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This paper describes a number of approaches that have been employed to reduce the size of features of self-assembled monolayers (SAMs) generated using microcontact printing (μCP). In μCP, an elastomeric stamp is used to print patterned SAMs of alkanethiolates on the surfaces of coinage metals and SAMs of alkylsiloxanes on Si/SiO_2. It is a convenient technique for generating patterned microstructures with feature sizes $\geq$ 500 nm. The capability of this technique could be extended to produce features smaller than 500 nm using the following approaches: (1) μCP with mechanical deformation of the elastomeric stamp—that is, with lateral compression or uniaxial stretching in the plane of the stamp and with pressure perpendicular to the plane of the stamp; (2) μCP with physical alternation of the elastomeric stamp—that is, with a stamp that has been swelled with a solvent or a stamp whose dimensions have been reduced by extraction of an inert filler; (3) μCP with reduction in the size of features resulting from processes taking place on the surface—that is, lateral reactive spreading of hexadecanethiol on gold; and (4) μCP with multiple impressions on the same surface. The advantages and disadvantages of each approach are evaluated and compared in this paper.

Introduction

Microcontact printing (μCP)[1] is a very convenient, nonphotolithographic technique that can generate patterned features of self-assembled monolayers (SAMs)[2] on both planar and nonplanar surfaces.[3] The concept of μCP is quite straightforward. An elastomeric stamp (usually made from poly(dimethylsiloxane), PDMS) is fabricated by casting a prepolymer of PDMS against a master whose surface has been patterned with a complementary relief structure using photolithography[4] or micromachining[5] or from a commercially available relief structure such as a diffraction grating.[6] When carrying out μCP on Au, a PDMS stamp is wetted with an "ink" (typically, an ~2 mM solution of hexadecanethiol in ethanol) and is brought into contact with the surface of gold for 5–10 s. The hexadecanethiol (HDT, $CH_3(CH_2)_{15}SH$) transfers from the stamp to the gold, forms a hexadecanethiolate ($CH_3(CH_2)_{15}S^-$), and generates patterns of SAMs on the surface of gold.

One of the important applications of μCP has been in forming patterned SAMs to be used as ultrathin resists.[7] SAMs are remarkably effective as primary resists in controlling the etching of the underlying substrates. Patterning of gold with a hydrophobic, long-chain SAM (typically, derived from HDT), followed by selective dissolution of the underivatized gold in chemical etchants (usually an aqueous solution containing $K_2S_2O_3/K_3Fe(CN)_6/K_4Fe(CN)_6$ or KCN/O_2),[8] produced patterned features of Au on the surface; these gold features could be subsequently used as secondary masks to define and direct the etching of the underlying substrates of SiO_2 and Si.[9,10] More recently, microcontact printing has been extended to form patterned SAMs of alkanethiolates on silver[10] and copper,[11,12] SAMs of alkylsiloxanes on hydroxyl-terminated surfaces,[13–16] and Pd colloids on Si/SiO_2.[17]

Features of patterned SAMs with dimensions larger than 1 μm can be routinely produced using μCP. It is more difficult to generate features with sizes less than 1 μm, primarily because fabrication of the corresponding masters in this range critically depends on the availability of advanced microlithographic techniques (for example, e-beam writing, deep UV, and X-ray photolithography) that are still in development.[18–20] Below 100 nm, material properties—especially deformation of the elastomeric stamp—may limit feature size (or at least require development of new materials optimized for this regime).

We are developing procedures that can extend the capabilities of μCP into the submicrometer range without requiring masters having submicrometer-sized features that have to be generated by less readily available advanced lithographic equipment. Basically, our strategy is to start with an elastomeric stamp having feature sizes of 2–4 μm (that is, easily made using routine photolithography) and to find *non*-photolithographic methods to produce patterned SAMs with feature sizes *smaller*

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(1) Kumar, A.; Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(2) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
(3) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *264*, 696.
(4) Moreau, W. M. *Semiconductor Lithography: Principles and Materials*; Plenum: New York, 1988.
(5) Xia, Y.; Zhuk, A.; Whitesides, G. M. *Chem. Mater.*, submitted.
(6) Xia, Y.; Tien, J.; Qin, D.; Whitesides, G. M. *Langmuir* **1996**, *12*, 4033.
(7) Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255.
(8) Xia, Y.; Zhao, X.-M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 2332.
(9) Xia, Y.; Kim, E.; Whitesides, G. M. *J. Electrochem. Soc.* **1996**, *143*, 1070.
(10) Kim, E.; Kumar, A.; Whitesides, G. M. *J. Electrochem. Soc.* **1995**, *142*, 628.
(11) Xia, Y.; Kim, E.; Mrksich, M.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 601.
(12) Moffat, T. P.; Yang, H. *J. Electrochem. Soc.* **1995**, *142*, L220.
(13) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.
(14) Jeon, N.-L.; Nuzzo, R. G.; Xia, Y.; Mrksich, M.; Whitesides, G. M. *Langmuir* **1995**, *11*, 3024.
(15) Jeon, N. L.; Clem, P. G.; Nuzzo, R. G.; Payne, D. A. *J. Mater. Res.* **1995**, *10*, 2996.
(16) St. John, P. M.; Craighead, H. G. *Appl. Phys. Lett.* **1996**, *68*, 1022.
(17) Hidber, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375.
(18) Dunn, P. N. *Solid State Technol.* **1994**, *June*, 49.
(19) Dagata, J. A. *Science* **1995**, *270*, 1625. Snow, E. S.; Campbell, P. M. *Appl. Phys. Lett.* **1994**, *64*, 1932.
(20) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Appl. Phys. Lett.* **1995**, *67*, 3114; *Science* **1996**, *272*, 85.

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than those of the original stamps (preferably, in the range $\leq 0.5\ \mu m$). We have reported three such methods (that is, controlled reactive spreading,[21] μCP with a PDMS stamp while it is under lateral compression,[22] and μCP with a PDMS stamp cast from V-shaped microtrenches etched in a Si(100) wafer[23]) by which patterned features with dimensions of ~100 nm have been generated from masters with feature sizes of ~2.5 μm. Other approaches, for example, μCP with a stamp that has been swelled with an organic solvent before printing, μCP with a PDMS stamp that has been reduced in dimensions by extraction of an inert filler intentionally added into the PDMS prepolymer before curing, and μCP with a PDMS stamp that is under uniaxial tension in the plane or vertical pressure perpendicular to the plane of the stamp, have also been used to produce patterned features of SAMs with reduced sizes. Here we report a complete list of the results of all these approaches, with an evaluation on the strengths and weaknesses of each one.

Experimental Section

Materials and Substrates. Au (99.999%), Ag (99.999%), Ti (>99.99%), $K_2S_2O_3$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and $CH_3(CH_2)_{15}SH$ were obtained from Aldrich. PDMS elastomers were obtained either from Dow Corning (Sylgard 184, Midland, MI) or from Hüls (PELD 15, Piscataway, NJ). Si(100) wafers (Cz, N/Phosphorous-doped, test grade, SEMI Std. flats.) were obtained from Silicon Sense (Nashua, NH). Hexadecanethiol (HDT) was purified under nitrogen by chromatography through silica gel. Thin films of Au (20 nm) and Ag (50 and 200 nm thick) were prepared by e-beam evaporation onto Si wafers primed with thin layers of Ti (2–3 nm thick).

