Using Patterns in Microfiche as Photomasks in 10-*μ*m-Scale Microfabrication

Tao Deng, Joe Tien, Bing Xu, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

Microfiche has been used as the photomask in 1:1 contact photolithography to generate structures of photoresist with features as small as 10 *μ*m. Optical reduction of images that were printed by a high-resolution image setter on transparent polymer sheets generated patterns in microfiche. The photoresist patterns generated using microfiche as the photomask are useful in the fabrication of elastomeric stamps/molds/membranes for soft lithography. Four test structures fabricated using microfiche as photomask and soft lithography are used to evaluate the utility and resolution of this technique.

Introduction

This paper describes the use of patterns in microfiche[1] as photomasks for contact photolithography. Microfiche offers a rapid, inexpensive, and generally accessible route to generate photoresist patterns with lateral dimensions as small as 10 *μ*m and with an edge roughness of ∼1 *μ*m. These patterns in photoresist, and the microstructures derived from them, are useful in making poly(dimethylsiloxane) (PDMS) stamps, molds, and channel systems for soft lithography[2] and microfluidics[3] and for fabricating microelectromechanical systems (MEMS),[4,5] microsensors,[6] organic microelectronic devices,[7] optical components,[8] and other types of devices that do not require submicron-scale patterning.[9]

The approach used commercially to generate photomasks uses a specialized device to raster a sharply focused spot of light or beam of electrons across a sensitized polymer film on a chrome plate;[10] input for the rastering tool consists of a digitized CAD pattern. The drawback of this procedure is that it requires specialized facilities and is relatively slow and expensive: a 6 in. × 6 in. mask with feature sizes between 5 *μ*m and 20 *μ*m costs ∼$100/in² and requires ∼1 day to image[11] (the total turnaround time from CAD file to chrome mask can be much longer—on the order of weeks—when using commercial facilities). Similar drawbacks hinder the widespread adoption of mask-making procedures based on laser ablation of polymers.[12]

---

* To whom correspondence should be addressed. Telephone: 617-495-9430. Fax: 617-495-9857. E-mail: gwhitesides@gmwgroup.harvard.edu.

(1) Here we refer to "microfiche" as a film containing microimages which are photographic records on a reduced scale of printed or other graphic matter (Webster's Collegiate Dictionary, 9th ed.).

(2) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550.

(3) Kopp, M. U.; Mello, A. J. D.; Manz, A. *Science* **1998**, *280*, 1046.

(4) Kovacs, G.; Petersen, K.; Albin, M. *Anal. Chem.* **1996**, *68*, 407.

(5) Macdonald, N. *Microelectron. Eng.* **1996**, *32*, 49.

(6) Muller, R. S. *Microsensors*; IEEE Press: New York, 1991.

(7) Rogers, J. A.; Bao, Z.; Raju, V. R. *Appl. Phys. Lett.* **1998**, *72*, 2716.

(8) Carts, Y. A. *Laser Focus World* **1994**, *30*, 67.

(9) Qin, D.; Xia, Y.; Rogers, J. A.; Jackman, R. J.; Zhao, X.-M.; Whitesides, G. M. In *Microfabrication, Microstructures and Microsystems*; Manz, A., Becker, H., Eds.; Springer-Verlag: Berlin, 1998; Vol. 194, p 1.

(10) Elliott, D. J. *Integrated Circuit Mask Technology*; McGraw-Hill: New York, 1985.

(11) Advance Reproductions Corporation (North Andover, MA); http://www.advancerepro.com.
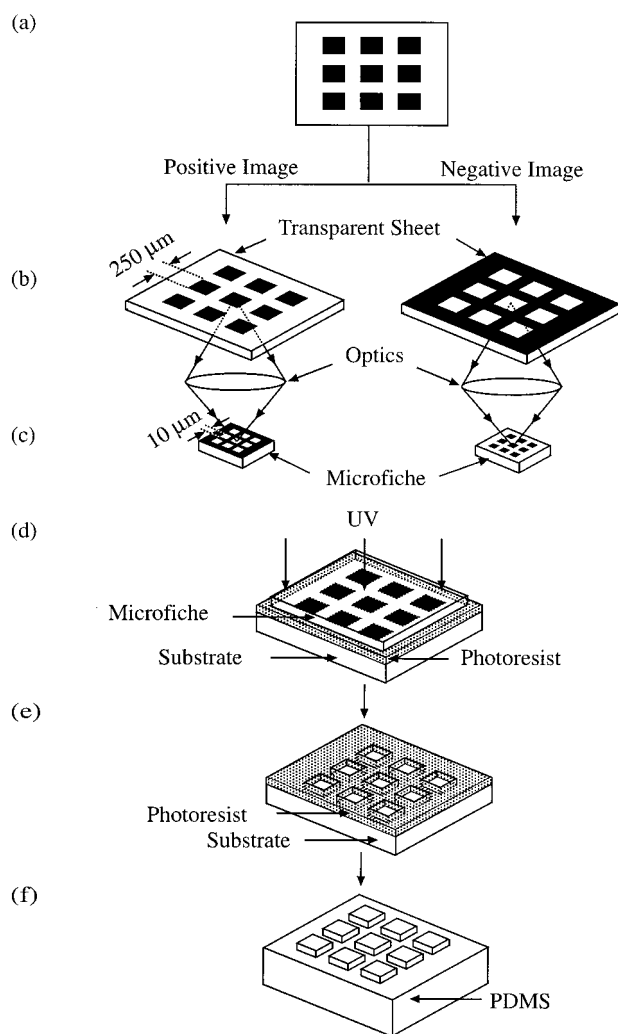

