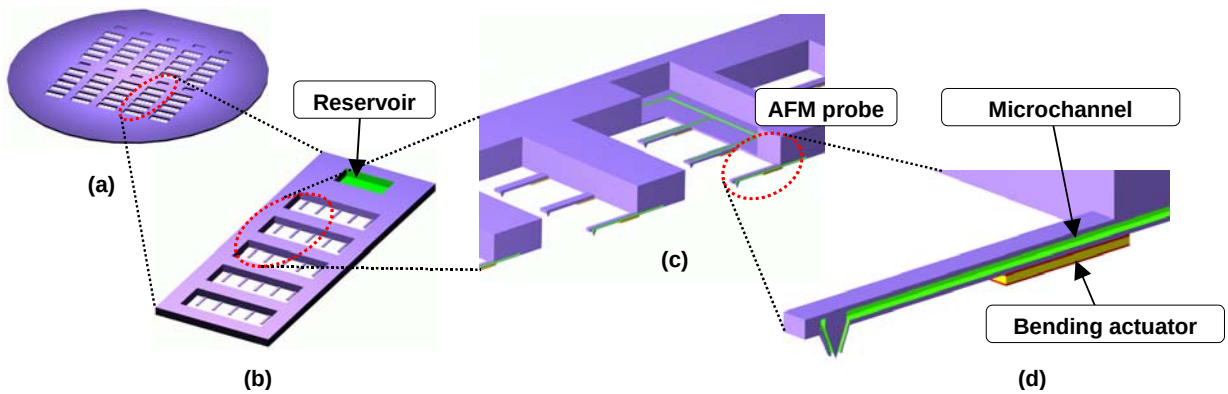

Figure 1. Schematic showing the concept of massively parallel cantilevers: (a) arrays of the device on a silicon wafer, (b) zoom-in view of a unit cell with a feeding reservoir, (c) embedded microfluidics network, (d) a cantilever with a dispensing tip, a microchannel and a bending actuator for vertical motion control.

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overcome the low speed of AFM, thousands AFM probes were integrated on a single chip for parallel writing/reading in data storage application, which eventually enhanced the overall writing speed [8]. Parallel DPN probe arrays on a single chip were also reported [9], which demonstrated DPN-mode writing using eight parallel probes, for linewidths ranging between 80 and 100 nm. However, the probes still need to be detached to replenish the writing species. In this paper, we propose a concept of novel AFM probes with embedded microchannels and an ink-dispensing mechanism, which are microfabricated using surface micromachining technology. We believe that this concept of fountain-pen nanolithography (FPN) will facilitate and expand the DPN technology substantially.

2. DESIGN

The concept of our FPN device is shown in Figure 1. The device consists of massively parallel microprobes and reservoirs integrated in a large size structure. The unit cell of the device, which comprises arrays of microprobes and reservoirs, is supposed to be cut and mounted to a commercial AFM or an X-Y scanner. Each individual microprobe consists of a cantilever, an embedded microchannel, an ink-dispensing tip, and a bending actuator for vertical motion control. In an individual microprobe, ink is fed through an integrated microchannel and transferred to a substrate by a dispensing tip, such that DPN-mode writing can be performed (see Figure 2). The goals of an initial prototype were i) integration of microchannels into AFM cantilevers, ii) development of the ink-dispensing microstructures, and iii) microfabrication of a chip with five cantilevers having the abovementioned features.

In order to implement integrated microchannels and ink-dispensing mechanism to AFM probes, a new method exploiting surface micromachining has been developed. The technique uses so-called volcano tips, a completely novel design for microfluidics, to transport ink from microchannels to substrates (Figure 3).

To assess the feasibility of this concept, we performed numerical simulations of the ink dispensing mechanism and fluid transport in the microchannels (Figure 4). A three-dimensional axially-symmetrical model was used. The channel considered was 0.5 µm high and 500 µm long. A series of simulations were performed using a commercial software (CFD-ACE+) for materials with different wetting angles and for different geometrical configurations of the tip. The simulation showed that the ink can flow to the end of

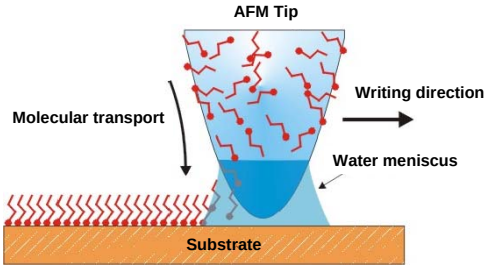

Figure 2. Dip-pen nanolithography [1]

