Micromolding of Polymers in Capillaries: Applications in Microfabrication

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This paper describes the use of micromolding in capillaries (MIMIC) to produce complex polymeric microstructures supported on different substrates and the applications of these microstructures in microfabrication. Patterned microstructures of several organic polymers—polyurethane, polyacrylate, and epoxy—were formed by molding in enclosed, continuous channels formed by conformal contact between a solid support and an elastomeric mold whose surface had been patterned with a relief structure having micrometer-scale dimensions. A liquid prepolymer filled these channels by capillary action and was allowed to cure photochemically or thermally. The mold was then removed. Polymeric microstructures formed on films of Saran Wrap could be folded into different shapes, while these microstructures retained their forms; they could also be stretched uniaxially to generate microstructures having distorted forms. The patterned polymeric microstructures formed on SiO_2, glass, and metals (Au, Ag, and Cr) could be used directly as resists in the selective etching of underlying substrates. Free-standing polymeric microstructures fabricated by lift-off were used as disposable masks to generate patterned microfeatures of metals on the surfaces of both planar and nonplanar substrates in two different procedures: (a) evaporation of gold through the polymeric mask supported on a substrate; (b) formation of patterned self-assembled monolayers (SAMs) by exposure of a silver film covered by a polymeric mask to hexadecanethiol (HDT) in vapor, followed by selective etching of the regions that were not exposed to HDT (that is, the parts of the surface protected by the mask) in an aqueous solution containing $K_2S_2O_3$ and $K_3Fe(CN)_6/K_4Fe(CN)_6$.

Introduction

Micromolding in capillaries (MIMIC) is a convenient technique for generating patterned microstructures of organic polymers on the surfaces of solid substrates.[1] In this technique, an elastomeric block (typically made from poly(dimethylsiloxane), PDMS) having a patterned relief structure in its surface is prepared by casting the elastomer against a master using procedures developed for use in microcontact printing (μCP);[2,3] the master can be prepared by photolithography or by a range of other techniques.[4,5] The PDMS mold that is placed on the surface of a substrate makes conformal contact with that surface; as a result, a network of channels is formed between the mold and the substrate. The substrates can be either planar or curved. When a low-viscosity liquid prepolymer is placed at the open ends of the network of channels, the liquid spontaneously fills in the channels by capillary action. After filling the channels and curing the prepolymer into a solid, cross-linked polymer, the PDMS mold is removed, and a network of polymeric material remains on the surface of the substrate. A variety of liquid prepolymers[6] (both thermally and ultraviolet curable) such as polyurethane (PU), polyacrylate, and epoxy can be used in this process. These polymeric microstructures can be released by dissolving the underlying substrates to form free-standing polymeric membranes (with an area of up to several cm^2). MIMIC has also been used to form patterned microstructures of inorganic materials, metals, and polymeric microbeads.[7]

Photolithography,[8] micromolding, and related techniques[9–13] are currently used to form patterned microstructures of polymeric materials. Microfabrication based on MIMIC is remarkable for its simplicity, for its economy, for the effectiveness with which the channels fill by capillary action, and for its fidelity in transferring the patterns from the mold to the polymeric structures that it forms. MIMIC is applicable to patterning a broader range of organic polymers—especially structural and functional polymers[14–16]—than is photolithography,

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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in which only certain specialized polymers are used as photoresists.[8]

In this paper, we report representative applications of MIMIC in microfabrication. These applications include (a) the formation of patterned polymeric microstructures on the surfaces of various solid substrates, (b) the use of these polymeric microstructures as resists to protect the underlying substrates from chemical etchants (for example, to prevent etching of SiO_2 or glass by aqueous HF/NH_4F solutions), (c) the use of MIMIC and selective etching to fabricate chrome masks for use in photolithography, and (d) the use of free-standing polymeric microstructures formed using MIMIC and lift-off as disposable masks in the deposition of patterned metals, and in the formation of patterned self-assembled monolayers (SAMs)[17] on both planar and nonplanar substrates. Most of these applications have not been optimized: they are intended to demonstrate principles that might underlie detailed development work.

Experimental Section

Materials. Poly(dimethylsiloxane) (Sylgard 184) was obtained from Dow Corning. Ultraviolet-curable polyurethanes (J-91 and NOA 60, 71, 72, 73, 88) were obtained from Summers Optical (Fort Washington, PA) and Norland Products (New Brunswick, NJ), respectively. Ultraviolet-curable polyacrylate (SK-9) was obtained from Edmund Scientific Co. Thermally curable epoxies (F113 and F114) were obtained from TRA-CON (Medford, MA). Au (99.999%), Ag (99.9999%), and Ti (99.99%) were obtained from Aldrich. Hexadecanethiol (HDT) was obtained from Aldrich and was purified under nitrogen by chromatography through silica gel.

