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Integrated microfluidic inking chip for scanning probe nanolithography

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This letter reports an architecture for a microfluidic chip that dresses (inks) multiple nanolithography tips in a high-density array in a parallel and multiplexed fashion. The microfluidic chip consists of multiple precision patterned thin-film poly(dimethylsiloxane) (PDMS) patches serving as porous inking pads. Inking chemicals are supplied from loading reservoirs to the inking pads through microfluidic channels. The gas-permeable thin PDMS membranes allow ink molecules to diffuse through while preventing bulk liquid from overflowing or evaporating. The inking chip provides high-density inking, easy loading of inks, and reduced evaporation losses. We present the fabrication process and inking of scanning probe contact printing probes and commercial nitride probes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1771453]

Scanning probe microscopy (SPM) has been widely used for patterning submicron features.^{1–5} In SPM technologies, a sharp tip (3–200 nm radius of curvature, normally made of silicon nitride) is located at the distal end of a cantilever and scanned across a surface of interest. By measuring the interaction force between the tip and surface, various surface properties can be measured down to molecular or atomic resolutions.

The SPM instrument can be used to place chemical and biological molecules with submicron precision for applications, such as producing deoxyribonucleic acid and protein arrays, and for patterning general organic or inorganic molecules. For example, dip pen nanolithography (DPN)^{6,7} utilizes the capability of SPM technology to deposit chemicals onto a substrate with sub-100-nm linewidth by coating the tip with a chemical of interest. When the probe is placed in contact with a surface, a meniscus forms and provides a pathway for the chemical to diffuse from the probe tip to the surface.

Recently, a technique called scanning-probe contact printing (SP-CP) was invented.⁸ It utilizes an SPM probe with an integrated tip made of poly (dimethylsiloxane) (PDMS). In the SP-CP process, chemicals are first absorbed into the elastomeric tip. The probe is then moved to a desired location using a commercial SPM. Each contact printing action creates individual dots, analogous to dot-matrix printing. This method combines the chemical versatility and performance advantages of microcontact printing^{9–14} with the production flexibility and accuracy of DPN.

The throughput of SPM-based nanolithography methods can be increased by using arrays of probes,¹⁵ arranged in one or two dimensions. Certain future applications require inking different tips with different chemicals. However, existing methods for inking such nanolithography probes all rely on exposure to a chemical vapor of interest or by immersing the

probes in a liquid, and are therefore not suitable for arrayed tips because of cross contamination, especially for high-density tip arrays (e.g., with tip-to-tip spacing on the order of 100 μm in one or two axes). Parallel inking, using open capillary wells, incurs rapid ink loss through evaporation.¹⁶ In addition, active control is required to maintain the desired liquid level to interact with tips successfully.

A method for parallel, multiplexed inking must be practical, robust, scalable (to potentially hundreds of tips per inking session, and low cost, while providing high-density and minimal ink loss.

We report a method of “inking” tips that takes advantage of thin PDMS membrane patches through which molecules can permeate. As shown in Fig. 1, a thin PDMS membrane (5 μm thick) is patterned in registration with vent holes made in a silicon wafer. PDMS can readily absorb many types of chemical inks with little distortion.¹⁰ Reservoirs and connecting fluidic channels, formed by PDMS molding, are

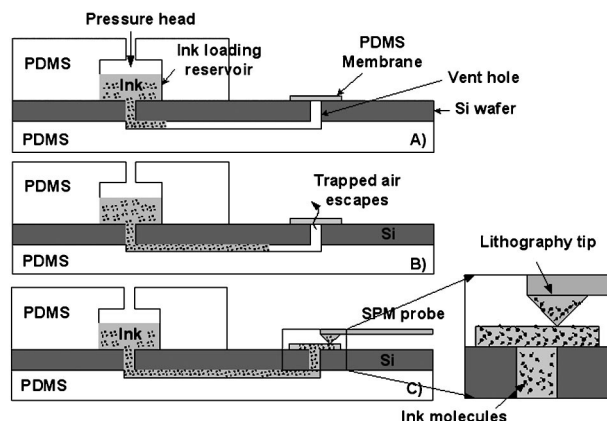


FIG. 1. Schematic side view of an inking chip. Positive pressure head at the reservoir moves the liquid ink toward the PDMS membrane since trapped gas can permeate through PDMS. In time, ink will diffuse through the PDMS membrane, allowing tips in contact with the membrane to pick up inking chemicals.

