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Pneumatically actuated elastomeric device for nanoscale surface patterning

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The authors present a simple polydimethysiloxane (PDMS) device for nanoscale surface patterning by controllably bringing a hard silicon nitride tip on a PDMS membrane in and out of contact with surfaces using pressurized gas to inflate the membrane. The writing process is analogous to contact printing. By regulating the pressured gas to actuate the silicon nitride tip on the PDMS membrane, the nanometer size features can be easily fabricated on substrates. Moreover, using the dot matrix method, this PDMS device can masklessly fabricate arbitrary patterns. In this letter, a nanometer scale three-line pattern is demonstrated. © *2007 American Institute of Physics*.

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Scanning probe nanolithography (SPN) is an emerging technique to generate nanoscale chemical patterns. It uses a sharp scanning probe or probe arrays to transfer chemical ink onto solid substrates. These inks include small organic molecules, peptides, proteins, oligonucleotides, and inorganic sol gel.[1–3] In the past several years, much progress has been made to develop micromachined tools for SPN, including passive or active scanning probes or probe arrays[4–7] and probe inking chips.[8–10] These advanced micromachined tools have tremendously expanded the capabilities of SPN. Among these micromachined SPN tools, the active probe or probe array demonstrated unique writing capability.[6,7] The current active probes are actuated by either thermal bimorph effect or electrostatic force. Both of them have serious cross-talk problems (heat or electrical field) that can deteriorate the performance of other probes in the same array, so new actuation methods need further exploration, e.g., pneumatic actuation.

Since the advent of soft lithography, an explosion of development has extended the use of elastomers for surface patterning. Elastomeric stamps can be used to pattern surfaces with monolayer-scale amounts of molecules, ranging in size from small molecules such as alkanethiols and silanes to large molecules such as DNA and proteins.[11,12] While the use of centimeter-scale elastomeric stamps for soft lithography allows the patterning of large areas at once, this comes at the expense of flexibility: a new stamp must be fabricated whenever a change in design is desired. Competing techniques based on finely controlled writing with a single pen, such as SPN and pipette-based patterning,[13–16] allow arbitrary patterns to be made in a maskless fashion, reducing the cost and turn-around time.

In this letter, we demonstrate a simple device that takes advantage of the elasticity of polydimethylsiloxane (PDMS) to create a surface-patterning tool with unique abilities. This active surface-patterning device is pneumatically actuated, based on the inflation of a PDMS membrane with a hard silicon tip using pressured gas. The inflation pressure controllably brings the tip into contact with the surface to write nanometer size features on the substrate. This unique device combines the simplicity and versatility of microcontact printing with the customizability and resolution of maskless, scanning probe based lithography methods.

Figure 1 is a schematic of a pneumatically actuated PDMS device for surface patterning. The device consists of a soft PDMS membrane hosting a silicon nitride pyramidal tip and a gas channel that provides pressured gas. Instead of bringing a large stamp into contact with surfaces like microcontact printing, a pressurized gas channel provides inflation pressure to controllably bring the tip in contact with the surface. Once the tip contacts the surface, molecular inks are transferred from the tip to the substrate and form monolayer chemical patterns on the substrate. When the inflation pressure is slightly reduced and the deformation of the PDMS membrane becomes smaller, the tip is detached from the surface and the ink transfer is stopped. The displacement of the tip on the PDMS membrane is approximately calculated using the analytical equation for the case of a circular plate under uniform pressure with a clamped boundary because the dimension of the tip is much smaller than that of the PDMS membrane.[17] This PDMS chip is mounted on the scanning head of a commercial atomic force microscopy (AFM) machine (M5, Digital Instrument, Santa Barbara,

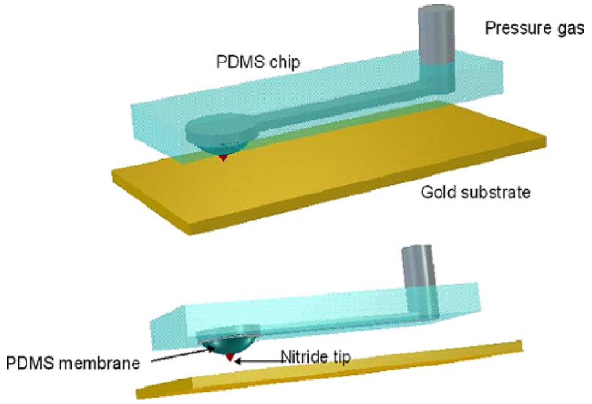

FIG. 1. Schematic of a pneumatically actuated PDMS surface-patterning device with a silicon nitride tip on a PDMS membrane.