Figure 1. Schematic diagram of the fabrication of a pattern in microfiche and of the use of this microfiche in lithography. (a) Patterns designed using Freehand or CAD software. (b) Patterns printed on a transparent sheet using a high-resolution image-setting system. Both negative and positive images can be printed. (c) Image reduced onto microfiche. (d) Use of microfiche as the photomask in photolithography. (e) Photoresist patterns after developing. (f) Generation of PDMS stamp/mold by casting PDMS on the photoresist master.
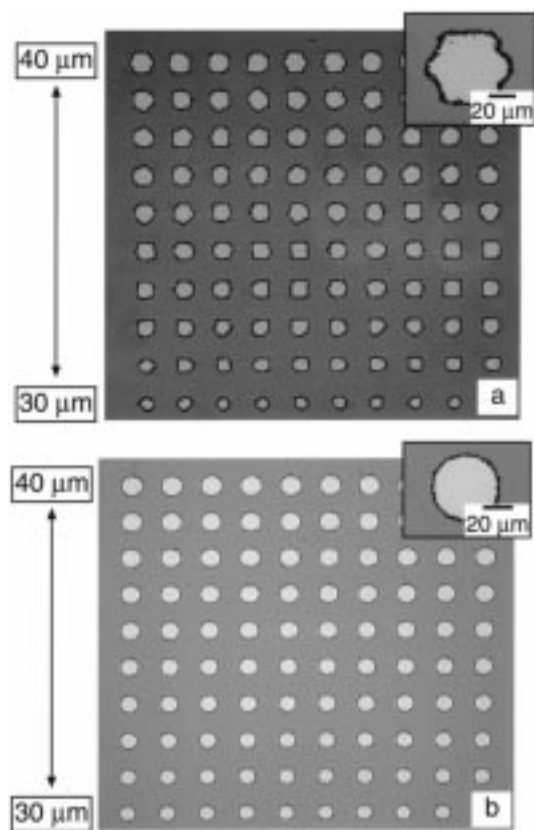
Figure 2. Optical micrographs of arrays of photoresist dots on silicon wafer fabricated using a transparent sheet printed by a high-resolution image setter and microfiche. The diameters of the dots change from 40 to 30 μm. The insets are the magnified views of dots with the diameter 40 μm. (a) Dot arrays generated using a transparent sheet as the photomask. (b) Dot arrays generated using microfiche as the photomask.

We and others have demonstrated that a high-resolution image setter (3386 dots per inch; Linotype-Hell Co.; available in commercial printing shops[13]) can quickly and inexpensively generate 50-μm patterns on flexible, transparent sheets with excellent quality and can generate features with sizes as small as 20 μm but only with marginal quality.[14] An 8.5 in. $\times$ 11 in. sheet produced using this image setter costs ~\$20 (i.e., ~\$0.20/in²) and requires ~1 h to print, regardless of feature size. We routinely use this procedure to make patterned masks for use in contact photolithography. After development, the patterns in photoresist become the master for casting PDMS stamps, and molds for use in soft lithography. The capability to produce 50-μm features routinely has had a strong impact on the ability of laboratories—especially those focused on chemistry, biology, condensed matter physics, and materials science—to prototype and produce small numbers (1–100) of simple microsystems. This capability, which we call "rapid prototyping", makes it possible to test concepts in structures that require feature sizes of 50–300 μm (for example, structures used in microfluidics, MEMS, and microsensors).[3–6]

The procedure for generating patterns by high-resolution printing using an image setter gives high-quality patterns with feature sizes of $\geq$50 μm. Smaller features (10–50 μm) require a new approach. The objective of this

(12) Goldie, D.; Cairns, J.; Verrall, M.; Coates, D. *Mater. Chem.* **1997**, *7*, 2013.
(13) We use the services of PageWorks, a division of Creamer Associates, Inc. (Cambridge, MA); http://www.pageworks.com.
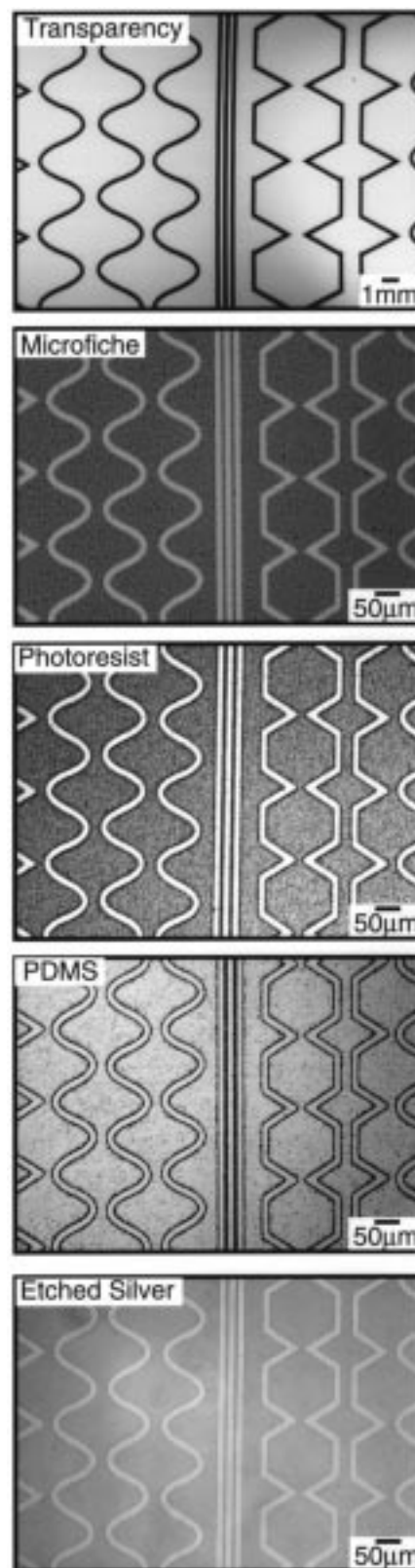(14) Qin, D.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 917.