Fabrication of PDMS Stamps. PDMS stamps used for normal μCP were fabricated from Sylgard 184 (the ratio between component A and B was 1:10) using the published procedure.[1] PDMS stamps used for μCP or micromolding with lateral compression in the plane were fabricated from Sylgard 184 (A:B = 1:20)[24] or PELD 15 soft silicone elastomer (A:B = 1:10).[22] The thickness of these PDMS stamps was ~1 cm. PDMS stamps used for μCP with uniaxial tension in the plane were made from PELD 15 silicone elastomer (A:B = 1:10); the thickness of these stamps was ~1 mm. The fabrication of other PDMS stamps is going to be described in the appropriate section.

Microcontact Printing and Chemical Etchings of Au and Ag. All printings of SAMs were carried out by hand. An ~2 mM solution of HDT in ethanol was used as the "ink". Before printing, substrates of Au and Ag were rinsed with ethanol and dried in a stream of N_2. After applying the HDT solution (by cotton Q-Tips) to the surface of the stamp, we dried the stamp in a stream of N_2 for ~1 min and then brought it into contact with the surface of Au or Ag for 5–10 s. Samples of Au and Ag that have been patterned with SAMs were etched in an aqueous solution containing KCN/O_2 or $K_2S_2O_3/K_3Fe(CN)_6/K_4Fe(CN)_6$ using the published procedures.[8]

Instrumentation. SEM was done on a JEOL JSM-6400 scanning electron microscope. Lateral compression of the PDMS stamp was achieved using a vice.

Results and Discussion

Figure 1 summarizes all the strategies that we have tried to reduce the size of features of SAMs produced using μCP. These strategies fall into four different categories: (1) Use the deformable character of the elastomeric material—μCP with lateral compression or uniaxial stretching in the plane of the stamp, and with pressure perpendicular to the plane of the stamp; (2) manipulate the cross-linked network of the elastomeric material—μCP with a stamp that has been swelled with a solvent or a stamp whose dimensions have been reduced by extraction of an inert filler; (3) control the surface chemistry for the formation of SAMs—lateral reactive spreading of HDT on gold; (4) take advantage of the convenience of μCP—multiple impressions of HDT on the same surface.

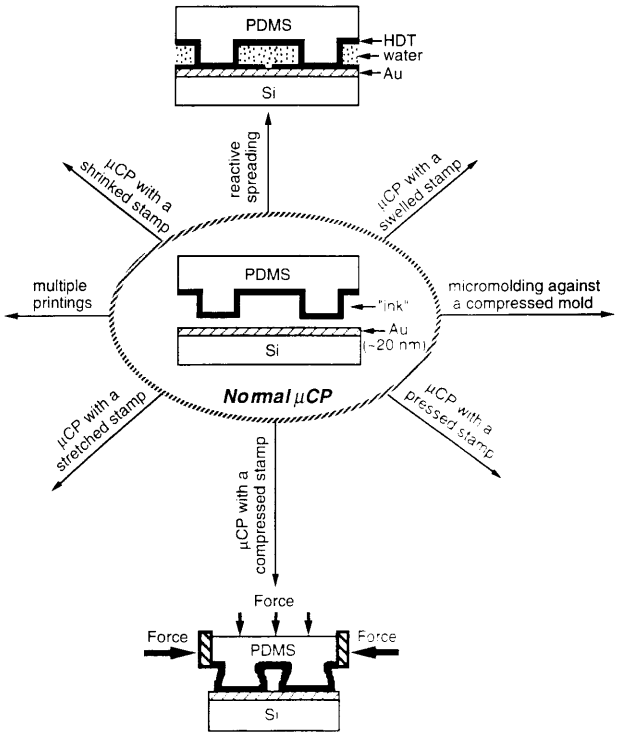

Figure 1. Summary of all procedures that have been used to reduce the size of features of SAMs generated using microcontact printing.

Microcontact Printing with a Stamp under Lateral Compression in the Plane. This procedure is shown in Figure 1 schematically. The lateral dimensions of the relief structures present on the PDMS stamp are reduced by the application of mechanical force using a vice. The resulting stamp is then used while under compression in μCP and is capable of forming patterns of SAMs with certain of its features reduced by a factor of more than two relative to the original features on the uncompressed stamp. The deformation caused by the vertical pressure during μCP further reduces the dimensions of the recessed regions of the stamp while increasing the dimensions of the raised regions slightly. Two-dimensional compression in the plane of the stamp was also possible.

Figure 2 shows SEM images of Ag patterns that were fabricated using μCP with a stamp under one-dimensional compression, in combination with selective chemical etching. The stamp had a simple test pattern of parallel lines (~2 μm in width and separated by ~1.6 μm) on its surface and was mechanically compressed to the indicated strain in the direction perpendicular to these lines. These samples were fabricated using a three-stage procedure: the first used a compressed stamp to print lines of HDT on a Ag surface; the second used the same or another compressed stamp to form lines of HDT on the same Ag surface with the lines perpendicular to those formed in the first step; and the third removed underivatized regions of Ag by chemical etching in an aqueous ferricyanide solution.[9] It was possible to achieve a substantial reduction in size of some of the features of the pattern but not others: areas in which the SAM was printed slightly increased their lateral size on compression, while bare regions in which no SAM was printed decreased in size.

(21) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274.
(22) Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 471.
(23) Wilbur, J. L.; Kim, E.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 649.
(24) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J. A.; Prentiss, M.; Whitesides, G. M. *Science* **1996**, *273*, 347.