Substrates. Si(100) wafers (Cz, phosphorous-doped, test grade, SEMI Std. flats, covered by native or thermal oxide) were obtained from Silicon Sense (Nashua, NH). Silver films (50 nm thick) were prepared by e-beam evaporation onto Si wafers (primed with a 2.5 nm thick layer of Ti). Silicon substrates having V-shaped grooves in their surfaces were prepared using published procedures.[18,19] Films of Saran Wrap (Stretch-tite) were obtained from Polyvinyl Films (Sutton, MA). Quartz plates covered by chrome were obtained from Hoya Inc. (Tokyo, Japan).

Micromolding in Capillaries (MIMIC). Elastomeric molds were fabricated from PDMS (Sylgard 184, A:B = 1:20) using the procedures described for μCP.[3] The thickness of the PDMS blocks used in MIMIC was usually ~2 mm. The PDMS mold was cut (using a razor blade) in such a way that it formed a network of channels having open ends when it was placed on the surface of a support (Figure 1). When a low-viscosity liquid prepolymer was placed at the open ends of the channels, the liquid spontaneously filled the channels by capillary action. The initial rate at which a liquid prepolymer of PU (NOA 73, $\eta \approx 150$ cP) filled a channel with cross-sectional dimensions of ~3.0 × 1.5 μm, over a Si/SiO_2 surface, was ~0.9 mm/min. Ultraviolet-curable polymers were cured with an ultraviolet light (Canrad-Hanovia 450 W medium pressure, mercury vapor lamp, type 7825-34) for ~20 min, with the lamp positioned at a distance of ~3 cm from the sample. Thermally curable epoxies were cured in an oven heated at ~60 °C for ~6 h. All the polymeric microstructures in this paper were made of PU (NOA 73) unless mentioned in the text.

Evaporation of Metals and Formation of SAMs through Polymeric Masks Supported on Solid Substrates. Free-standing polymeric microstructures that were used as disposable masks for the deposition of patterned gold and for the formation of patterned SAMs were prepared using a two-stage procedure: (i) a continuous polymeric microstructure having micrometer-scale features in it was formed using MIMIC on a Si wafer covered with 0.2 μm-thick thermal oxide; (ii) the polymeric microstructure was freed from the support by dissolving the sacrificial layer of SiO_2 in an aqueous HF/NH_4F solution (250 mL of H_2O, 165.5 g of NH_4F, and 40 mL of 48% HF) for ~20 min.

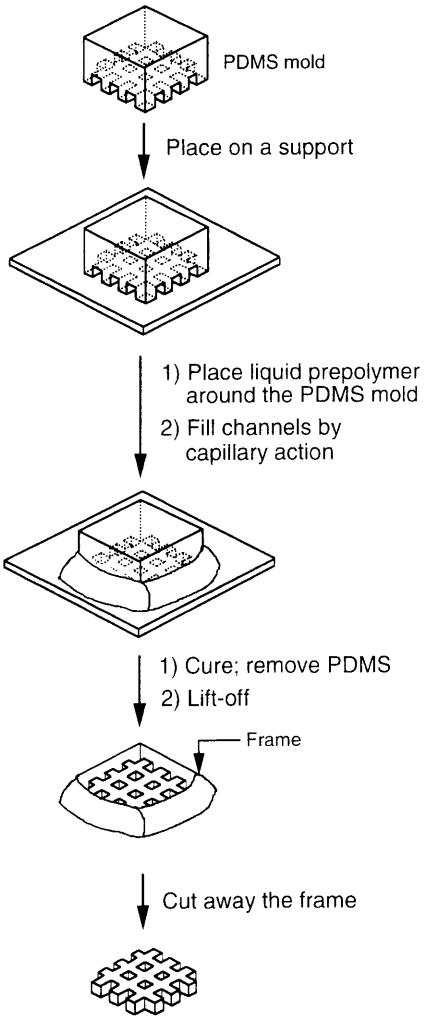

Figure 1. Schematic illustration of MIMIC. After filling the network of channels with a liquid prepolymer, the prepolymer was cured either thermally or photochemically. The PDMS mold was then peeled away carefully. The patterned polymeric microstructure remained on the support and could be released from the surface of the support by dissolving the support.

In the present procedure, a liquid prepolymer was placed around the PDMS mold. The liquid filled the channels from all sides. After curing, the excess polymer that remained outside the PDMS mold formed a "frame"—that is, a relatively thick, strong polymeric structure around the thinner, more fragile, patterned microstrcuture (Figure 1); leaving this frame attached made it easier to handle this free-standing polymeric microstructure: it could be placed on the surface of a planar substrate using tweezers and used subsequently as the mask in the deposition of patterned gold. The frame could also be cut away using a razor blade. This free-standing polymeric microstructure without a frame was allowed to float on the surface of water and then picked up by a nonplanar substrate (for example, a glass capillary or a contoured silicon surface) from underneath.

Instrumentation. Gold was evaporated through polymeric masks supported on solid substrates using argon plasma sputtering (Hummer II, Technics Inc.). SEM was done on a JEOL JSM-6400 scanning electron microscope. An accelerating voltage of 3 kV was used for glass substrates and 15 kV for silicon wafers. Polymeric microstructures were sputtered with gold (~100 nm thick) before imaging by scanning electron microscope.