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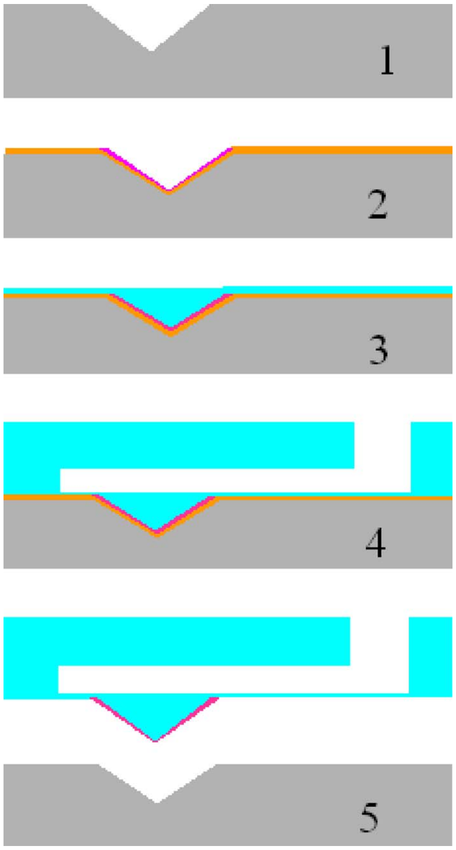

FIG. 2. (a) Pneumatically actuated PDMS device fabrication process: (1) cavity etching on silicon wafer; (2) ZnO and silicon nitride layers deposition and patterning; (3) spin coating the thin PDMS layer; (4) PDMS bonding with the pneumatic actuation PDMS layer; (5) PDMS device releasing.

CA). The precise movement of AFM stage enables the PDMS chip to precisely fabricated patterns at any location on the substrate.

The PDMS chip fabrication process is briefly diagramed in Fig. 2. Starting with a ⟨100⟩-oriented silicon wafer, we use anisotropic etching to create an inverted pyramidal tip. A 2500 Å thick layer of ZnO is sputtered conformably on the tip silicon mold as a sacrificial layer. Then a 1 μm thick layer of silicon nitride thin film is deposited and then photolithographically patterned. This is followed by spin coating the patterned silicon wafer with PDMS (Dow Corning Sylgard 184) prepolymer solution mixed at a 20:1 base: cross-linker ratio at 2000 rpm for 1 min. Separately, 5:1 PDMS prepolymer solution is poured onto a microchannel silicon mold. After baking for 15 min at 65 °C, the pieces are removed from the oven, and access holes are drilled in the stiff (5:1) block using a sharpened 18 gauge hypodermic needle after peeling the stiff block from the substrate. The molded piece of PDMS layer with integrated channels for delivering pressure is bonded with the thin PDMS layer using a home-built aligner. A subsequent bake is performed for more than 30 min at 90 °C. Finally, the PDMS device is released from the silicon substrate by etching off the sacrificial layer after two days etching inside diluted HCl acid solution. An optical micrograph of the silicon nitride tip on top of the PDMS membrane is shown in Fig. 3. The inset is a close-up view of the silicon nitride tip. The length at the base of the tip is approximately 20 μm.

The writing experiments are conducted using a thermo-microscope M5 AFM machine (Digital Instrument, Santa Barbara, CA). The AFM scanning head is modified by the addition of a two degree-of-freedom tip-tilt stage to the end of the scanner. The stage allows devices to be tilted side to side by ±14° and front to back by ±20°, both with a resolution of ~0.1°. The PDMS device is mounted to a shaped plastic holder on the stage. A 20-gauge stub needle is used to connect a plastic tube to the PDMS device. The pneumatic pressure is delivered through the plastic tube using a home-made computer controlled regulator. Before surface patterning, the PDMS chip needs be aligned with the surface of the substrate. The device-to-substrate surface alignment is assisted using a video microscope that provides a front view of the tip on the inflated PDMS membrane. As the tip approaches the substrate, it is clearly visible with its reflection in the gold surface. Alignment is accomplished by adjusting the tilt stage until the device is parallel with its reflection. Once the tip approaches the surface, a 1–2 μm overdrive is needed to make sure that the tip physically contacts the surfaces. After the tip finishes writing at a position, it moves up 5 μm to detach from the surface and then moves to the next position for the writing.

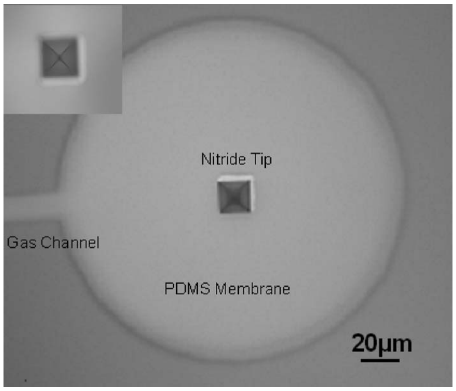

FIG. 3. Optical micrograph of a circular PDMS membrane with a silicon nitride tip. The inset is a close-up view of the silicon nitride tip.

