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HTML ABSTRACT + LINKS

Rapid and convenient method for preparing masters for microcontact printing with 1–12 μm features

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Mechanical scribing can be employed to create surfaces with recessed features. Through replica molding elastomeric copies of these scribed surfaces are created that function as stamps for microcontact printing. It is shown that this new method for creating masters for microcontact printing can be performed with a computer-controlled milling machine (CNC), making this method particularly straightforward and accessible to a large technical community that does not need to work in a particle free environment. Thus, no clean room, or other specialized equipment is required, as is commonly needed to prepare masters. Time-of-flight secondary ion mass spectrometry confirms surface pattering by this method. Finally, it is shown that feature size in the scribed master can be controlled by varying the force on the tip during scribing. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1781385]

Microcontact printing (μCP)[1] and replica molding (REM)[1,2] have emerged as powerful methods for surface modification and pattern transfer. In μCP an elastomeric stamp is cast from a patterned surface (a master). This master is typically made in a clean room using semiconductor processing equipment and techniques. Surface patterning is performed by coating the stamp with a compound of interest (ink) and then pressing it against a surface to transfer the ink. In REM a replica of a surface is made by first transferring its pattern to a polymer, to make it negative, and then transferring the pattern from the negative to another polymer. These two methods have been combined by Whitesides and coworkers who generated masters for μCP by laser ablation, cast poly(dimethylsiloxane) (PDMS) stamps (negatives) from these masters, and then cast replica PDMS stamps from these negatives.[3]

The work described in this article represents an approach to master production for μCP through mechanically scribing a surface. While it is true that the present work will probably be of little interest to those fabricating semiconductor devices, it should be of real significance to a large community of scientists who regularly use microcontact printing to pattern a variety of surfaces, such as gold, quartz, and polymers with monolayers,[4–9] polymers,[10–13] cells,[14,15] proteins,[16,17] DNA,[18,19] small molecules,[20] and/or colloids,[21] and even hydrophobic and hydrophilic spots for matrix/peptide solutions for matrix assisted laser desorption ionization mass spectrometry (MALDI).[22] Many in this community would like to be able to quickly prepare different masters for microcontact printing using facilities that are readily available so that rapid prototyping (creation of many different patterns on surfaces) could be possible. For many in this community the dust-free environment of a clean room is unimportant, as they already do their μCP in an open laboratory. Indeed, a significant fraction of this community either has no access to a clean room, or is completely unfamiliar with clean room equipment and procedures. Thus, a technique that would allow masters for microcontact printing to be rapidly and inexpensively made with readily available equipment, and with micron features, outside of a clean room would be of great benefit to a large number of researchers.

Here it is shown that masters for μCP with 1–12 μm features can be rapidly made with high precision over large (many centimeter) areas using only a computer numerical controlled milling machine (CNC), a diamond tip, and a tip holder (an end-effector). Patterns are transferred from scribed glass to poly(methylmethacrylate) (PMMA) by embossing. Elastomeric stamps in PDMS are then cast from the PMMA negatives. Microcontact printing is confirmed using time-of-flight secondary ion mass spectrometry. Because CNCs are readily available to a much larger number of researchers than the clean rooms, clean room equipment, or lasers that to date have been needed to prepare masters for μCP, this development should make microcontact printing, and especially rapid prototyping with this method, much more accessible to the technical community.

Other methods for directly patterning surfaces by a method analogous to writing, including Whitesides and coworker's micromachining (mechanical scribing) of thiol monolayers on gold in the air followed by immersion of the

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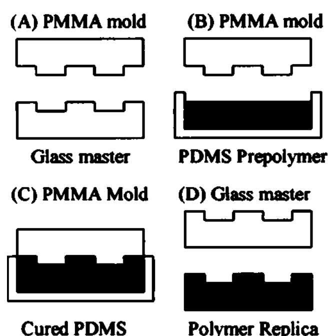

FIG. 1. PDMS stamp preparation for microcontact printing: (a) a PMMA mold is formed from a glass template by embossing; (b) the mold is placed in a PDMS prepolymer; (c) the PDMS is cured; and (d) a replica of the template has been created.