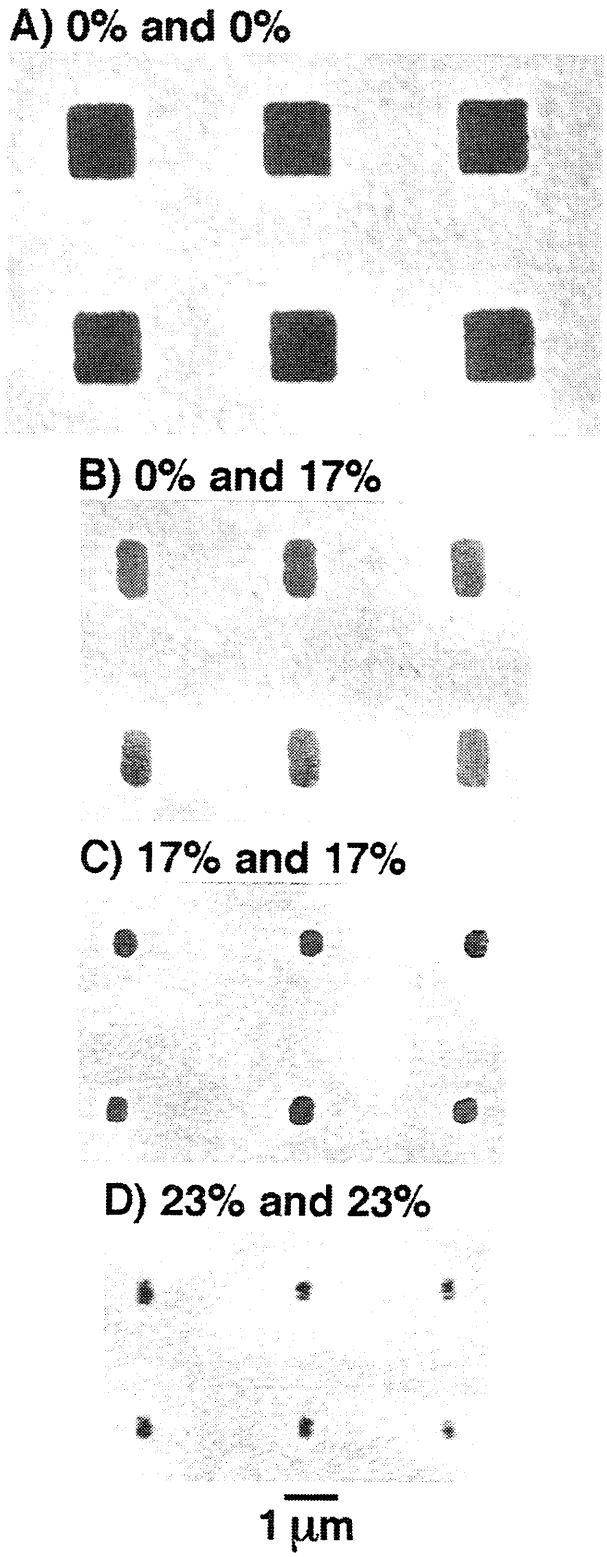

Figure 2. SEM images of Ag patterns (50 nm thick) that were fabricated with a PDMS stamp of parallel lines that had been compressed in the direction perpendicular to the lines. Each pattern was formed by printing twice with the direction of lines rotated by 90° before making the second printing. The first number indicates the compressive strain in the vertical direction. The bright regions are Ag; the dark regions are Si where the unprotected Ag has dissolved in an aqueous ferricyanide solution.

Right now, the smallest features that we have generated using this procedure are ~200 nm in dimension; the accuracy of this procedure is limited by the mechanics of the system used to compress the stamp laterally.

Since PDMS deforms isotropically under mechanical

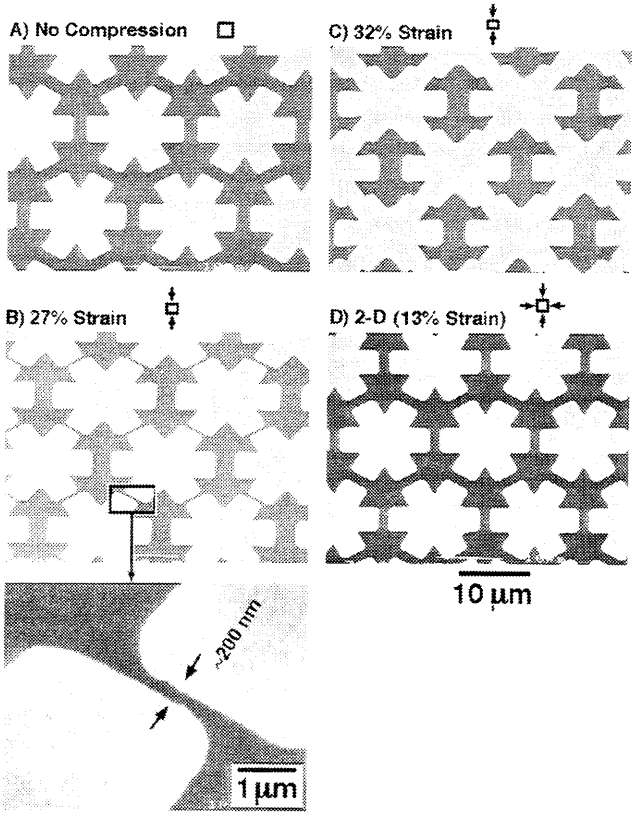

Figure 3. SEM images of Ag patterns (50 nm thick) that were fabricated using microcontact printing with a PDMS stamp that was under one-dimensional (A–C) and two-dimensional (D) compression. The one-dimensional compression was in the vertical direction. The bright regions are Ag; the dark regions are Si where the unprotected Ag has dissolved in an aqueous ferricyanide solution.

compression, both the shapes and sizes of the features present on the surface of the PDMS stamp change in a controllable manner. This procedure can be easily extended to more complex patterns. Figure 3 shows SEM images of silver patterns that were fabricated using this procedure with a moderately complex pattern that has features with acute angles and nonuniform sizes. The stamp was under one- and two-dimensional compression during μCP, respectively. It is obvious that the size of certain features of a test pattern with such a complexity can also be reduced using this procedure, while retaining the regularity in the original pattern.

This procedure for generating submicrometer-sized features is general. It indicates a new type of microlithography, in which dimensions of selected regions of the pattern can be made smaller or larger by deforming the stamp mechanically. It also suggests a potential route to the fabrication of "smart stamps", that is, stamps whose surfaces can be deformed locally with certain spatial resolution.

Replica Molding against a PDMS Mold under Mechanical Compression. The reconfigurated relief structures on the surface of a compressed PDMS stamp could also be replicated into a second polymeric material and then used to cast new PDMS stamps.[24] Figure 4 outlines the procedure schematically. The size of features is reduced in the lateral compression of this stamp. The compressed features are replicated by molding an ultraviolet-curable, liquid prepolymeric polyurethane (PU) against the compressed stamp. This procedure is iterative: a new PDMS stamp can be prepared, by casting against the relief structures on the surface of the PU replica, and then compressed and replicated. Each time

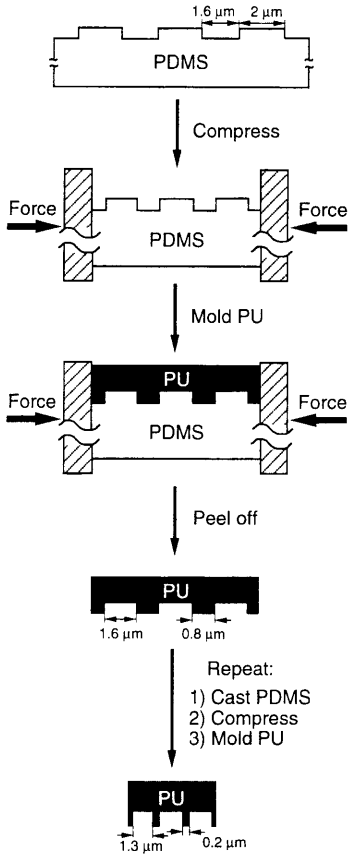

Figure 4. Schematic procedure for replica molding of polyurethane (PU) against a laterally compressed PDMS mold.