Figure 3. Optical micrographs of test patterns in microfiche, and the microstructures generated from the microfiche. The micrographs from top to bottom are as follows: the original line patterns printed on a transparent polymer sheet using a high-resolution image-setting system; these patterns in microfiche, after 25$\times$ optical reduction; photoresist patterns generated by contact photolithography using the microfiche as the photomask; a PDMS stamp fabricated from the photoresist patterns; silver patterns produced by microcontact printing of hexadecanethiol using this PDMS stamp and by etching the unstamped regions.
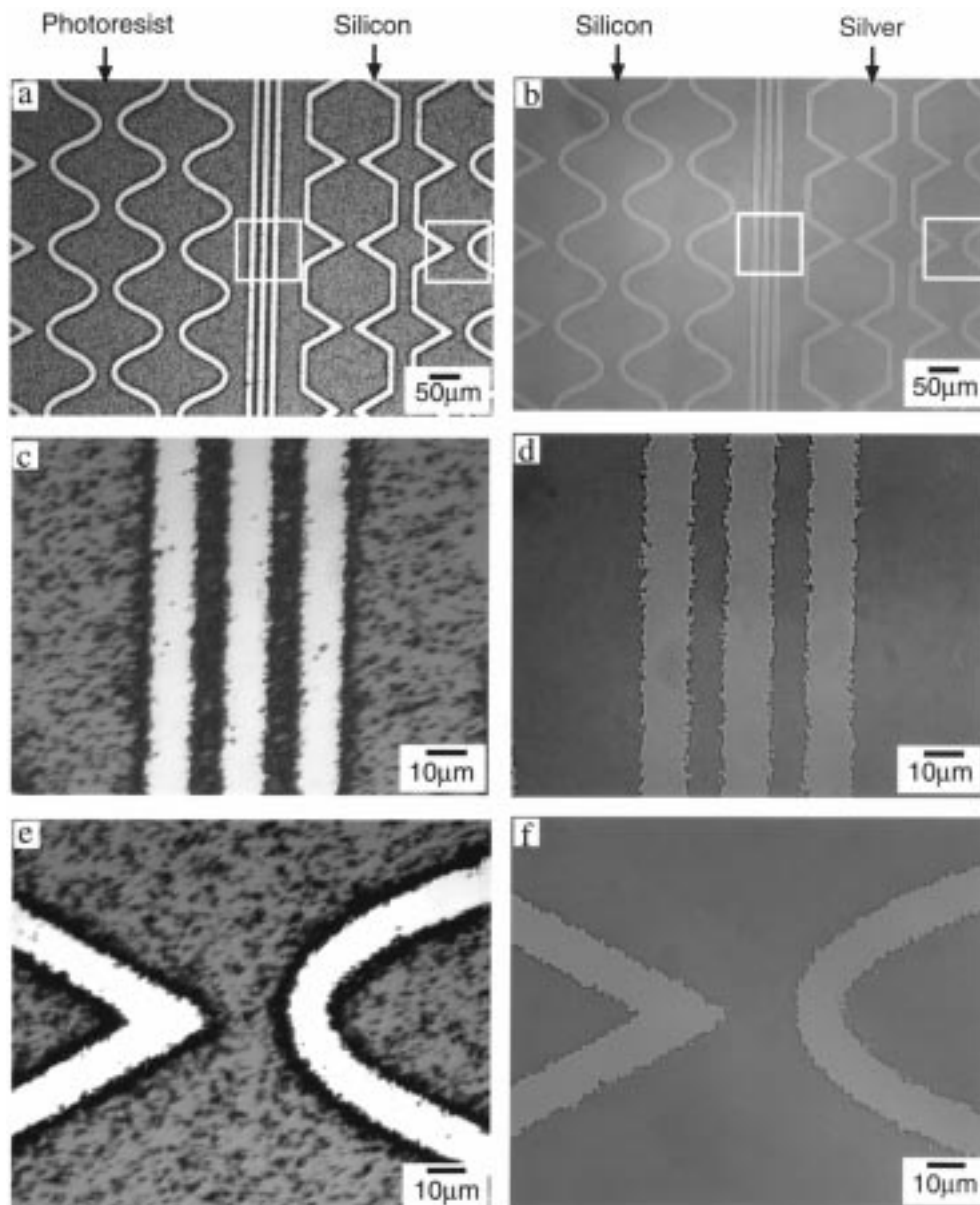
Figure 4. Optical micrographs of the smallest lines generated using microfiche as the photomask. Parts a, c, and e are pictures of photoresist patterns generated from lithography using microfiche as the mask: (a) test pattern; (c and e) magnified views of the highlighted areas in part a. The silicon lines are ~10 μm. Parts b, d, and f are optical micrographs of silver lines after microcontact printing with a PDMS stamp cast from the photoresist pattern and etching with ferricyanide.