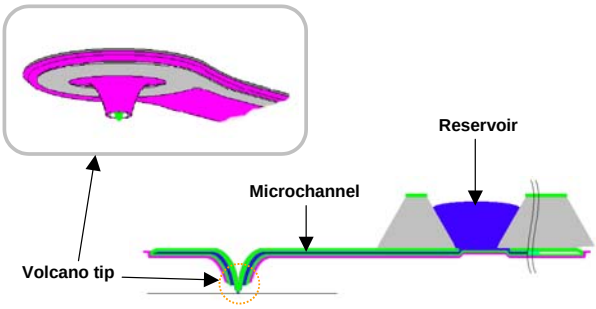

Figure 3. FPN probe with a volcano tip and a reservoir

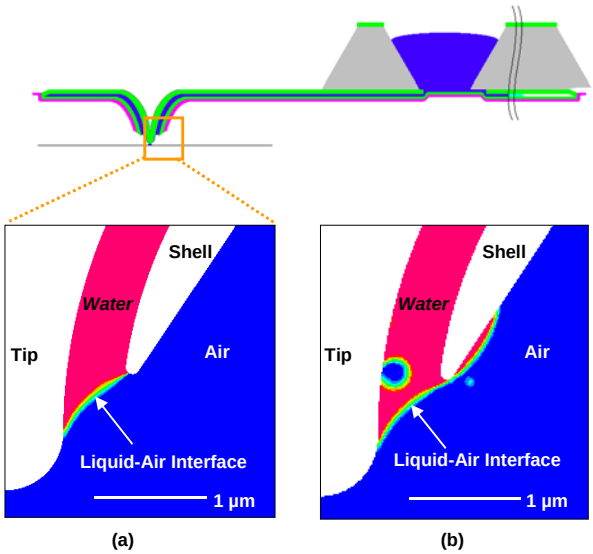

Figure 4. Liquid-air interface at the device tip for two different combinations of tip and microchannel materials. The contact angles of the fluid with the tip and shells are: (a) C_t = 20° and C_s = 65°, tip made of SiO_2 and shell made of Si_3N_4, (b) C_t = 20° and C_s = 20°, tip and shell made of SiO_2

the channel, due to the capillary force resulting from the small channel dimensions, for various channel materials. Moreover, the results showed how the equilibrium liquid-air interface is determined by both the geometry of the device and the contact angles of the liquid on the solid wall surfaces. For some cases, leaking of the liquid outside the channel and formation of vapor bubbles due to cavitation were observed.

3. FABRICATION

The fabrication process for making integrated microchannels is presented in Figure 5. It is based on deposition and patterning of a stacked three-layer film, sacrificial layer etching, and selective oxidation. Firstly, 0.5 µm of low-stress silicon nitride was deposited through low pressure chemical vapor deposition (LPCVD) on a {100} silicon wafer, and a silicon oxide layer (0.5-µm-thick) was subsequently deposited as sacrificial layer by plasma enhanced chemical

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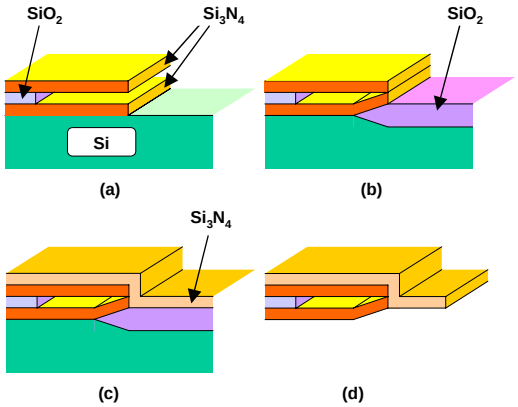

Figure 5. Schematic for the fabrication process of sealed microchannels by underetching and selective oxidation

vapor deposition (PECVD). Deposition of another 0.5 µm of LPCVD silicon nitride followed to complete the stacked three-layer film. Photolithography was performed to define the structures for channels. Those three layers were selectively etched through by reactive ion etching (RIE) with CF_4. The middle silicon oxide layer was underetched in buffered HF. The amount of underetching defined the width of microchannels, which was about 6 µm for this case. In the following thermal oxidation process, only the exposed silicon part was oxidized resulting in a bird's beak structure, which lifted the end of the bottom nitride layer closing the channel. Subsequently, an extra layer of PECVD silicon nitride was deposited to ensure the sealing of the channel. The sealing layer was patterned defining the shape of cantilevers, and finally the cantilevers were released by etching in potassium hydroxide (KOH) solution. Figure 6 shows released cantilevers with integrated microchannels. The cantilevers are bent up due to the release of residual stress, which favors the later integration of cantilevers in arrays of AFM probes.

