Non-Photolithographic Methods for Fabrication of Elastomeric Stamps for Use in Microcontact Printing

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Received April 22, 1996[⊗]

This paper describes several methods that generate patterned relief structures for casting the elastomeric stamps required in microcontact printing (μCP). The relief structures include the following: (1) patterns etched in thin films of silver (200 nm thick) with printed SAMs of hexadecanethiolate as resists; (2) patterned polymeric structures assembled on the surface of a thin film of silver (or gold) that has been patterned with SAMs of hexadecanethiolate; and (3) polystyrene microspheres assembled on a flat surface. Commercial diffraction gratings were also useful as masters. Microcontact printing with poly(dimethylsiloxane) stamps cast from these relief structures was used in combination with selective wet etching to generate patterns in thin films of silver and gold. Although some of these techniques used photolithography once in fabricating the initial masters, they could produce patterns more complex than those on the initial masters. These procedures provide a convenient route to moderately complex patterns with feature sizes ranging from ~100 nm to ~100 μm.

Introduction

Microcontact printing (μCP)[1,2] is a non-photolithographic technique for generating patterned self-assembled monolayers (SAMs)[3] on the surfaces of a variety of substrates, for example, gold,[1,2] silver,[4] copper,[5,6] and silicon dioxide.[7−9] In this technique, an elastomeric stamp (typically, made from poly(dimethylsiloxane), PDMS) is prepared by casting against a master that has a relief structure on its surface. Patterned SAMs with feature sizes larger than 0.5 μm can be produced routinely using this technique; and in some cases, features with sizes down to ~100 nm have also been fabricated.[10−12] Patterned SAMs formed using μCP have been used as nanometer-thick resists in selective chemical etching of underlying substrates[1,2,4−9] and as templates for selective adsorption of proteins and selective attachment of cells.[13,14] Because μCP involves conformal contact between an elastomer stamp and a substrate, it can be used to print patterned SAMs on curved surfaces.[15]

The utility of μCP is limited mainly by the availability of masters used to cast PDMS stamps. These masters are usually made by photolithography in thin films of conventional resists.[1,2] Photolithography is a wonderfully versatile and precise technique that generates submicron features routinely.[16] It has, however, a number of disadvantages, especially for potential users of microtechnology who do not have routine access to microfabrication facilities. Only specialized polymers can be used as resists. It is not applicable to nonplanar surfaces. It requires a different chrome-mask for each pattern to be produced. The cost of making a chrome-mask and the cost of maintaining clean room facilities make this technique less than accessible to the chemistry community.

In this paper, we describe several methods that use photolithography seldom or not at all to generate the masters required for casting PDMS stamps.[17] The masters that we used for the present work include the following: (1) commercial diffraction gratings; (2) patterns etched in thin films of silver (200 nm thick); (3) polymeric relief structures assembled on surfaces of silver or gold patterned with SAMs; and (4) polystyrene microspheres assembled on flat surfaces. For those techniques that used photolithography once in fabricating the original PDMS stamp used in μCP, they were able to produce patterns more complex than those on the original PDMS stamp. The smallest features that have been generated so far were trenches and cavities etched in silver or silicon with dimensions of ~100 nm.

Experimental Section

Materials. Au (99.999%), Ag (99.9999%), Ti(99.99%), $K_2S_2O_3$, KOH, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and $CH_3(CH_2)_{15}SH$ were obtained from Aldrich. Poly(dimethylsiloxane) (PDMS, Sylgard 184) was obtained from Dow Corning. Polished Si(100) wafers (Cz, N/phosphorus-doped, 1−10 Ωcm, test grade, SEMI Std. flats) were obtained from Silicon Sense (Nashua, NH). Hexadecanethiol was purified under nitrogen by chromatography through silica gel. Gold films (20 nm) and silver films (50 nm) were prepared using e-beam evaporation onto titanium-primed (~2 nm) silicon wafers. Ultraviolet-curable polyurethanes (PU) were obtained from Summer Optical (J-91, Fort Washington, PA) and Norland Products (NOA-73, New Brunswick, NJ). Blazed diffraction gratings were obtained from Edmund Scientific (Stock # E43206, epoxy replicas from diamond-ruled masters, 600 grooves/mm). Polystyrene microspheres (dispersions in water) were obtained from Polysciences (Warrington, PA).