The writing substrates are prepared from a ⟨100⟩ silicon wafer and etched with different alignment marks using a DRIE (deep reactive ion etching) machine. The alignment marks on the substrates are used as location references for the later pattern imaging. Then the wafer is diced into small chips (approximately 3 by 5 mm^2), cleaned with acetone/isopropanol/water and piranha solution (38% $H_2SO_4:H_2O_2 = 700$ ml:300 ml) for half an hour. After the surfaces are dried by nitrogen gas, a 5-nm-thick chromium thin film and a 20-nm-thick gold thin film are then deposited by thermal evaporation. The samples are stored in a vacuum chamber to prevent the surface oxidation until use (between 1 and 24 h).

The inking of the silicon tip is performed using thermal vapor-inking method. The PDMS device with the silicon nitride tip is mounted on a cover using double side tape and sealed inside a metal container that is full of solid octadecanethiol (ODT) chemical. The container is put on a hot plate and heated to 70 °C and held for 30 min, and then allowed to slowly cool down for about 30 min. The vapor coating process is repeated (typically two to three times) until the tip is sufficiently coated with ODT for the following printing experiments.

After the PDMS device finishes inking, it is mounted on the customized AFM scanning head to print dot array on the substrate with the different contact times. Figure 4(a) is dif-

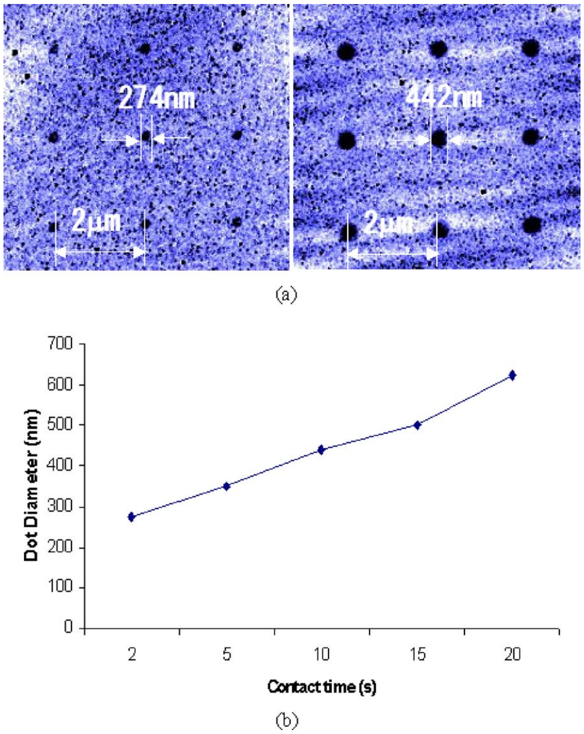

FIG. 4. (a) Lateral force microscopy (LFM) images of ODT dot array made by the pneumatically activated silicon nitride tip on the PDMS membrane at contacting times of 2 and 10 s. The temperature and the relative humidity are 23 °C and 38%, respectively. (b) Characterization of the pneumatically actuated PDMS device with the nitride tip on the PDMS membrane at different contacting times.

ferent AFM scanning images at different contact times at 2 and 10 s. The size of the dot is found as a function of the contact time [Fig. 4(b)]. The experiments are conducted at a temperature of 23 °C and 38% relative humidity. Besides these simple dot arrays, the PDMS device can also write arbitrary shape patterns on the substrate using the dot matrix method. A three-line pattern is demonstrated using the overlapped dot matrix. Figure 5 is a lateral force microscopy (LFM) image of the three-line pattern formed by the overlapped dot matrix. Theoretically, the PDMS device can make any shape or complicated pattern using the same dot matrix method.

A PDMS device with a hard silicon tip for nanoscale surface patterning has been demonstrated. By using the dot matrix method, the PDMS device can write arbitrary shape nanoscale patterns on the substrate. This pneumatically actuated PDMS device presents an option for AFM-driven nanoscale patterning techniques. The nature of the actuation presents advantages for creating arrays, since there are heat transfer or electrical field related cross-talk issues, as seen in thermally or electrically actuated patterning devices. The scalability, pneumatic addressability, and ease of fabrication

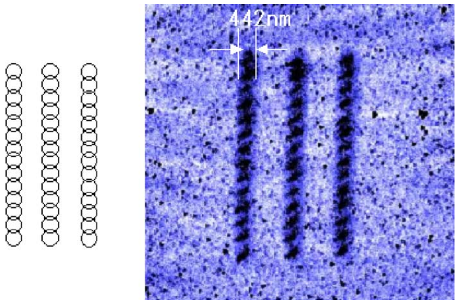

FIG. 5. LFM image of a three-line pattern made by the pneumatically actuated PDMS device with the silicon nitride tip using the dot matrix printing format at contact time of 5 s, 24 °C, and 40% relative humidity (scanning area is 6 by 6 μm^2).

of the PDMS device presented here offer a clear advantage for creating arrays and expanding the capabilities of nanopatterning devices.

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