A cross-section of a microchannel in one of the released cantilevers is shown in Figure 7. Unexpected deposition of PECVD nitride occurred inside the channels after the sealing process. The reason is because, through the selective oxidation process, the top nitride layer was lightly lifted up, resulting in a small open gap at the margin of the channels (Figure 8). This allowed the inside deposition, due to the highly conformal PECVD process. The small open

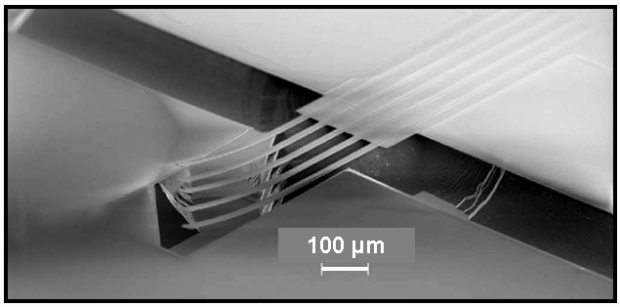

Figure 6. Released cantilevers with integrated microchannels

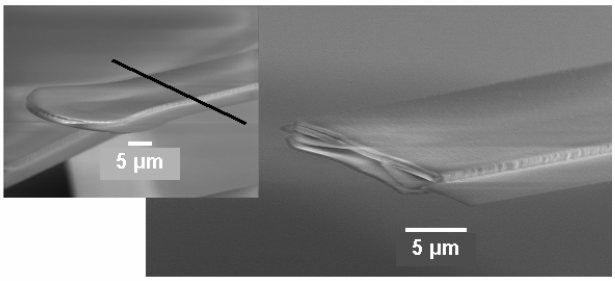

Figure 7. Cross-sectional view of microchannels integrated in a cantilever

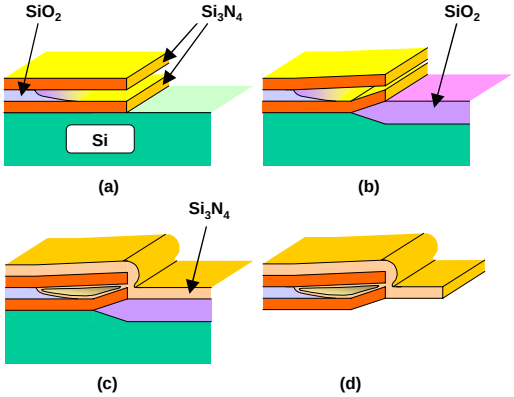

Figure 8. Schematic showing the reason for the inside deposition during the sealing process

gap at the edge was soon closed in such a way that a much thinner layer formed inside the channel than outside. This inside deposition was not such critical to the dimension of the channels. The obtained channels were still tall enough to deliver liquid (~0.4 µm, which is 0.1 µm shorter than targeted).

Tips were microfabricated on silicon wafers by either wet or dry etching, followed by oxidation sharpening. Over these tips, the before-mentioned process for microchannels was used to produce volcano tips and microchannels for AFM probes. The tip fabrication implied the deposition of an LPCVD nitride or thermal oxide layer on {100} silicon wafers, patterned with CF_4 RIE to define precursor caps, which were used as masks in the following etching steps to form tips. Different shapes, dimensions and processes were experimented for the precursors etching. Several circular-shape precursor caps with diameters varying between 7 µm and 12 µm were used for defining precursors by isotropic etching. One set of precursor caps consisted in 12 µm x 12 µm squares with 10-µm-long and 2-µm wide beams at the corners of the squares. These shapes were used for anisotropic etching of precursors [10]. Tips were etched in either acid mixtures (HF-CH_3COOH-HNO_3) or KOH solution, and terminated before the precursors started to fall off. After the precursors were removed, the wafers went through an oxidation sharpening process. One micron of oxide was thermally grown at low temperature (950 °C), to take advantage of the stress-induced oxidation reduction [11].

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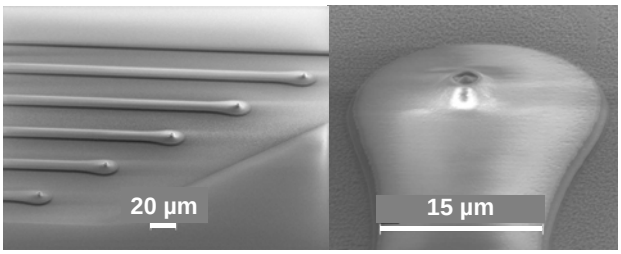

Figure 9. Cantilevers with integrated microchannels and volcano tips (prior to release)