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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S0743-7463(96)00387-3 CCC: $12.00

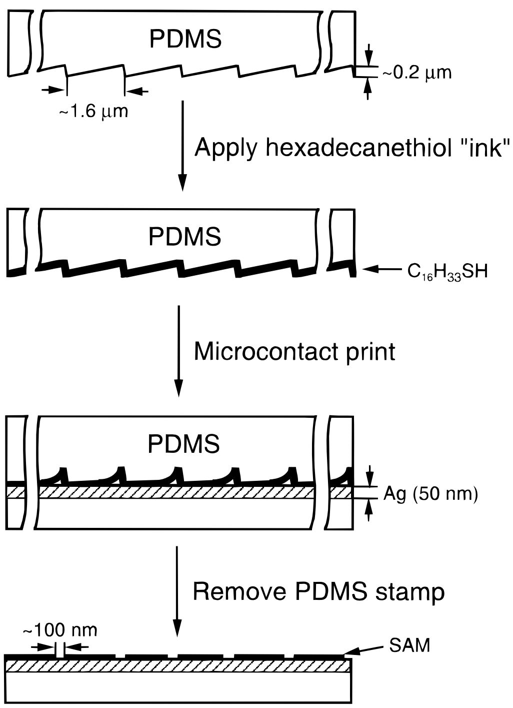

Figure 1. Schematic procedure for microcontact printing using a PDMS stamp cast from a commercial blazed diffraction grating.

Microcontact printing (μCP). PDMS stamps were fabricated according to the published procedure.[1,2] A solution of hexadecanethiol in ethanol (~2 mM) was used as the "ink" for μCP. After the hexadecanethiol solution was applied (by cotton Q-tip) to the PDMS stamp, the stamp was dried in a stream of N_2 for ~1 min and then brought into contact with the surface of silver (or gold). After ~5 s, the stamp was separated carefully from the silver surface. In some cases, μCP was carried out under water:[10] a piece of silver substrate was put in a petri dish that was half-filled with deionized water, and the inked stamp was then brought into contact with the silver surface. After ~5 s, the stamp was separated from the silver substrate while under water, the water was replaced with several volumes of clean water to remove alkanethiol floating on its surface, and the silver substrate was then removed from the water and dried in a stream of N_2.

Assembly of Organic Polymers on SAM-Patterned Surfaces.[18,19] After the surface of a silver (or gold) film was patterned with hexadecanethiol, a drop of prepolymer of polyurethane was placed on the patterned area; the substrate was then carefully tilted to drain off the excess prepolymer. The remaining prepolymer selectively wetted and covered the hydrophilic regions (that is, bare regions of Ag or Au) of the surface and was cured with a medium-pressure mercury vapor lamp (type 7825-34, Canrad-Hanovia) for ~20 min, with the lamp positioned at a distance of 1−2 cm from the sample. This simple procedure is highly reproducible and can form patterned polymeric relief structures over an area of several square centimeters.

Etchings of Silver, Gold, and Silicon. The etchants used for SAM-patterned films of silver and gold were aqueous solutions containing thiosulfate and ferri/ferrocyanide.[4,20] Anisotropic etching of silicon was carried out in an aqueous solution of KOH and 2-propanol at 65 °C (400 mL of H_2O, 92 g of KOH, 132 mL of 2-PrOH).[7] Prior to silicon etching, the native oxide on silicon was removed by dipping in an unbuffered aqueous HF solution (~1% w/w).

Instrumentation. SEM was done on a JEOL JSM-6400 scanning electron microscope. AFM images were obtained using a Topometrix TMX 2010 scanning electron probe microscope (Mountain View, CA); the images were obtained in the contact mode with supertips (Model # 1700-00).