work was to test the usefulness of images in microfiche as masks for photolithography at this size scale. This investigation is based on several attractive qualities of microfiche. First, microfiche is inexpensive to make (<$1/in²), and commercial facilities for reduction onto microfiche are widely available. Second, it is capable of extraordinary resolution for a silver halide-based photographic technique (the emulsion on microfiche can, in principle, resolve ≥500 lines/mm or, equivalently, ≥25 000 dots per inch).[15] Third, microfiche is flexible and can be wrapped around curved substrates. Fourth, the transparency of the film extends to ~300 nm in the UV; it can therefore be used directly in photolithography using standard light sources at 330−450 nm.

The process described here has four steps: (i) The desired pattern is designed in a CAD file with features expanded by 25×. (ii) The expanded pattern is printed onto a smooth, transparent sheet using a high-resolution

image-setting system.[13] (iii) This printed pattern is photoreduced by a factor of 25 onto microfiche. (iv) The images in microfiche are used as contact masks in photolithography. The combination of CAD, high-resolution printing, and size reduction onto microfiche makes photomasks that can generate features in photoresist as small as 10 μm. This process makes features of this size routinely available for use in soft lithography and microfabrication. It therefore extends, by a small but significant amount, the resolution that can be obtained using readily available, commercial facilities, without the complexities and delay of commercial mask houses, and provides an alternative method for making patterns with intermediate feature sizes for use in microfabrication.

Methods

Figure 1 illustrates the procedure for making microfiche and for using them to pattern photoresist. Figure 1a−c outlines the procedure for making microfiche photomasks.

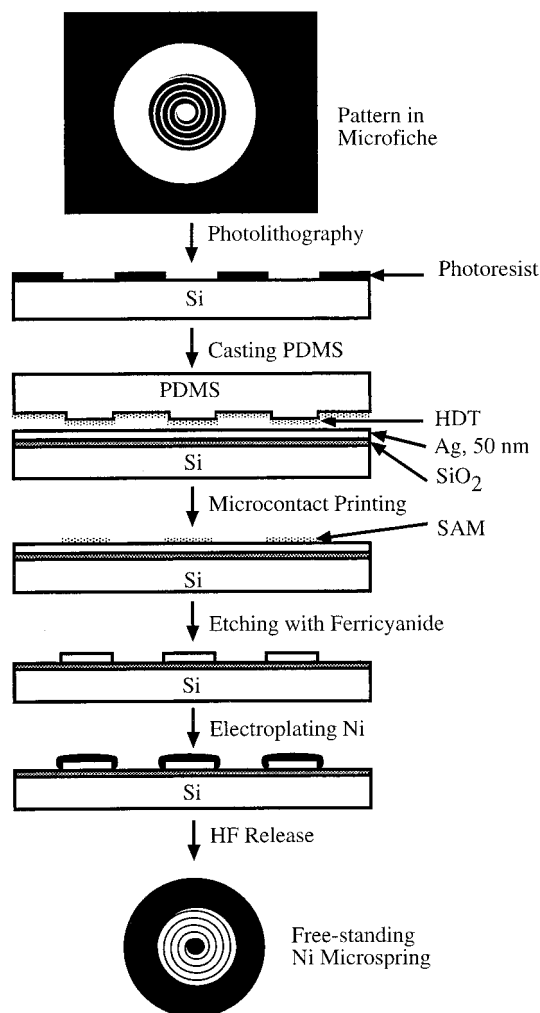(15) New England Micrographics (Manchester, NH).

Figure 5. Scheme for fabricating a microspring. The microspring pattern in microfiche was transferred into photoresist using conventional photolithography. The PDMS stamp used in μCP was fabricated by casting PDMS on the photoresist master. Silicon wafers having a 20−400 nm thermally grown layer of silicon dioxide were coated with titanium (∼5 nm) and silver (∼50 nm). Microcontact printing with hexadecanethiol patterned a SAM on the silver surface. Wet chemical etching removed silver not derivatized in the printing step. Immersion in 1% HF solution removed exposed titanium. Electroplating of nickel formed rigid structures with the thickness 1−2 μm. A free-standing structure resulted after dissolving the silicon dioxide layer in 12% aqueous HF.

This procedure consists of three steps: computer design, high-resolution printing,[14] and photoreduction. We designed the patterns using CAD software and printed them as positive or negative images on transparent sheets with a high-resolution image-setting system. We then reduced these patterns optically onto microfiche.[15] Figure 1d and e describes the generation of patterns in photoresist; this bas-relief pattern can be used directly to generate the PDMS molds/stamps for soft lithography (Figure 1f) or for other purposes, such as microelectrochemistry. The molds/stamps were made by casting PDMS directly on the developed pattern of photoresist and curing the PDMS at 60 °C for 2 h.