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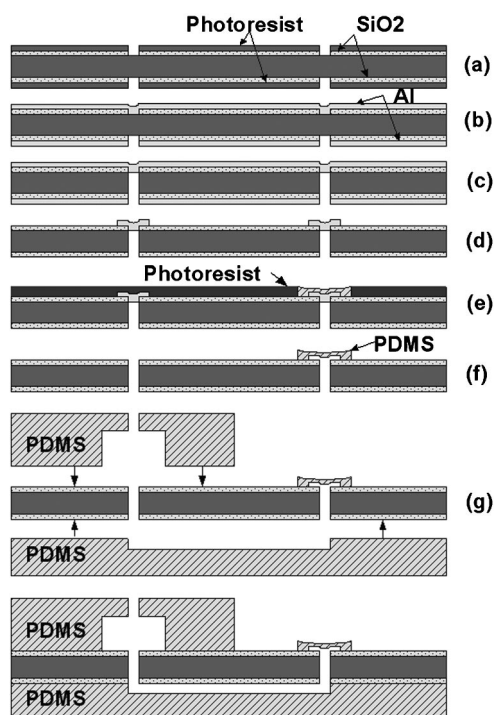


FIG. 2. Schematic diagram of the microfabrication process of the inking chip.

reversibly bonded on two sides of a silicon wafer. Once the reservoir is filled with ink [Fig. 1(A)], the positive pressure head at the reservoir moves the “ink” toward the inking site (membrane). Trapped air escapes through the thin PDMS membrane [Fig. 1(B)], allowing inking liquid to contact the bottom of the membrane. The ink, over time, diffuses through the membrane to the other side and is picked up by a tip in contact mode. The diffusion of ink molecules through the membrane follows the Fick’s first law,

$$J = -D \frac{dC}{dx}, \quad (1)$$

where D is the diffusion coefficient of the ink molecule in PDMS, C is the concentration of the ink in the solution, and x is the thickness of the PDMS membrane. The diffusion coefficient D is an experimental parameter that varies with the ink molecules and the PDMS elastomer.

Advantages of this method include: (i) No active pumping or valving is required to gain precision leveling of liquid at inking spots, (ii) cross contamination of adjacent PDMS membranes is minimal, (iii) Rapid evaporation of liquid and bubble clogging are avoided. (It was found that 5 μl of an ethanol-based solution in a reservoir lasted more than 10 h before drying up.), (iv) High-density inking sites are possible by routing microfluidic channels.

The fabrication process to realize the integrated inking chip is shown in Fig. 2. (a) First, a 1- μm -thick SiO₂ layer is thermally grown on a Si substrate ({100} orientation (International Wafer Service, Portola Valley, CA). Using photolithography with double side alignment, the SiO₂ layer at the front and back side are wet etched at sites where through holes are to be made. (b) 2000-Å-thick Al films (99.999%, Alfa Aesar, Ward Hill, MA) are deposited on the front and back side of the wafer. (c) The film on the back side is photolithographically patterned, serving as mask for the sub-

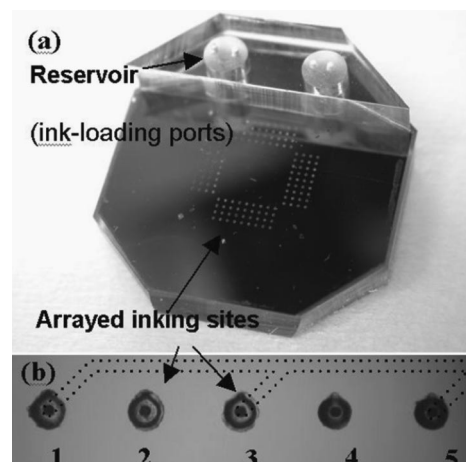


FIG. 3. Optical micrograph of an assembled inking chip with eight inking sites. (a) Perspective view showing four reservoirs and PDMS membranes. The Si wafer is 250 μm thick; (b) Close-up view of individual PDMS patch membranes, each 200 μm in diameter.

sequent deep reactive ion etching to create through wafer holes for liquid communication. (d) The front-side Al film is patterned to overlap with the through holes with 20- μm -radial margins. The back-side Al film is removed in this step. (e) A 10- μm -thick AZ 4620 photoresist is spin coated and lithographically patterned to create molds for PDMS patterning, following a recently developed PDMS patterning method.¹⁷ Uncured PDMS (10:1 mixing ratio with curing agent, Dow Corning Sylgard 184, Midland, MI) is used to define PDMS patches, overlapping with aluminum thin-film patterns. The approximate thickness of PDMS patches is 5 μm .¹⁷ (f) After curing, the PDMS at 60°C for 2 h, the photoresist layer is removed with acetone followed by Al etching. (g) Finally, the top and bottom pieces of PDMS molded separately¹⁸ are aligned and assembled. Figure 3 shows the assembled chip with 144 (four groups of 4 \times 9 arrays) inking sites.