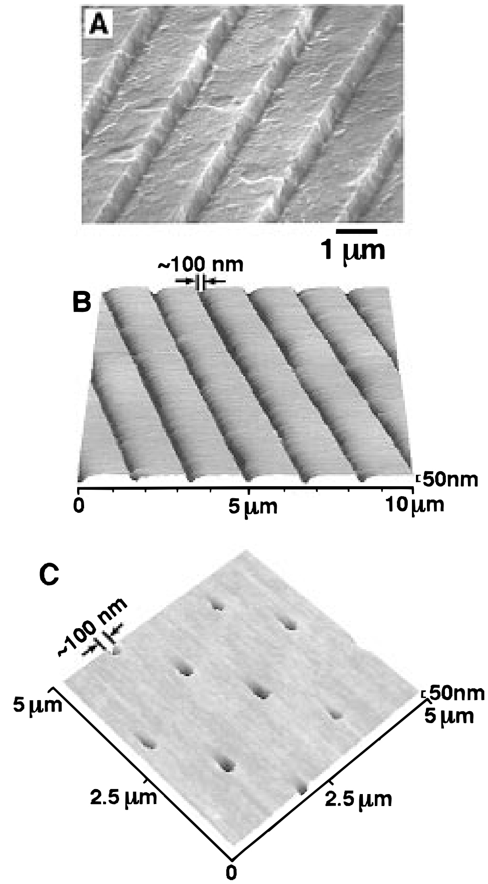

Figure 2. (A) SEM of the commercial blazed diffraction grating used for casting PDMS stamps. (B and C) AFM images of two representative patterns of silver (50 nm thick) that were generated using μCP with a PDMS stamp cast from the blazed grating, followed by selective etching. The pattern of (C) was generated using double-printing, with the orientation of the lines of the second printing rotated by ~90°.

Results and Discussion

PDMS Stamps Cast from Blazed Diffraction Gratings. The relief structures (usually generated from replicas prepared using diamond ruling or holography) present on the surfaces of commercially available diffraction gratings could be used directly to cast PDMS stamps with simple patterns such as parallel lines and arrays of dots. The unusual cross-sectional profile of a blazed diffraction grating provides useful access to feature sizes not easily prepared using relief structures made with the square shape usually found in conventional resist films patterned using photolithography.

Figure 1 illustrates the procedure for μCP on silver with a PDMS stamp cast from a blazed diffraction grating. We speculate that when the stamp is in contact with the silver surface, the raised areas of the stamp deform as a result of the attractive force between the stamp and the substrate. The lateral dimension of the areas of the pattern in which the SAM is printed is therefore much larger than that of the bare areas. Under the conditions we normally used for μCP, the resulting bare areas on the silver surface had a width of ≤300 nm, depending on the softness of the PDMS stamp and the period of time during which the stamp was in contact with the silver surface.

Figure 2A shows an SEM image of the blazed diffraction grating used for the present work. Figure 2B and C shows AFM images of two typical patterns of silver that were

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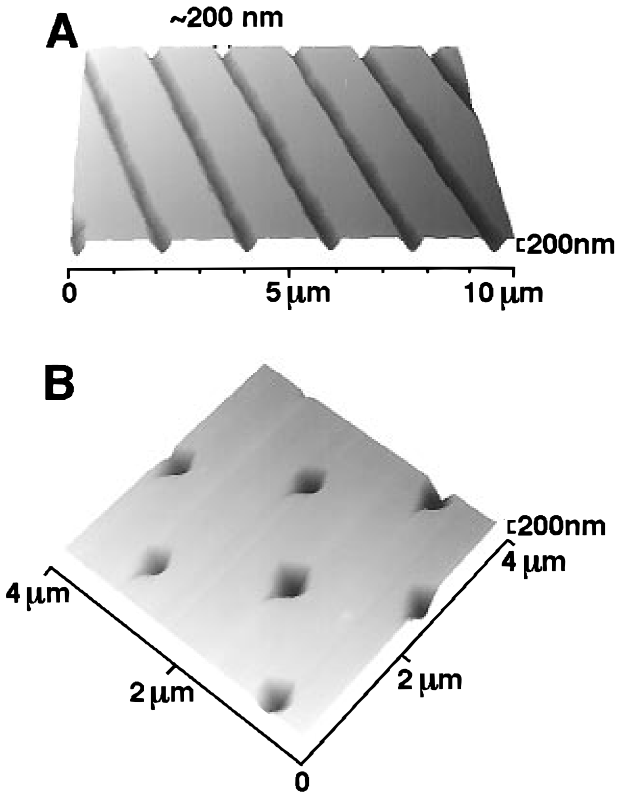

Figure 3. AFM images of trenches and pyramids anisotropically etched in silicon using patterned silver films as resists. (A) The sample of Figure 2B was etched in an aqueous KOH/2-PrOH solution for ~20 s at 65 °C; (B) the sample of Figure 2C was etched for ~1 m. After etching silicon, the silver masks were removed by dipping in aqua regia. The dimension of the trenches in silicon is wider than that in silver due to undercutting.

easily generated using μCP with a PDMS stamp cast from this grating, followed by selective chemical etching in an aqueous ferricyanide solution.[20] At present, the smallest features that we have produced using this method had dimensions of ~100 nm. The rough edges of the silver lines were caused by the roughness of the features on the original master (Figure 2A). The height of the relief structure on the PDMS stamp is important in obtaining high-contrast patterns of SAMs. If the height is less than 200 nm, no patterns of SAMs form on the silver surface: the SAMs cover the entire area of the substrate that is covered by the stamp.