Results and Discussion

Quality of Patterns Generated with Microfiche.
The most important issue regarding the attractiveness of microfiche as a mask is the quality of the patterns in photoresist that can be generated from it: Does using
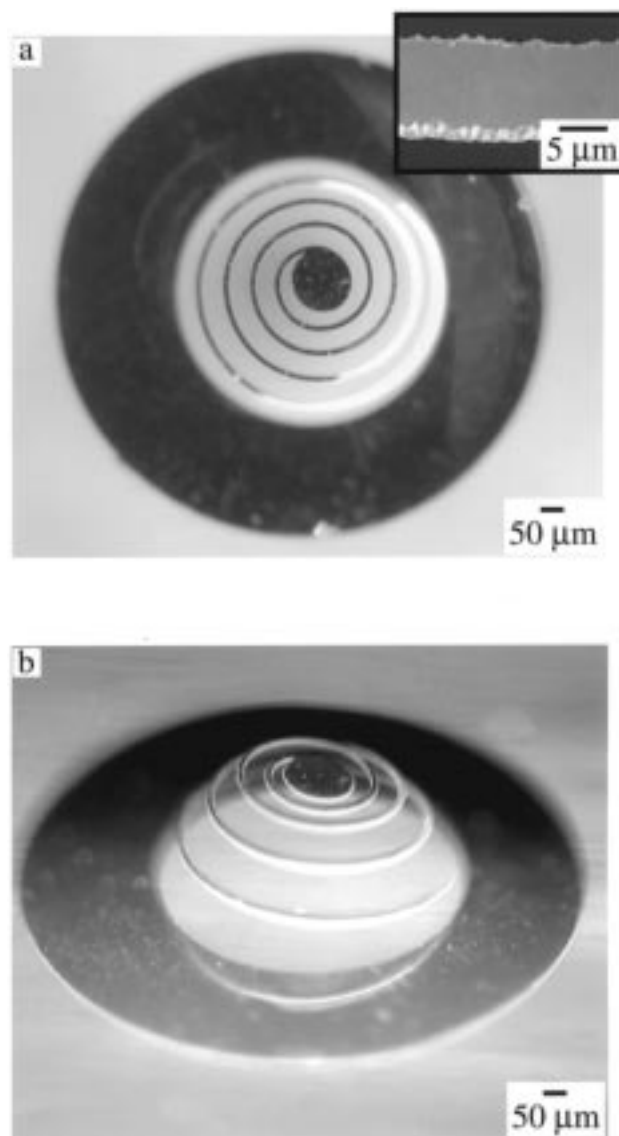

Figure 6. Microspring fabricated using microfiche as the photomask. (a) Top view of the microspring. The inset is a magnified view of the spiral wire in the spring. The line width of the wire is ∼10 μm, and the dimension of the spring is ∼1.5 mm × 1.5 mm. (b) Side view of the microspring. The internal stresses in the spring caused the center of the spring to pop out after release from the substrate.

this technique result in more regular patterns than using high-resolution printing? What is the resolution of this technique? Can these patterns be used in soft lithography? Figures 2−4 address these questions.

Figure 2 compares dots of photoresist fabricated using a transparent sheet with the pattern printed by a high-resolution image setter as a mask with those made using microfiche as a mask. The pattern consists of circles with diameters ranging from 40 to 30 μm. Dots generated using a pattern of circles printed directly on a transparency as a photomask are not circular (Figure 2a), because the resolution is limited by the discrete step size of the image setter. In contrast, dots made with microfiche as a mask are circular. This effect arises from the process for generating microfiche. To make dot arrays with diameters of 30−40 μm on the microfiche, we printed dot arrays with diameters of 750−1000 μm onto the transparent sheet and then photoreduced the printed image onto the microfiche. The quality of the dot arrays printed on the transparent sheet was high when the diameters were in
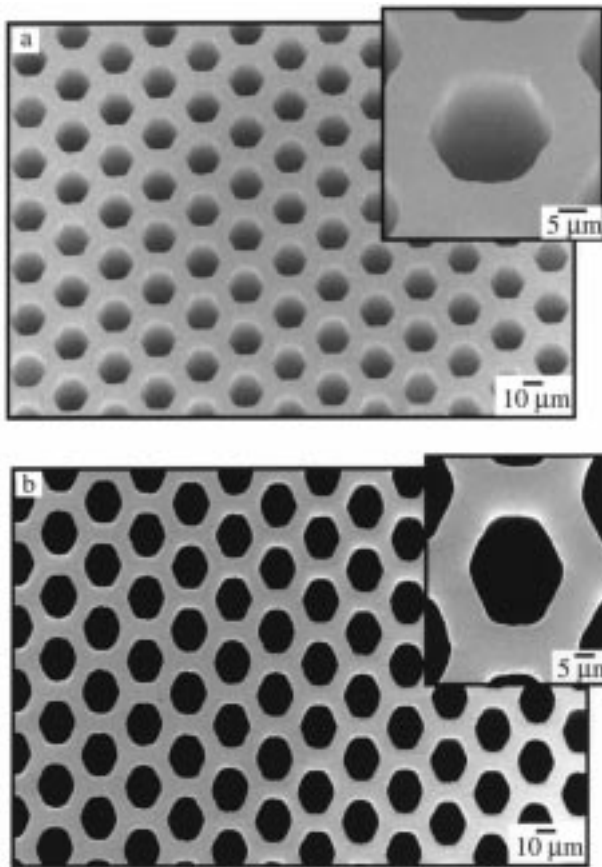
Figure 7. Scanning electron micrographs of a honeycomb structure fabricated from SU-8 photoresist. Insets are magnified views of a single honeycomb cell. (a) Viewed from a 60° tilt. (b) Viewed from the top. The line width of each cell is ~15 μm, and the height of each cell is ~80 μm. The edge roughness of each cell is ~0.5 μm.

the range of 750−1000 μm. Both the high quality of the images on the printed transparent sheet and the high quality of the optical lenses we used in the optical reduction step contribute to the increased resolution obtained when using microfiche as photomask relative to images printed directly by the image setter.