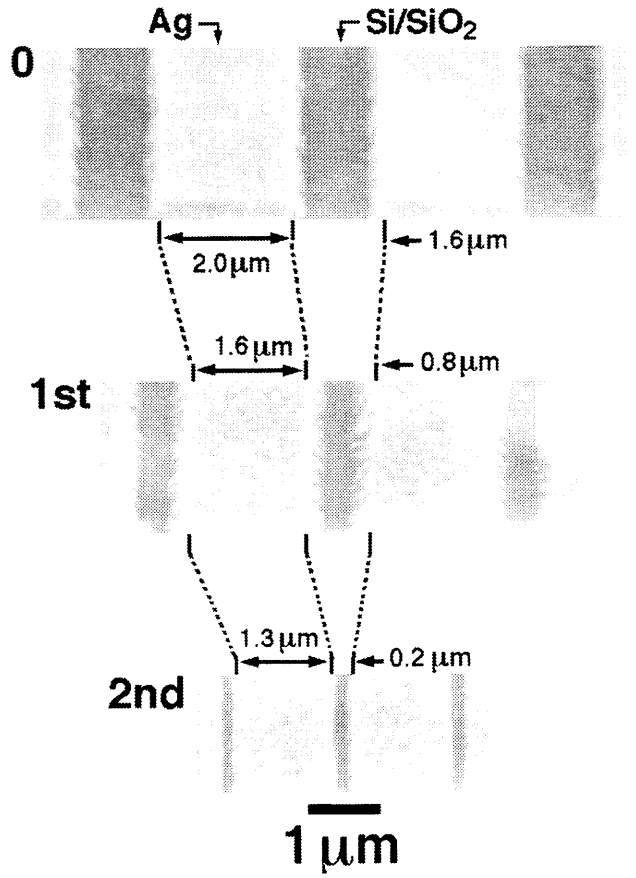

Figure 5. SEM images of Ag patterns (200 nm thick for the first two and 50 nm thick for the last one) that were fabricated using microcontact printing with PDMS stamps cast from PU replicas during different cycles of compression and replica molding.

that the PDMS master is compressed, the recessed areas decrease more in dimension than the raised areas. Using a test structure of parallel lines, two cycles of compression and replica molding reduced the size of some features from ~1.6 μm to ~200 nm.[24]

The PDMS master formed in each repeating cycle could be used as the stamp in μCP to generate patterned SAMs of alkanethiolates on the surfaces of gold and silver. Figure 5 shows SEM images of patterned silver lines that were generated by μCP with hexadecanethiol using PDMS stamps cast from the PU structures, followed by selective chemical etching. The period of the pattern decreased during each cycle of compression and replica molding; the dimensions of the recessed regions decreased more than those of the raised regions in each cycle.

This method provides a very simple and efficient route to submicrometer-sized structures. Besides those advantages mentioned for μCP with a compressed stamp, this method provides a convenient procedure for preparing PDMS stamps with a range of different feature sizes starting from a single master. Each stamp can be subsequently used in μCP for more than 100 times to transfer patterns to the surfaces of other solid substrates.

Microcontact Printing with a Stamp under Uniaxial Stretching in the Plane. Cross-linked PDMS has very high mechanical strength. Thin films made from high molecular weight prepolymers of PDMS can be stretched mechanically with a uniaxial elongation up to 800%.[25] Under uniaxial elongation, the dimensions of the microfeatures on the PDMS stamp increase along the stretching direction and decrease in the perpendicular direction.

Figure 6 shows SEM images of test patterns of gold that were fabricated using μCP with a PDMS stamp that was under uniaxial stretching along the direction of the lines. The thin stamp (~1 mm thick) was cast from the soft silicone elastomer (PELD 15, Hüls) that has a maximum elongation of ~700%. In this uniaxial elongation, the dimensions of the recessed regions on the stamp decreased more significantly than those of the raised regions.

This approach is most useful for simple test patterns such as parallel lines. The dimensions of the features on the PDMS stamp decrease in the direction perpendicular to the stretching while increasing along the stretching. Since the elongation can be accurately measured and controlled easily, this procedure is convenient to use in practice.

Microcontact Printing with a Stamp under Pressure Perpendicular to the Surface. A thin PDMS stamp was fabricated on a glass slide using the following procedure: a drop of PDMS prepolymer was placed between a master and a piece of glass plate; the two rigid substrates were compressed against each other using a pair of book clamps; the PDMS prepolymer was cured, and these two substrates were separated carefully. A thin PDMS stamp was formed and grafted to the surface of a glass plate via the chemical reaction between the silanol groups on glass and the Si–H groups of the PDMS prepolymer. A similar stamp was also made on a gold substrate covered with SAMs of vinyl-terminated alkanethiolates. The cross-linked PDMS was grafted to the gold surface via the reaction between the vinyl groups on the surface of gold and the Si–H groups of the PDMS prepolymer.

In carrying out μCP, the inked PDMS stamp was pressed against the gold substrate with some pressure (Figure

(25) *Silicon Compounds: Register and Review*; Hüls America; Piscataway, NJ, 1991.

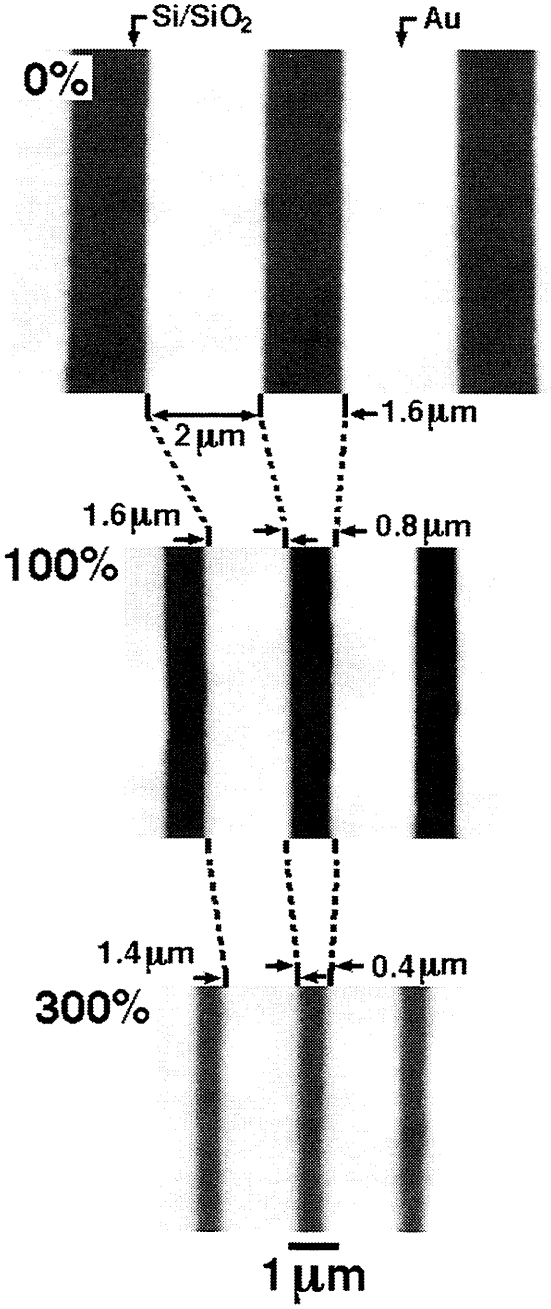

Figure 6. SEM images of Au patterns (20 nm thick) that were fabricated using microcontact printing of HDT with PDMS stamps that were stretched along the direction of the lines (the strain was 0%, 100%, and 300%, respectively), followed by selective chemical etching.