Anisotropic etching of silicon with the patterned silver films as secondary masks produced V-shaped trenches and pyramids in silicon having base dimensions ≤ 300 nm (Figure 3). These featured surfaces could be further used as masters to cast PDMS stamps for fabricating structures of metals or polymers with features in the ~300 nm range of sizes.[12,21−23]

PDMS Stamps Cast from Relief Structures Etched in Silver Films. Silver is a relatively inexpensive metal and can be etched rapidly in a variety of aqueous solutions with printed SAMs of alkanethiolates as resists.[4] The relatively high (~200 nm) relief structures formed in silver using the combination of μCP and selective etching could be used to cast PDMS stamps for use in μCP (Figure 4). The silver pattern formed by μCP with this new PDMS stamp and selective etching is complementary to the original silver pattern. This method, therefore, provides a convenient route to negative patterns without further access to the photolithographic facilities. By using

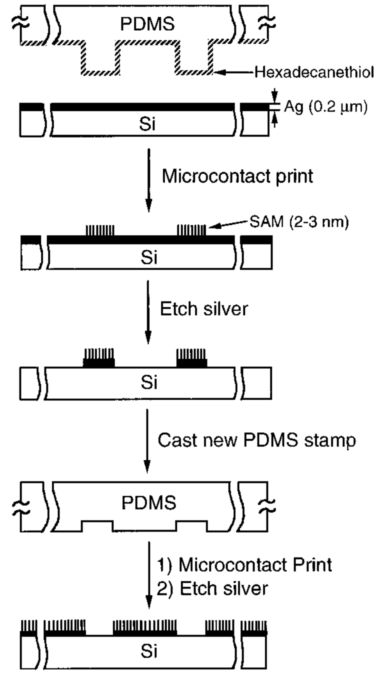

Figure 4. Schematic procedure for casting PDMS stamps from relief patterns etched in silver films.

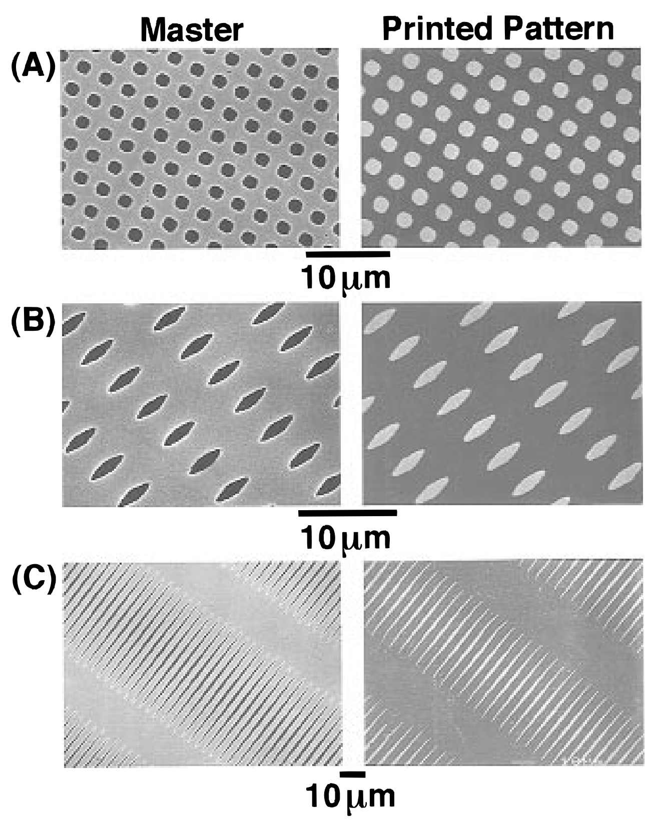

Figure 5. SEMs of some representative patterns of silver (50 nm thick) that could be generated by double-printing using a PDMS stamp having parallel lines on its surface. The masters were generated in 200 nm-thick films of silver by μCP with hexadecanethiol, followed by selective etching. In generating the masters, the direction of the lines of the second printing was rotated by (A) ~90°, (B) ~45°, and (C) ~2°. The bright regions are silver; the dark regions are silicon, where the silver has been dissolved.