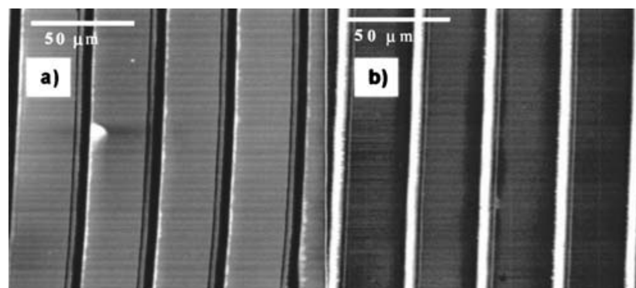

FIG. 2. (a) AFM height image of glass scribed with a CNC milling machine using a diamond tip in the end effector. Line widths are ~12 μm (b) AFM height image of PMMA embossed from the glass substrate on the left. The depth and height of the features in (a) and (b), respectively, is 702 nm. The curvature of the lines in the image on the left is an artifact of the AFM.

surface in a different thiol solution,[23] Mirkin and co-worker's dip-pen nanolithography,[24] Liu and co-worker's nanoshaving with an AFM,[25] Ewing and Mancia's rapid marker masking,[26] and Linford and co-worker's chemomechanical surface patterning[27,28] have also recently been reported.

To produce masters for μCP, a glass microscope slide is mechanically patterned by scribing in the air with a diamond tip. The tip is held by a compliant,[29] friction-free, end effector[30] that has tremendous flexibility in its axial direction, and great stiffness in the plane. The end effector was manufactured in the BYU Mechanical Engineering Department. The force on the end effector can be controlled by changing the amount it is flexed. The end effector is attached to a CNC, which moves the end effector to pattern the surface as it has been programmed. The pattern in the glass slide is then transferred by embossing to a piece of 1/8 in. thick PMMA[31] [see Fig. 1(a)], i.e., the two surfaces are clamped together and heated at 130 °C for 30 min. A polydimethylsiloxane stamp is then cast[32] from the embossed PMMA according to standard protocols for μCP[1] [see Figs. 1(b) and 1(c)]. The thickness of the PDMS stamp varied from 1/4 to 1/8 in. depending on the size of the mold vessel and the amount of PDMS poured over the PMMA master. The entire process of scribing the glass, embossing the PMMA, and casting the PDMS only takes a few hours. Finally, microcontact printing is performed with the PDMS stamp. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed with a TOF-SIMS IV from ION-TOF (Münster, Germany). Atomic force microscopy (AFM) was performed with a Digital Instruments Dimension 3100 AFM. A Millmaster B-3V Shizuoka computer numerical controlled (CNC) milling machine was used for all scribing work. It has 2.5 μm resolution and is capable of patterning large areas (16 in. × 24 in.).

AFM, which is unparalleled in its ability to determine surface topography at micron and nanometer scales, was used to characterize patterned glass and PMMA surfaces. Figure 2(a) shows ~12 μm parallel lines that were scribed on a glass microscope slide with a diamond tip (VWR) in the end effector in the CNC. The lines are straight and their center-to-center distance is ~30 μm. The AFM height image in Fig. 2(b) reveals that the scribed pattern in glass can be faithfully transferred to PMMA by embossing.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) acts as a chemical microscope with high lateral and mass resolution. Figure 3 shows representative ToF-SIMS images of the fluoride ion from a surface that was microcontact printed using a PDMS master that was cast from the PMMA surface shown in Fig. 2(b), and then inked with a 2 mM solution of a fluorinated silane [$ClSi(CH_3)_2(CH_2)_2(CF_2)_5CF_3$] in toluene. This figure shows that μCP printing occurs according to the raised (unscribed) features of the original glass surface [see Figs. 1 and 2(a)]. Plots of the first few principal components from a principal components analysis (PCA) and the total ion images of the data showed similar chemical contrast.

More complicated features can also be patterned onto glass with the CNC and end effector, and control of feature width is possible by varying the deflection (force) on the end effector. In order to know when the tip first touched the surface to have a zero point for deflecting the end effector, a linear variable displacement transducer was placed on top of