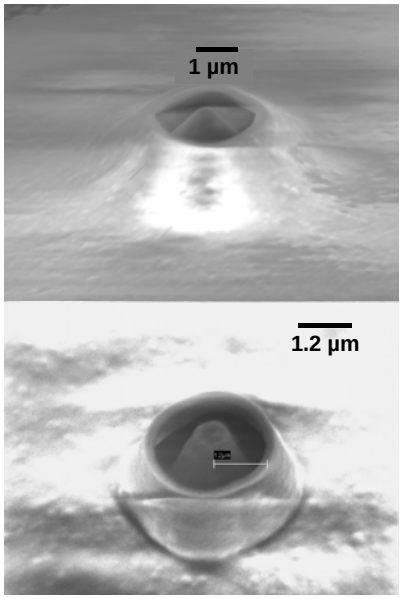

Figure 10. Volcano tip made by deposition of 3 layers followed by selective etching and removal of sacrificial layer; tip formed by etching in acid mixture solution (top) and KOH (bottom)

The oxide was subsequently removed in buffered HF, leaving sharpened tips. Tips radii achieved so far are better than 30 nm.

After sharpening, three layers of films, which comprised a PECVD oxide layer sandwiched between two LPCVD nitride layers, were deposited and the process for microchannels was performed. Photoresist was spun over the microfabricated microchannel structures, and subsequently, RIE etching was fulfilled in such a way that only the photoresist over the end of the tip was etched away. In this way, a portion of the top nitride layer at the end of the tip was exposed to RIE and etched until the middle oxide layer beneath was exposed. After that, the wafer was immersed into buffered HF to remove the sacrificial oxide layer, completing the volcano-tip structures and making the connection with the microchannels. Figure 9 and Figure 10 show the volcano tips on AFM probes.

4. CONCLUSIONS

Unique AFM probes with volcano tips and integrated microchannels were designed and fabricated using surface micromachining technology. Materials and geometries for volcano tips were selected based on the results of numerical simulations. A chip with single cantilevers with microfluidics capabilities was microfabricated.

5. ACKNOWLEDGEMENT

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6. REFERENCES

[1] Piner, R. D., Zhu, J., Xu, F., Hong, S., and Mirkin, C. A., “Dip-Pen Nanolithography,” *Science*, Vol. 283, pp. 661-663, 1999.

[2] Hong, S., Zhu, J., and Mirkin, C. A., “Multiple Ink Nanolithography: Toward a Multiple-Pen Nano-Plotter,” *Science*, Vol. 286, pp. 523-525, 1999.

[3] Hong, S. and Mirkin, C. A., “A nanoplotter with both parallel and serial writing capabilities,” *Science*, Vol. 288, pp. 1808-1811, 2000.

[4] Lewis, A., Kheifetz, Y., Shambrodt, E., Radko, A., Khatchatryan, E., and Sukenik, C., “Fountain pen nanochemistry: Atomic force control of chrome etching,” *Appl. Phys. Lett.*, Vol. 75, No. 17, pp. 2689-2691, 1999.

[5] Shalom, S., Lieberman, K., Lewis, A., Cohen, S. R., “A micropipette force probe suitable for near-field scanning optical microscopy,” *Rev. Sci. Instrum.*, Vol 63, No. 9, pp. 4061-4065, 1992.

[6] Lieberman, K., Lewis, A., Fish, G., Shalom, S., Jovin, T. M., Schaper, A., Cohen, S. R., “Multifunctional, micropipette based force cantilevers for scanned probe microscopy,” *Appl. Phys. Lett.*, Vol. 65, No. 5, pp. 648-650, 1994.

[7] Hong, M.-H., Kim, K. H., Bae, J., Jhe, W., “Scanning nanolithography using a material-filled nanopipette,” *Appl. Phys. Lett.*, Vol. 77, No. 16, pp. 2640-2606, 2000.

[8] Vettiger, P., Despont, M., Drechsler, U., Durig, U., Haberle, W., Lutwyche, M. I., Rothuizen, H. E., Stutz, R., Widmer, R., Binnig, G. K., “The Millipede – More than one thousands tips for future AFM data storage,” *IBM J. Res. Develop.*, Vol. 44, No. 3, pp. 323-340, 2000.

[9] Zhang, M., Bullen, D., Chung, S.-W., Hong, S., Ryu, K. S., Fan, Z., Mirkin, C. A., Liu, C., “A MEMS nanoplotter with high-density parallel dip-pen nanolithography probe array,” *Nanotechnology*, Vol. 13, pp. 212-217, 2002.

[10] Offereins, H. L, Kühl, K., and H. Sandmaier, “Methods for the fabrication of convex corners in anisotropic etching of (100) silicon in aqueous KOH,” *Sensors and Actuators A*, Vol. 25-27, pp. 9-13, 1991.

[11] Ravi, T. S. and Marcus, R. B., “Oxidation sharpening of silicon tips,” *J. Vac. Sci. Technol. B*, Vol. 9, No. 6, pp. 2733-2737, 1991.

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