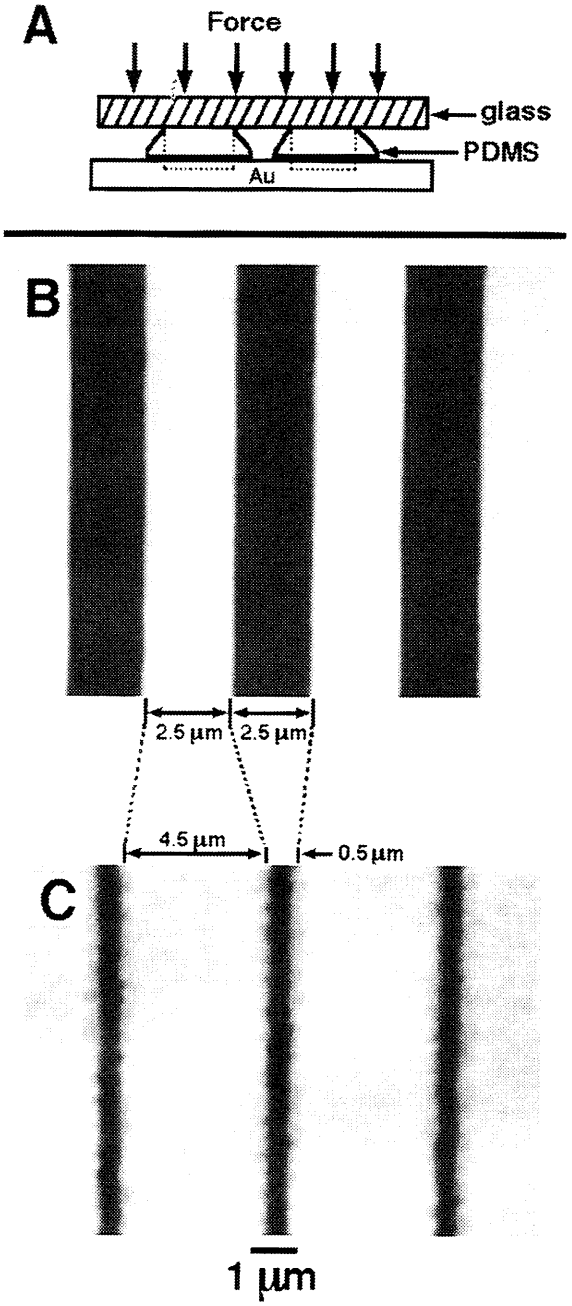

Figure 7. (A) Illustration of size reduction by mechanically pressing a PDMS stamp against the gold substrate while conducting microcontact printing. The dashed lines represent the original profiles of the microstructures on the stamp. (B and C) SEM images of Au patterns (20 nm thick) that were fabricated using microcontact printing with PDMS stamps without and with vertical pressure, followed by selective etching in an aqueous cyanide solution.

7A). The raised features on the PDMS stamp deformed in this process of compression: the vertical dimensions of the raised features decreased while the lateral dimensions increased. As a result, the lateral dimensions of the recessed regions decreased (Figure 7B and C).

This approach does not reduce the period of the pattern; it can only be used to reduce the lateral dimensions of the bare regions of gold (that is, regions not derivatized with SAMs). Much effort is required to measure and control the vertical pressure; therefore, this procedure cannot generate features with the required size reproducibly, unless we invest in a certain amount of mechanical apparatus.

Microcontact Printing with a Stamp That Has Been Swelled in a Solvent. Cross-linked PDMS can be swelled in a number of "good" solvents, such as toluene and hexane.[26-28] A swelled PDMS stamp still has good mechanical strength to be used in μCP. For normal PDMS stamps, the dimensions of both recessed and raised regions increase after swelling in the solvent. We only observed size reduction for certain features for those thin stamps that are grafted to a rigid support (Figure 8A). These special stamps were fabricated using a similar procedure as described for the fabrication of stamps used for μCP under vertical pressure. Figure 8B and C shows SEM images of Au patterns that were fabricated using a PDMS stamp without and with swelling in toluene for ~30 min.

(26) Bueche, A. M. *J. Polym. Sci.* **1955**, *XV*, 97.
(27) Pierre, L. E. ST.; Dewhurst, H. A.; Bueche, A. M. *J. Polym. Sci.* **1959**, *XXXVI*, 105.
(28) DeBolt, L. C.; Mark, J. E. *Macromolecules* **1987**, *20*, 2369.

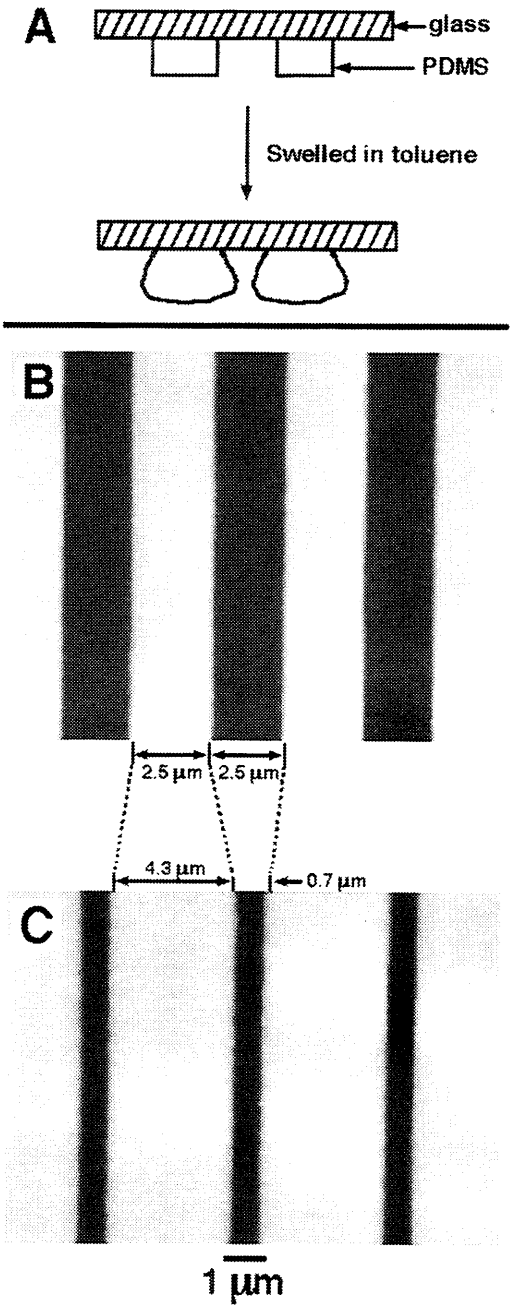

Figure 8. (A) Illustration of size reduction by swelling the PDMS stamp in toluene for ~30 min before conducting microcontact printing. (B and C) SEM images of Au patterns (20 nm thick) that were fabricated using a PDMS stamp without and with swelling in toluene, followed by selective chemical etching in a cyanide solution.