Inking of tips with organic molecules has been performed by filling the two reservoirs with a 4 mM ethanolic 1-Octadecanethiol (ODT) solution. 5 μl of the solution was fed into the reservoir. Ink travels to the membrane sites in 2–3 s. After 6 h of allowing the PDMS membrane to become saturated with ODT, SPM tips are made to contact the inking pads to initiate ink transfer from the pad to the tips (Fig. 4). It was found the 5 μl of solution completely dries up in approximately 12 h. With bigger reservoirs (~100 μl), the concentration change in the ink due to evapo-

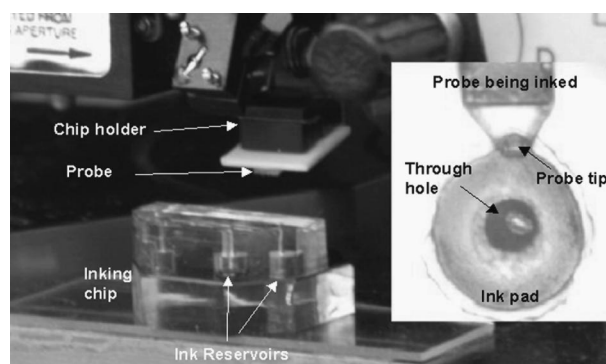


FIG. 4. The operational setup in a SPM nanolithography station. The inset shows a single SP-CP probe contacting a PDMS membrane at the periphery.

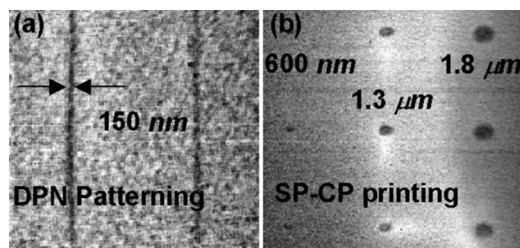


FIG. 5. (a) Atomic force microscopy scan image of lines drawn by a nitride DPN tips. (b) ODT dots created by a single SP-CP probe. Large size dots are useful to print coarse features for selected applications.

ration could be reduced. Nanolithography tips (including a silicon nitride Microlever tip and a SP-CP tip) were then placed directly on top of the PDMS inking patches but not over the vent hole aperture (to avoid accidental puncturing). After 30 min of inking, the nitride probe and SP-CP probe were used to write on Au surfaces. For comparison, “inking” by making contact to bulk PDMS soaked for 12–24 h in a solution takes at least 10 min. The inking speed is still limited by diffusion but parallelism and ink multiplicity capabilities are gained. Figure 5(a) shows lines drawn by a commercial nitride probe with a writing speed of $0.1 \mu\text{m/s}$. Increasing the writing speed results in narrower linewidths as shown in Fig. 6. Figure 5(b) shows multiple pixels drawn by a SP-CP probe. For contact time of 10 s, 30 s, and 1 min, the diameters of dots are 600 nm, $1.3 \mu\text{m}$, and $1.8 \mu\text{m}$, respectively.

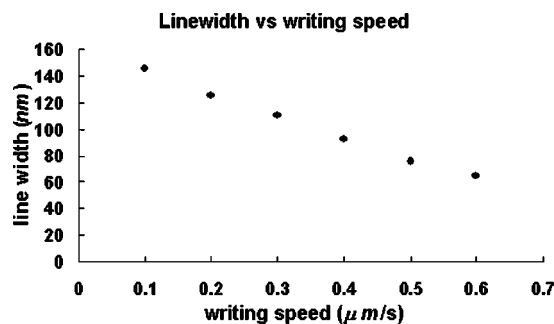


FIG. 6. Writing speed and resulting linewidth plot for commercial nitride probe in DPN writing mode.

A cross-contamination test was performed by supplying ODT to every other inkpad (i.e., Nos. 1, 3, and 5 inkpads) as shown in Fig. 3(b) and making contact to inkpad No. 2, which was not being fed ink from the channel side. We performed writing after 30 min of contact, but no ODT pattern was detected. We concluded that no appreciable cross contamination occurs even 6 h after chemicals introduction.

In conclusion, this letter reports a method for inking scanning probes for direct soft lithography. Thin PDMS membranes were used as inkpads, which minimized the evaporation of the ink and thus cross contamination between inking sites. Inking operation has been confirmed for both DPN and SP-CP modes.

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