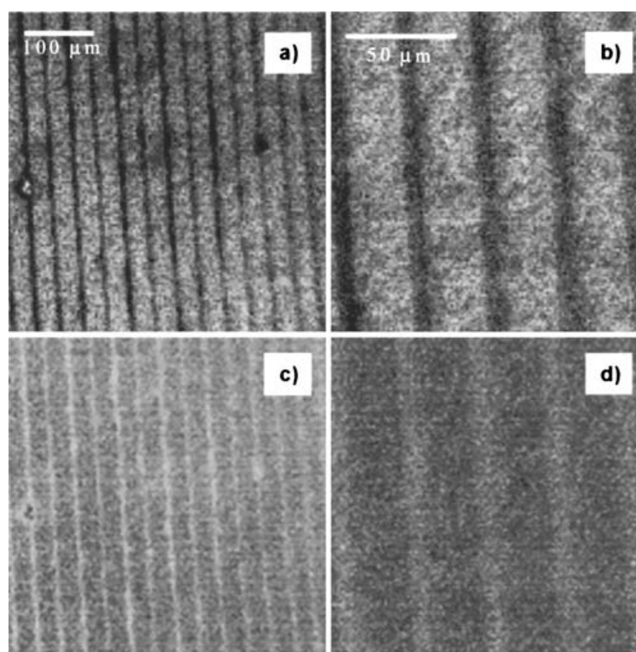

FIG. 3. (a) ToF-SIMS F^- ion image of a microcontact printed silicon surface, (b) a closeup of image (a). The brighter lines indicate higher concentrations of F^-; (c) and (d) the first principal component of a PCA analysis of the mass spectra from which (a) and (b) were taken, respectively, which further demonstrate the expected chemical contrast of the patterned surface. PCA was performed with the ToF-SIMS instrument software.

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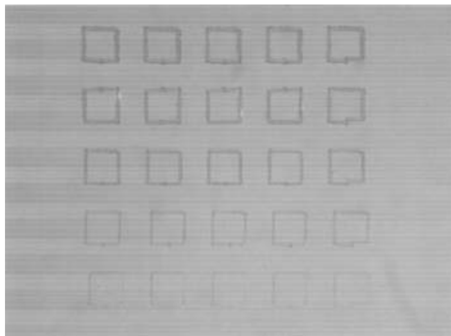

FIG. 4. Optical micrographs of an array of 100 μm $\times$ 100 μm squares scribed on a glass slide using the end effector and a diamond tip. Progressing down from the top row, the force on the diamond tip and average line width for each row are 0.072 N (4.0 μm), 0.054 N (3.6 μm), 0.037 N (2.5 μm), 0.019 N (2.2 μm), and 0.0017 N (0.7 μm). The linear velocity of the tip was 0.3 in./min during scribing. The force-displacement curve for the end effector was linear with a slope (spring constant) of 3.49 $\times 10^{-4}$ N/μm.

the end effector. Using this inexpensive device and accompanying electronics (Iomega) displacements as small as 5 μm could be detected. Figure 4 shows optical micrographs of 100 μm $\times$ 100 μm squares that were scribed in glass using different forces on a diamond tip in the end effector. The line widths of these features vary from $\sim$4 μm down to $\sim$1 μm. The size of the features appears to be a function of both the force on the tip and the tip geometry. These results suggest that virtually any pattern that can be programmed into the CNC can be scribed on a surface.

Other surfaces, including silicon, thick layers of SiO_2 on silicon, PMMA, and polypropylene, were also scribed. Glass and PMMA could be scribed more satisfactorily than the other materials.[33] While it should be possible to produce masters for μCP in metal using a CNC with more traditional machining tools than the end effector, glass, quartz, and silicon substrates are preferred because they are available with great flatness. Also, while it is possible to make PDMS stamps directly from scribed glass masters, the roughness of the scribed lines (see Fig. 5), which become raised features in the PDMS stamps, create problems during printing. The stamps and patterns produced by these methods may also be valuable in other soft lithographic techniques including microtransfer molding (μTM),[34] micromolding in capillaries (MIMIC),[35] solvent assisted micromolding (SAMIM),[36] and standard replica molding (REM).[2]

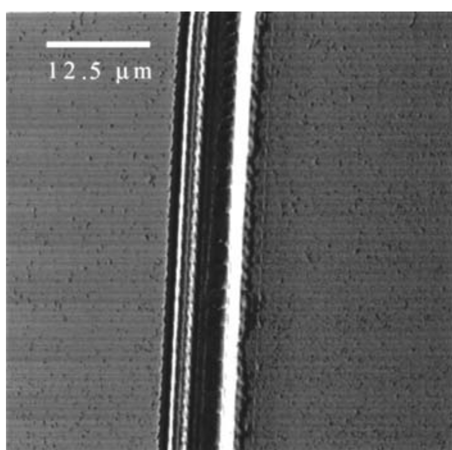

FIG. 5. AFM deflection image of CNC-scribed glass. The scan size is 50 μm $\times$ 50 μm, the scan rate was 1.00 Hz, and the data scale was 150 mV.

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