After being swelled in toluene, the raised features on the stamp increased in size, and this increase caused a reduction in the distance between the raised features.

The swelling process was reversible: the PDMS block returned to its original shape after the solvent had evaporated. The shape of a swelled PDMS stamp could be locked into place by using a solvent that can be grafted to the PDMS network or that can be cross-linked into a solid material via thermal or ultraviolet treatment. In general, this approach to reducing sizes is not as convenient as others.

Microcontact Printing with a Stamp Whose Dimensions Have Been Reduced by Extraction of an Inert Filler. In making a PDMS stamp, we added an inert filler into the prepolymer mixture before curing the system. After cross-linking (at 65 °C for ~10 h) the PDMS prepolymer into a solid material, the inert filler was

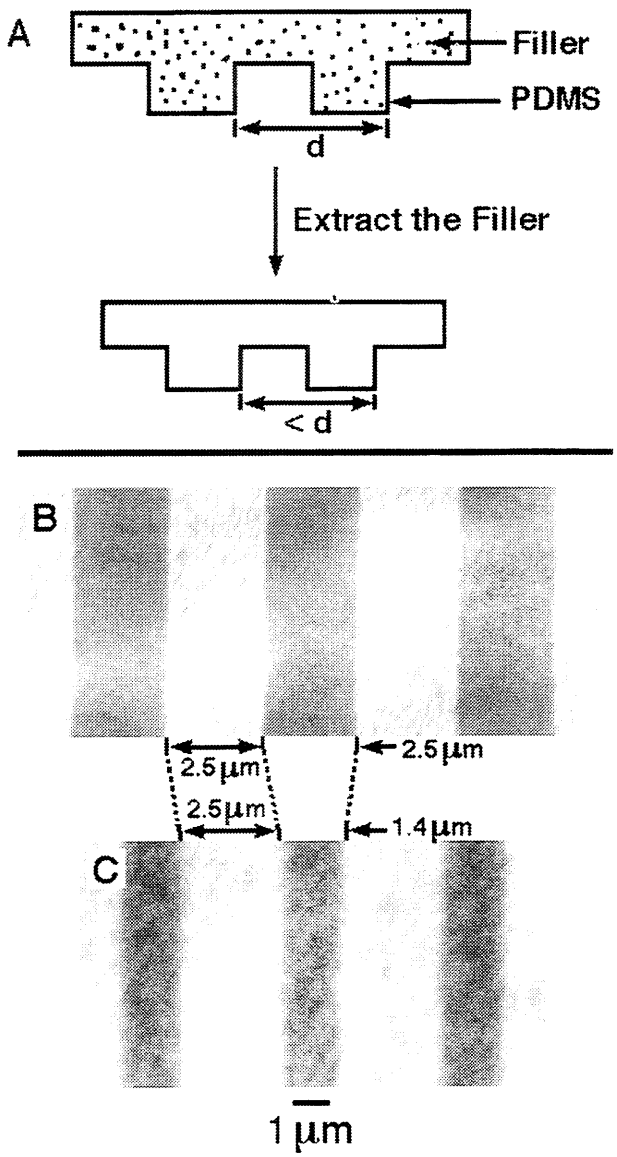

Figure 9. (A) Illustrations of size reduction by extraction of the inert filler that was added into the PDMS prepolymer before curing. (B and C) SEM images of Au patterns (20 nm thick) that were fabricated using a PDMS stamp before (B) and after (C) removing the filler. The bright regions are Au; the dark regions are Si where the unprotected Au has dissolved in an aqueous cyanide solution. In this example, ~54% (w/w) of PS041 was added into the Sylgard 184 mixture (A:B = 1:10).

removed by extraction with a solvent to reduce the volume (and, therefore, the dimension in each direction) of the PDMS block.[26-28] We have used a number of linear, low molecular weight oligomers of PDMS such as silicone fluids (PS039, PS040, PS041, Hüls) as the fillers. These fluids mix well with the Sylgard silicone prepolymer and can be extracted easily with toluene. After extraction of the filler, the volume of the PDMS block as well as the dimensions of the microfeatures on its surface decreased isotropically in all three directions (Figure 9A). We have been able to load as much as ~68% (w/w) of PS041 to the mixture of Sylgard prepolymer. The calculated reduction in the size of features was inconsistent with that measured using a light diffraction method. Figure 9B shows lines of gold that were fabricated using microcontact printing with a PDMS stamp that has ~54% (w/w) PS041 in it. Figure 9C shows gold lines that were fabricated using this same stamp after the PS041 has been extracted by immersing in toluene for ~30 min. The period of the pattern and the dimensions of both lines and the spacings between lines were reduced in this process. However, after the extrac-

tion of the filler, the stamp became very soft. When we brought the stamp into contact with the gold surface for printing, the raised areas of the stamp deformed again and resulted in the characteristics observed in the SEM photographs shown here, that is, less reduction in the dimensions of the lines than in the dimensions of the spacings between lines.

This approach can only be used to achieve size reduction by a factor of ~1.4. It was the only procedure that allowed us to reduce the size of the microfeatures in all three direction. We can design an iterative procedure (such as that shown in Figure 4) that will allow us to achieve more significant reduction (by a factor of >5) in the size of the features.

Microcontact Printing Using Controlled Reactive Spreading. This process is shown in Figure 1 schematically. The lateral spreading of HDT liquid (predominately from the edge of the patterned SAM beyond the area of the stamp in contact with the substrate) on the surface of gold reduces the dimensions of the bare regions (Figure 10A and B). The alkanethiol used in this process must be insoluble in water; thus, the water acts as a barrier to the diffusion of HDT from the recessed regions of the stamp to the surface of gold. The distance d (μm) over which the edge of the SAM advances through reactive spreading is related to the concentration of HDT [C] (mM) and the printing time t (min) by the empirical equation $d^2 \approx (0.16[C]^{1/2})t$. The dependence of d on t is consistent with a model proposed for the spreading of a liquid on a solid surface.[29,30]

Conducting μCP under water is critical for the success of this procedure. If printing was carried out in air, HDT liquid did not spread on gold: it formed an autophobic system—a liquid in contact with a surface modifies the chemistry of the surface and lowers its solid–vapor and solid–liquid surface tension, and the liquid retracts spontaneously.[31] In this case, the stamp cannot be kept in contact with the gold surface for intervals longer than 30 s; otherwise, disordered SAMs also formed on those regions not in contact with the stamp by the diffusion of HDT from the recessed regions of the stamp to the gold surface through the vapor phase.