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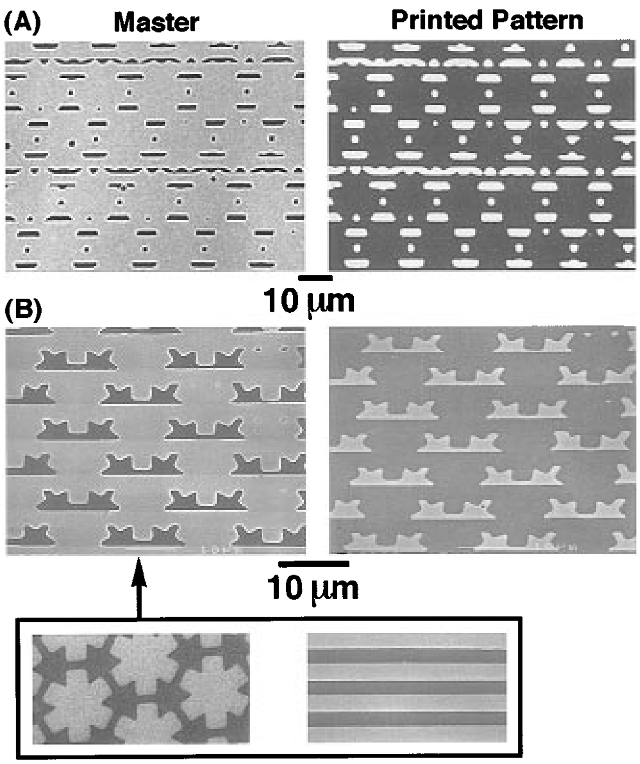

Figure 6. SEMs of some representative patterns of silver (50 nm-thick) that were generated by double-printing with two PDMS stamps: one of them has lines on its surface, and the other has a star pattern (see the inset). The bright regions are silver; the dark regions are silicon, where the silver has been dissolved.

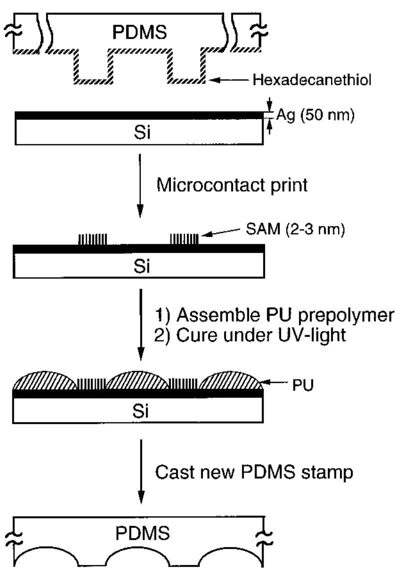

Figure 7. Schematic procedure for casting PDMS stamps from microstructures of polyurethane assembled on surfaces of silver patterned with SAMs.

multiple-impression printing with PDMS stamps having different relief structures, we can generate moderately complex patterns and structures from simple initial patterns. The edge resolution of the second silver pattern is <100 nm, a value that is good enough for many applications.

Figure 5 shows some representative patterns that have been fabricated using this procedure with a single PDMS stamp that has parallel lines (2 μm in width and separated by 2 μm) on its surface. The patterns on the surfaces of the masters were generated in 200 nm-thick silver films; the final patterns fabricated using the newly cast stamps were in 50 nm-thick silver films. By rotating the orientation of the lines of the second print, we could easily generate