Figure 3 shows the transformation of a set of lines from transparency to microfiche, to photoresist, to PDMS, and to metal. These pictures show the fidelity of pattern transfer in these five stages and establish the compatibility of microfiche with soft lithography. Figure 4 shows magnified views of these line patterns in photoresist and metal. The line width of these patterns is ~10 μm; the edge roughness is ~1 μm. Fabrication of the microfiche is an optical, analog process, so digitization of the image does not occur, and the edge roughnesses for straight lines and for curves are the same.

Figure 4 also shows that the dark regions in microfiche are not completely opaque. Gaps between the silver grains in microfiche[15] allow light to pass through and expose small areas of photoresist where exposure is not desired. This exposure creates "pockmarks" in positive resist after development; in negative resist, the exposure cross-links small regions in the resist, but these areas are removed during development.

Fabrication of Microstructures Using Microfiche. We have tested the capabilities of this method for forming patterns with four test structures.

A Microspring. Figure 5 shows the procedure used to fabricate a microspring using patterns in microfiche, and
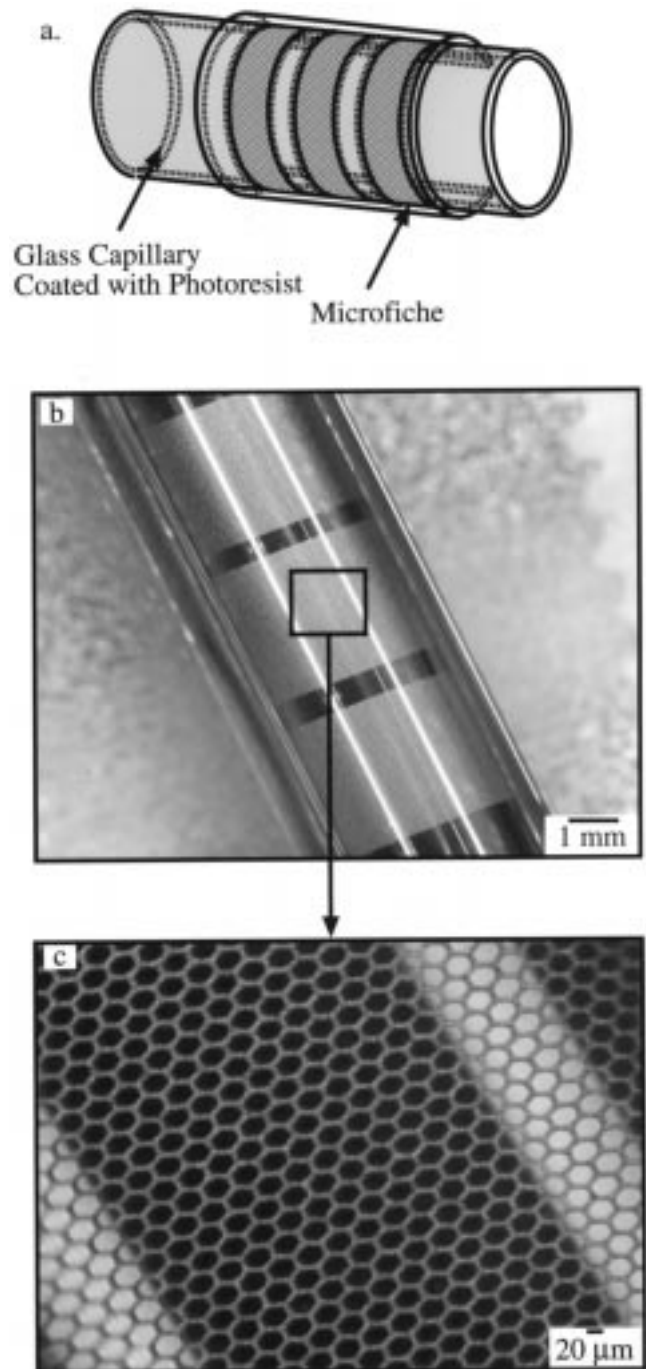

Figure 8. Honeycomb structure fabricated on a glass capillary. (a) Schematic indicating how structures were generated on the surface of the capillaries. We coated the capillary with a thin film of resist by pulling the capillary from bulk photoresist. After wrapping the capillary with microfiche, exposing the capillary to UV light, and developing the exposed resist, we evaporated chromium (~5 nm) and silver (~50 nm) onto the capillary. Dissolving the unexposed photoresist and electrodepositing nickel on the capillary formed a nickel honeycomb. (b) Micrograph of the nickel honeycomb generated on the glass capillary. The diameter of the capillary is ~3 mm. The two white lines in the capillary are artifacts caused by light reflected from the inside of the capillary. (c) Magnified view of the honeycomb structure in Figure 8b. The line width of the honeycomb is ~10 μm.