This method only reduces the dimensions of certain features—bare regions of gold underivatized with SAMs. The dimensions of the whole patterned area cannot be shrunk by using this technique alone. In combining with selective etching of gold, this method can be used to fabricate arrays of nanometer-sized trenches or grids in gold that are separated by several micrometers (Figure 10C and D).

Microcontact Printing with Multiple Impressions on the Same Surface. Multiple printings of SAMs on the same surface were also possible: we could use this approach to reduce the size of certain features of SAMs or to generate more complex patterns from a single stamp only having simple patterns on its surface. Figure 11A and B illustrates the use of this procedure for size reduction. The dimensions of the printed regions (that is, regions derivatized with SAMs) increased after the second printing while the dimensions of the bare regions decreased. Figure 11C shows the application of multiple printings in forming new patterns. The gold patterns (20 nm thick) were generated by a double-printing procedure: a PDMS stamp having parallel lines on its surface was first contacted with the Au surface for ~10 s; it was then removed, cleaned with ethanol, rewetted with HDT ink, and recontacted with the Au surface for ~10 s, with the orientation of the lines rotated by ~2°. The printed samples were then etched in an aqueous cyanide solution

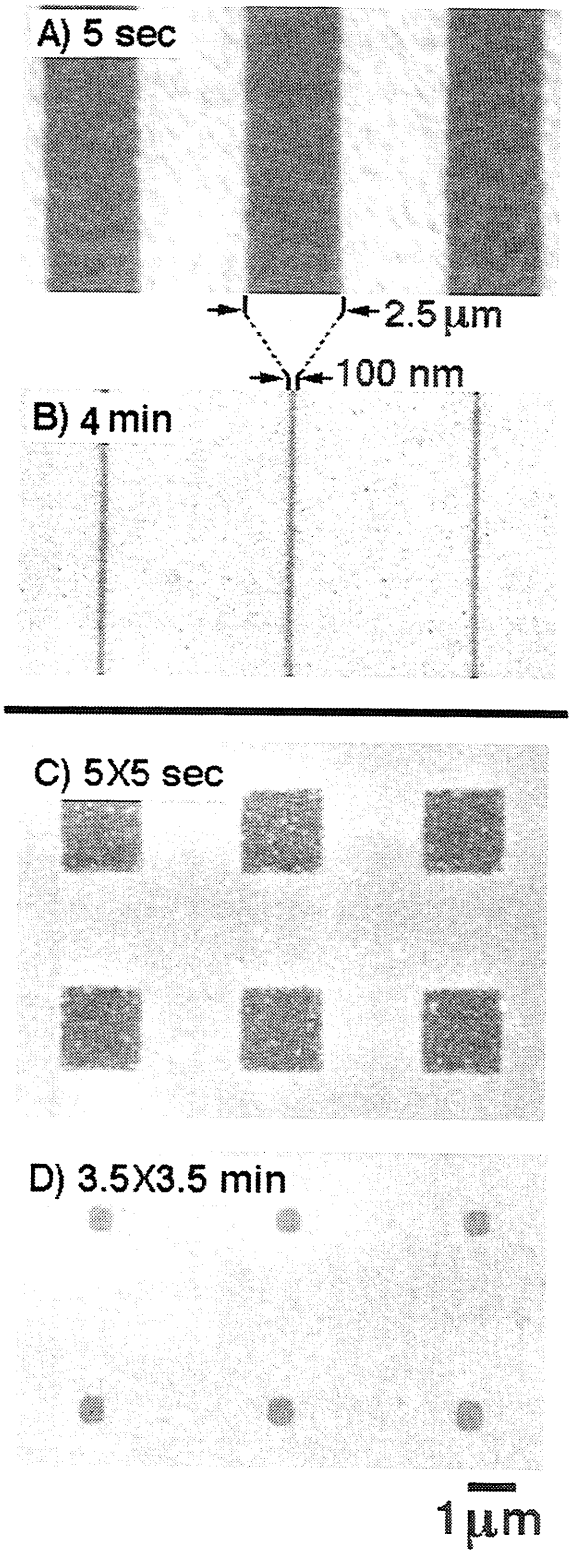

Figure 10. SEM images of Au patterns (20 nm thick) that were fabricated using microcontact printing of HDT under water, followed by selective chemical etching in an aqueous cyanide solution. By carrying out microcontact printing under water for several minutes, it was possible to achieve a substantial reduction in dimension for the bare Au (that is, not covered by the SAMs) from ~2.5 to ~0.1 μm (A and B). By cross-stamping with this procedure, it was possible to fabricate an array of Au grids with submicrometer-sized features (C and D). The bright regions are Au covered by SAMs; the dark regions are Si where the underivatized Au has been removed by etching in CN^-/O_2.

(29) Lopez, J.; Miller, C. A.; Ruckenstein, E. *J. Colloid Interface Sci.* **1976**, *56*, 460.
(30) Greenspan, H. P. *J. Fluid Mech.* **1978**, *84*, 125.
(31) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581.