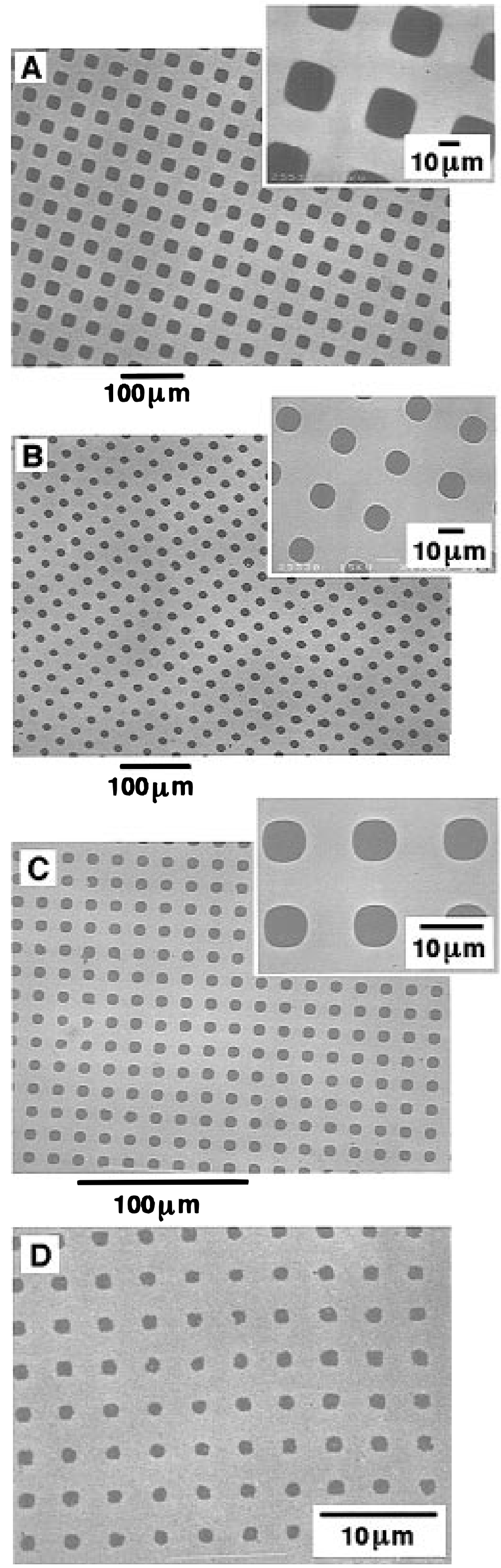

Figure 8. SEMs of silver patterns (50 nm-thick) that were generated by μCP using PDMS stamps cast from assembled microstructures of polyurethane, followed by selective etching. In making the polymeric microstructures, the silver surface was patterned with parallel lines of hexadecanethiol, the stamp was then rotated by 90°, and another printing was made. Polyurethane prepolymer liquid only assembled on those regions of silver that were not covered by hexadecanethiolate SAMs. The bright regions are silver; the dark regions are silicon, where the silver has been dissolved.

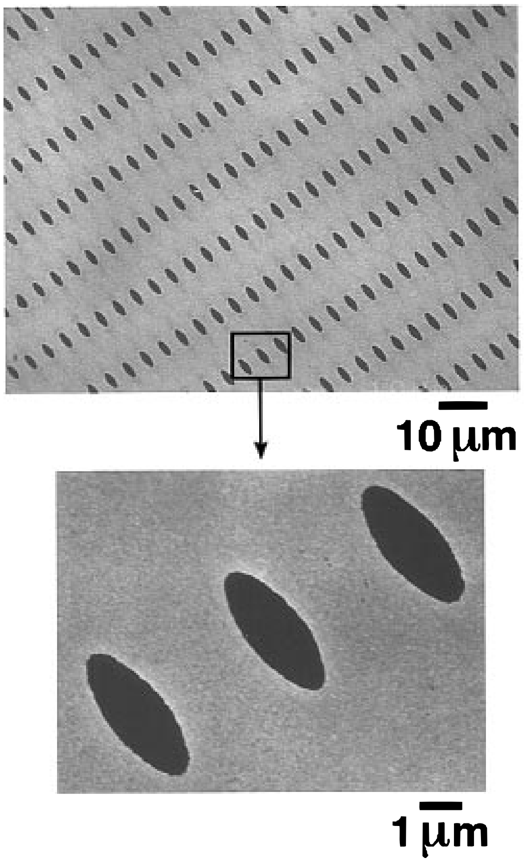

Figure 9. Same as Figure 8, except that the direction of lines was rotated by ~2° in making the second printing and that μCP with the newly fabricated PDMS stamp was carried out under water.

microfeatures with different shapes: for example, squares, rhomboids and parallelograms.

Figure 6 shows two examples of complex patterns that can be generated using this procedure with two PDMS stamps: one with parallel lines on its surface and the other with a star pattern. In order to generate well-controlled, complex patterns using this procedure, we need a high-resolution translational stage to register the position and orientation of the pattern formed in each printing.

PDMS Stamps Cast from Polymeric Microstructures Assembled on Surfaces of Silver (or Gold) Patterned with SAMs. When a liquid prepolymer of polyurethane is placed on a silver (or gold) surface that has been patterned with SAMs of hexadecanethiolate, the prepolymer selectively dewets from the hydrophobic regions (that is, regions covered by SAMs) of the surface. The remaining prepolymer is then cured into a cross-linked, solid polymeric material. This simple procedure has been used to fabricate polymeric resists used in selective chemical etching,[7] arrays of microlenses,[18] and multimode waveguides.[19] Here we demonstrate that such polymeric relief structures formed on Ag or Au can also be used as masters to cast PDMS stamps for use in μCP (Figure 7).