Figure 6 shows the structure. This type of microspring may find use as a sensing or actuating element in MEMS. The patterns in microfiche were transferred into PDMS using photolithography and replica molding. The PDMS stamp was used for microcontact printing (μCP) on a silver

film; wet chemical etching followed by electrodeposition of nickel gave the metallic structure of the spring. The free-standing nickel microspring was obtained by releasing it from the substrate by dissolving SiO_2 using a buffered HF solution (Figure 6). The line width of the wire is ~10 μm, and the dimension of the spring is ~1.5 mm × 1.5 mm. Figure 6b is a side view of the microspring. The Experimental Section gives a more detailed description.

A Microhoneycomb. Figure 7 presents a honeycomb-shaped structure fabricated using patterns in microfiche. This type of structure can form part of a honeycomb composite[16] or be used as a filter with defined pore geometries. This structure was fabricated using SU-8 photoresist. The line width of the honeycomb cell is ~15 μm, and the height of the cell is ~80 μm. The aspect ratio (width/height) is ~1:5. Because the microfiche is not completely opaque to UV light, we could not fabricate structures in SU-8 with aspect ratios larger than 1:5. Figure 7b is the honeycomb viewed along the perpendicular to the plane. The inset is the magnified view of a single honeycomb cell. The edge roughness of the cell is ~0.5 μm.

Microstructures on a Curved Surface. Figure 8 shows honeycomb-shaped structures fabricated on the outer surface of a glass capillary using microfiche as the photomask. The diameter of the glass capillary is ~3 mm. We wrapped microfiche around a capillary coated with photoresist and exposed the resist through the microfiche with UV light. Liftoff with evaporated thin films of chromium and silver generated thin metallic honeycombs on the capillary. Electrodeposition of nickel on these thin honeycomb structures gave the thick Ni structures shown in Figure 8b.

Microstructures Fabricated Using Two Stacked Microfiche Masks. Figure 9 shows an array of hexagons fabricated using two stacked microfiche masks. Each microfiche mask had half of the component of the final pattern: one consisted of an array of three solid lines; the other consisted of an array of three dashed lines (Figure 9a). Stacked and aligned, the two masks functioned as a photomask of an array of hexagons, each with three solid and three dashed edges (Figure 9b). Lithography with these stacked masks reproduced the array of hexagons in photoresist, with smallest features of ~15 μm. The error of registration[17] during the alignment of the two microfiche masks was ~20 μm over an area of 0.5 cm². This error was mainly due to the nonconformal contact between the two microfiche masks during the alignment. To align the two masks, we fixed one mask on the substrate and the other one on the mask aligner using Scotch tape. The contact between the mask and substrate was not conformal because of the deformation of the Scotch tape and the mask. By the same token, the contact between the mask and mask aligner was also nonconformal. These nonconformal contacts caused nonconformal contact between the two masks and some error in registration during the alignment.

Conclusions

We have demonstrated a new technique for fabricating photomasks to be used in contact photolithography—that is, images in microfiche, fabricated by optically reducing a pattern printed on a sheet of polymer transparency. This method for generating microscale patterns does not use the specialized tools required for making chrome
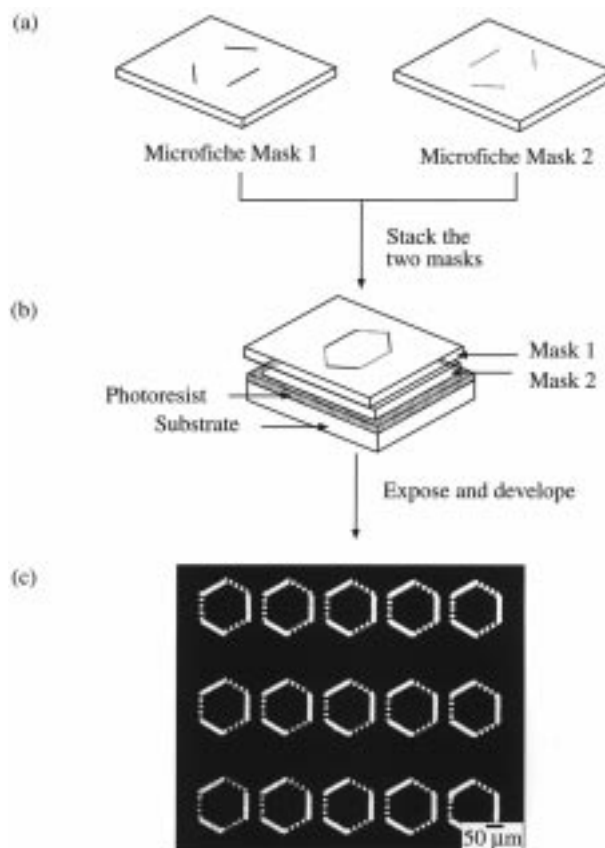

Figure 9. Microstructures of photoresist fabricated using two stacked microfiche masks. (a and b) Schematic of generating structures using two stacked microfiche masks. Only a single hexagonal cell is shown in the figure. (c) Optical micrograph of an array of hexagons fabricated using two stacked microfiche masks. The white features outlining the hexagons are photoresist, and the dark part in the image is the Si substrate with native oxide. The line width of the edge is ~15 μm.