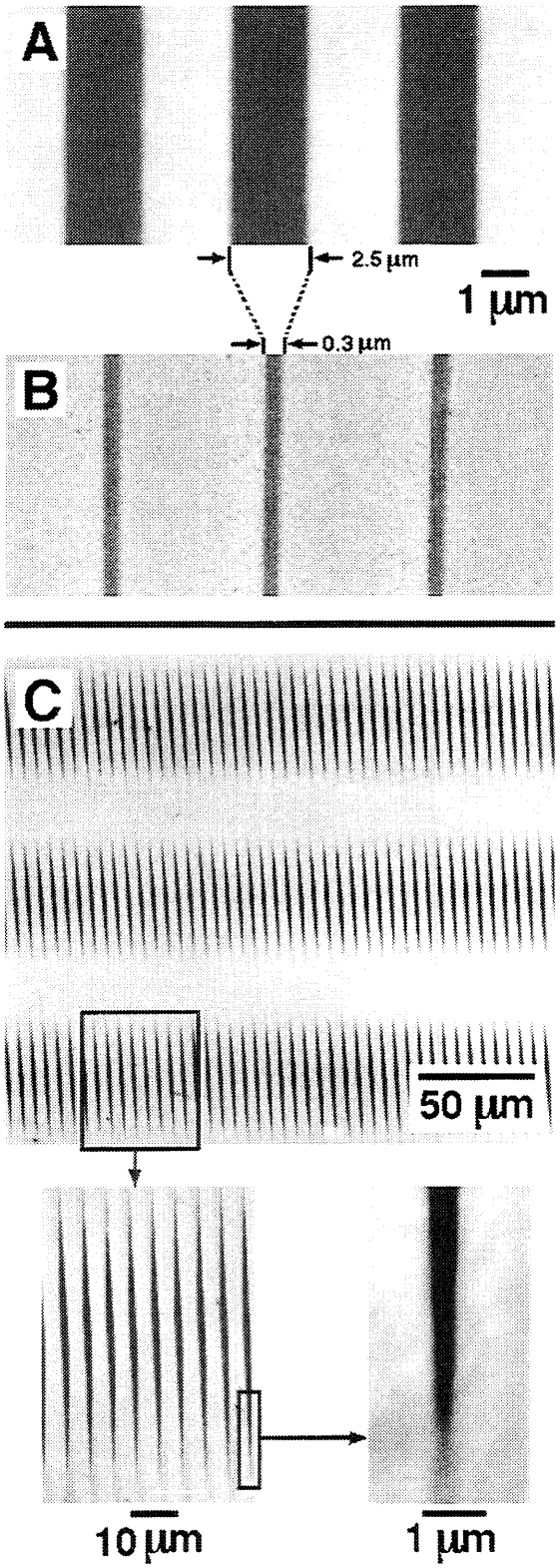

Figure 11. (A and B) Illustration of size reduction by double-printing. The gold patterns (20 nm thick) were fabricated by (A) stamp once and (B) stamp twice (after the first printing, the stamp was removed from the Au surface, it was translated in the direction perpendicular to the lines for a certain distance, and the second printing was made). (C) Illustration of making new patterns using double-printing. The lines were rotated by a small angle (~2°) before making the second printing.

to remove the unprotected gold. Note that the dimensions of the features etched in the gold film are only ~200 nm at the tip.

By rotating for different angles between these two printings, we could produce patterns with a variety of

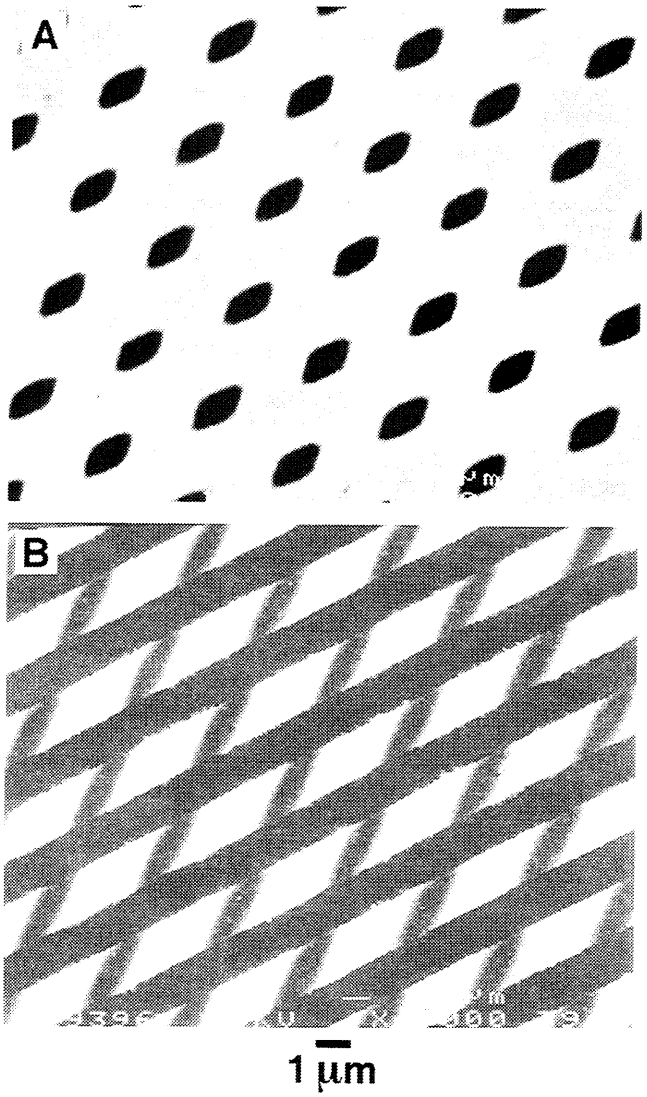

Figure 12. Two more examples to illustrate the application of double-printing in making new patterns. (A) SEM image of a test pattern of Au (20 nm thick) generated by double-printing, followed by selective wet etching in an aqueous ferricyanide solution. (B) SEM image of another test pattern of Au that was fabricated using a modified procedure for double-printing (see the text for details). The bright regions are Au covered by SAMs; the dark regions are Si where the underivatized Au has dissolved. The stamp used here only had parallel lines on its surface.

shapes and sizes (for example, Figure 12A, rotated by ~45°). Moreover, we could remove hexadecanethiolate SAMs on Au by immersing the patterned sample in piranha solution (a mixture of H_2SO_4 (98%) and H_2O_2 (30%) at the ratio of 7:3). This property opens the door to generate new forms of patterns that cannot be produced simply by double-printing. Figure 12B show the SEM image of a gold pattern that was fabricated using a five-stage procedure: (1) lines of hexadecanethiolate SAMs were printed on a Au surface; (2) this sample was etched in an aqueous ferricyanide etchant for ~7 min; (3) the hexadecanethiolate SAMs on the remaining Au were removed by immersing the sample in piranha solution for ~5 s; (4) lines of hexadecanethiolate SAMs were printed on this Au surface, with the orientation of the lines rotated by ~45°; (5) this sample was etched in the ferricyanide etchant for another ~7 min. The Au pattern generated in this way was complementary to that fabricated using the normal procedure of double-printing (Figure 12A).

At present we conduct microcontact printing by hand, and it is difficult to achieve accurate alignment between

the stamp and the substrate. Once a good procedure for registration is available, we believe that this approach can be used to generate features with sizes of ≤500 nm routinely.

Conclusions

We have demonstrated a number of strategies that can be used to reduce the size of features of SAMs generated using microcontact printing. In combination with selective chemical etchings of coinage metals, SiO_2, and Si, we could fabricate patterned microfeatures (<500 nm) in these materials without using advanced photolithographic techniques. These demonstrated strategies help to establish μCP as a microlithographic technique for the generation and manufacturing of submicrometer-sized features. Some of these strategies also suggest a new route for the preparation of patterns with small lateral dimensions, in which these dimensions are achieved by manipulating the elastomeric template[32] rather than by fabrication of a rigid mask with small features.

Microcontact printing illustrates a largely unexplored, non-photolithographic technique for forming micropatterns and microstructures. This technique is capable, in a research setting, of generating submicron features over relatively large areas (~50 cm^2). The limitations of this technique after serious development remain to be defined. The elastomeric character of the master provides many new opportunities for μCP; for example, we can easily manipulate the size and shape of features present on a PDMS stamp using mechanical compression, bending, and stretching. It also causes some problems for μCP; for example, it is more difficult to achieve high-resolution registration with an elstomeric material; the sagging of the elastomeric structures when a PDMS stamp comes in contact with a surface limits the utility of μCP only for certain types of micropatterns and microstructures. We are beginning to address these issues associated with μCP in our research, and we believe that we will find cures for most of them in the near future by bringing new materials, new designs, and new configurations into this area.

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(32) Finkelmann, H.; Brand, H. R. *Trends Polym. Sci.* **1994**, *2*, 222.