Figures 8−10 are SEM images of silver patterns that were generated using a three-stage procedure. First, a silver surface was patterned with lines of hexadecanethiolate using μCP; the same stamp was then used to print a second set of lines with their orientation rotated by ~90°. Second, a liquid prepolymer of polyurethane was assembled onto the hydrophilic regions (bare Ag or Au) of the surface and cured into a solid polymer. Third, a new

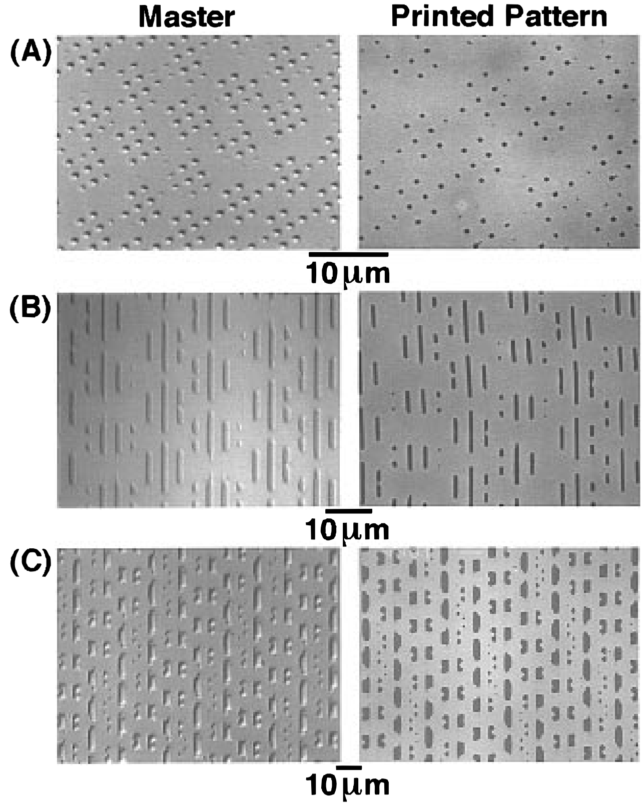

Figure 10. Optical micrographs of polyurethane masters assembled on silver surfaces that had been double-printed using two different PDMS stamps: parallel lines and a star pattern. SEM images of the corresponding silver patterns (50 nm-thick) generated by μCP (under water) using PDMS stamps cast from these polymeric microstructures. The bright regions are silver; the dark regions are silicon, where the silver has been dissolved.

PDMS stamp was made by casting against the assembled relief structures of polyurethane, and this stamp was then used to make patterned SAMs of hexadecanethiolate on a silver surface. Those regions of a patterned silver surface uncovered by SAMs were subsequently removed by etching in an aqueous ferricyanide solution.[4] Figure 8 shows patterns formed using PDMS stamps with parallel lines (different widths and spacings). As the dimension of the bare silver decreases, the height of the assembled PU relief structures decreases, and the shape of the polymeric features also changes from squares to circles as a result of the rounding of the corners caused by the surface tension of the prepolymer liquid. When the dimension is less than 5 μm, the height of the polymeric relief structures becomes so small that it is very difficult to obtain high-contrast patterns of SAMs by printing with the fabricated PDMS stamps (Figure 8D). In Figure 9, the lines between the first and the second printing were rotated by ~45°; thus the assembled polymeric features have an elliptical shape. In Figure 10, the two PDMS stamps have different patterns on their surfaces: one has parallel lines, and the other has a star pattern. Again, in order to form well-controlled, complex patterns using this procedure, precise alignment is required for the second printing step.