masks and thus provides a convenient and economical approach to make photomasks and stamps/molds for soft lithography. This technique can be used to fabricate microstructures at the 10−50-μm scale for laboratories centered in chemistry, biology, and materials science. These images in microfiche, when used as masks, can generate curves as narrow as 10 μm on both planar and curved surfaces, albeit with an edge roughness of ~1 μm. The flexibility of the microfiche enables us to pattern microstructures on cylindrical surfaces and fabricate composite structures using stacked masks. This method works better with a positive resist (that is, a resist in which exposed resist dissolves in development) than with a negative resist; the slight transparency of the dark regions in microfiche does limit the applicability of this technique when used with negative resist. We have yet to optimize the emulsion and conditions for use of microfiche, and our demonstration has not tested the ultimate resolving power of this technique; its extension to features smaller than 10 μm requires, however, the use of reducing lenses with higher resolution than the ones presently available to us.

Experimental Section

Materials. Ag (99.99%), Cr (>99.99%), Ti (>99.99%), $Na_2S_2O_3$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $CH_3(CH)_{15}SH$, tricholoroethylene (TCE), acetone, methanol, propylene glycol methyl ether acetate (PG-MEA), and hexamethyldisilazane (HMDS) were obtained from Aldrich. Poly(dimethylsiloxane) (Sylgard 184) was ordered from Dow Corning. Microposit 1813 photoresist (Shipley Co., Inc.;

(16) Xu, B.; Arias, F.; Whitesides, G. M. *Adv. Mater.* (submitted).
(17) We define the error of registration as the displacement of the final position of one pattern from the ideal position of that pattern.

Malborough, MA), Microposit 351 developer (Shipley Co., Inc.; Malborough, MA), and SU-8 photoresist (Microchem Co.; Newton, MA) were used as received. Thin films of Ag (~50 nm) were prepared by thermal evaporation onto silicon or glass primed with Cr (~5 nm) or Ti (~5 nm).

Fabrication of Microfiche. The test patterns were designed in CAD or Freehand files. We sent the files to Pageworks, and they printed the images onto transparent sheets using an image-setting system with resolution 3386 dpi. The printed images were then sent to New England Micrographics and optically reduced onto microfiche (Fuji Super HR, ~70 μm thick) with 25× reduction.

Use of Microfiche as Photomasks and in Soft Lithography. *1. Using Microfiche on Positive Photoresist.* Substrates were cleaned in TCE, acetone, and methanol using sonication, followed by drying in an oven at 180 °C for 10 min. We primed the substrates with HMDS and then spin-coated the substrates with 1813 photoresist at 4000 rpm for 40 s. The photoresist-coated substrates were baked for 3.5 min on a 105 °C hot plate and exposed through a microfiche mask with a Karl Suss MJB3 contact aligner for 15 s (10 mJ·cm^{-2}·s^{-1} at 405 nm). The photoresist was developed for 1 min in dilute 351 developer (351 developer/H$_2$O = 1:5 v/v).

2. Using Microfiche on Negative Photoresist. The substrates were cleaned and dried in the same manner as described above. We spin-coated SU-8 photoresist directly onto the substrates at 1500 rpm for 20 s. The substrates were baked at 95 °C for 15 min, followed by exposure through a microfiche mask for 1 min (10 mJ·cm^{-2}·s^{-1} at 405 nm) and baking at 90 °C for 1 min. The photoresist was developed in PGMEA for ~20 min with magnetic stirring.

3. Using Microfiche on Curved Surface. The photoresist (positive) patterns generated on a curved surface were prepared by the same procedure as described in the first section with the following two exceptions: (1) We coated capillaries with 1813 photoresist by pulling the capillaries from a bulk solution of resist, and (2) microfiche masks were wrapped around the glass capillaries during exposure.

4. Using Stacked Microfiche To Fabricate Composite Structures. We stacked two microfiche masks using the Karl Suss contact aligner. One mask was fixed on the substrate using Scotch tape. The other mask was fixed on the mask holder using Scotch tape. The positions of the two masks were aligned with respect to each other before they were brought into contact. The photoresist-coated substrates were exposed through the stacked masks for 30 s (10 mJ·cm^{-2}·s^{-1} at 405 nm), followed by developing in dilute 351 developer.

5. Using Patterns Generated from Microfiche in Soft Lithography. Photoresist patterns fabricated using microfiche as photomasks were used as masters to generate PDMS molds/stamps for soft lithography.[18] For microcontact printing, substrates of Ag were rinsed with ethanol and dried in a stream of N$_2$. We then applied a solution of hexadecanethiol (~2 mM in ethanol) with cotton Q-Tips to the surface of the PDMS stamp, dried the stamp in a stream of N$_2$ for ~30 s, and brought the stamp into contact with the surface of Ag for 5−10 s. Films of Ag that were patterned with SAMs were etched in an aqueous solution containing 0.1 M Na$_2$S$_2$O$_3$/0.01 M K$_3$Fe(CN)$_6$/0.001 M K$_4$Fe(CN)$_6$.[19]

Instrumentation. SEM was done on a LEO Digital scanning electron microscope, Model 982.

LA990372P

(18) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

(19) Xia, Y.; Zhao, X.-M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 2332.