PDMS Stamps Cast from Polystyrene Microspheres Assembled on Flat Substrates. Extensive studies have been carried out on the formation and potential applications of two-dimensional arrays of polystyrene microspheres on flat substrates.[24−28] The prepa-

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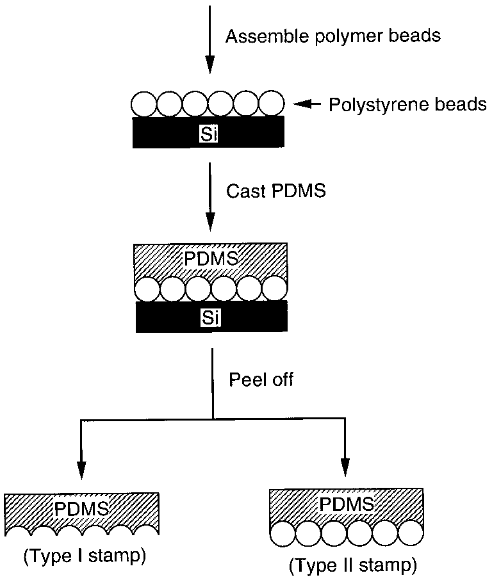

Figure 11. Schematic procedure for casting PDMS stamps from microspheres of polystyrene assembled on a flat surface.

ration of these arrays usually involves deposition of a thin layer of a suspension of monodispersed microspheres on a flat surface, followed by evaporation of the solvent. These microspheres usually form a hexagonal dense packing, as driven by a laminar flow and attractive capillary forces.[27,28] The arrays of closely packed microspheres have been used as masks for metal evaporation to generate hexagonal arrays of nanofeatures.[26] Here we use these assembled microspheres as relief structures to cast PDMS stamps for use in μCP.

Figure 11 outlines the procedure schematically. Two types of stamps were obtained. In the first, the relief structures on the surface of the stamp were made from PDMS. In the second, the relief structures were made from the polystyrene beads. Silver patterns generated using these two types of stamps are complementary to each other (Figure 12). Because the polystyrene is not a good elastomer, there is no conformal contact between the substrate and the second type of stamp. As a result, the quality of the SAMs printed using this kind of stamp is not as good as that printed using an elastomeric stamp (Figure 12B). Polystyrene beads with diameters as small as ~200 nm were suitable for this process. This procedure is only suitable for generating regular patterns having areas of ~500 μm^2, since these microspheres usually form domain structures on large flat substrates.[24]

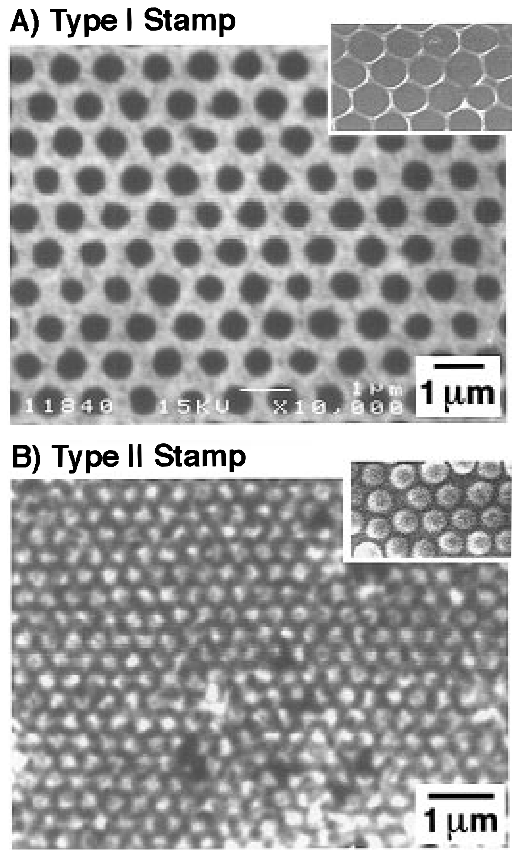

Figure 12. SEM images of gold patterns generated by μCP with the PDMS stamps (the insets) cast from assembled polystyrene microspheres, followed by selective etching. The bright regions are gold; the dark regions are silicon, where the gold has been dissolved.

Conclusions

This paper demonstrates several non-photolithographic methods to fabricate PDMS stamps with feature sizes ranging from ~100 nm to ~100 μm for use in μCP. Microcontact printing is an extremely convenient technique for generating patterned SAMs on a variety of substrates. Its utility has been limited mainly by the availability of PDMS stamps that have various patterns and features on their surfaces. We believe that the methods described here will be useful in providing PDMS stamps with certain types of moderately complex patterns, especially for those who want to use μCP but have no access to the clean room and photolithographic facilities.

Acknowledgment. This work was supported in part by ONR and ARPA. This work made use of MRSEC Shared Facilities supported by the National Science Foundation (Grant DMR-9400396). We would like to thank Mr. Yuan Lu and Mr. Stephen Shepard for their assistance in using SEM and photolithographic instruments. J.T. is grateful to the NSF for a predoctoral fellowship.

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