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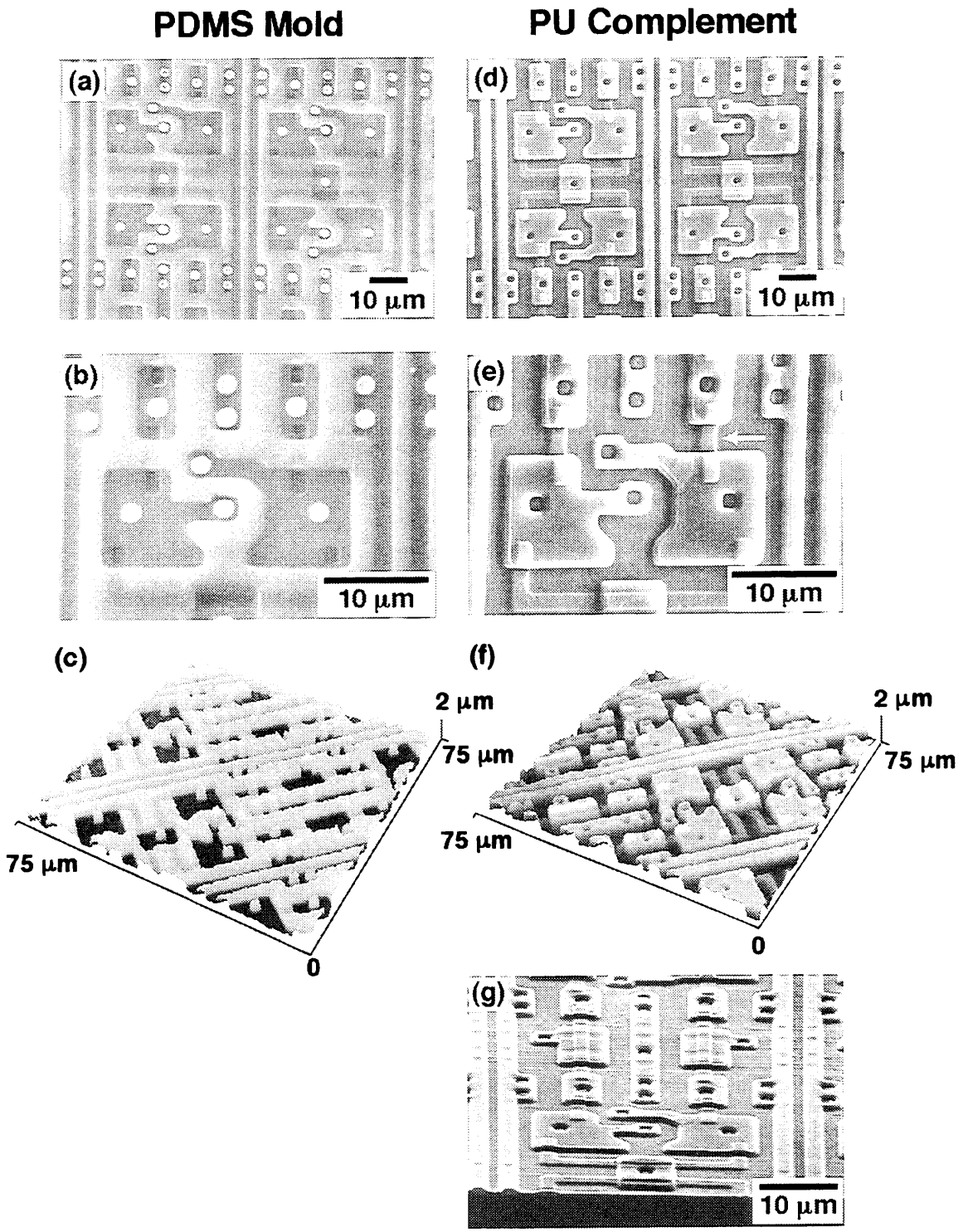

Figure 2. Comparison of a PDMS mold with a topologically complex surface and the complementary PU structure made against it using MIMIC. (a, b) SEM images of the PDMS mold at two different magnifications. (c) AFM image of the PDMS mold. (d, e) SEM images of the corresponding PU microstructures formed on a Si/SiO_2 surface. The patterned PU layer has features with different thicknesses; the thinnest parts of the layer (indicated by the arrow in (e)) are less than 100-nm thick. (f) AFM image of the PU complement. (g) Fracture view by scanning electron microscopy (at 60°) of the PU layer.

Results and Discussion

Micromolding in Capillaries (MIMIC). Figure 1 shows the procedure used in MIMIC schematically.[1] The choice of PDMS as the material to fabricate the mold is important for the success of this process;[20] it faithfully replicates the features of the master structure (photolithographically formed pattern,[3] diffraction grating,[21] micromachined silicon[4] or wax[5] structure, etc.); the elastomeric character of PDMS enables it to make a conformal contact with the substrate; the relatively low interfacial free energy of the surface of PDMS ($\gamma_{PDMS/air}$ = 21.6 dyn/cm)[20] gives adequate adhesion between the mold and the substrate but allows it to be separated from both the support and the polymeric microstructures formed by MIMIC. The surface of cured PDMS

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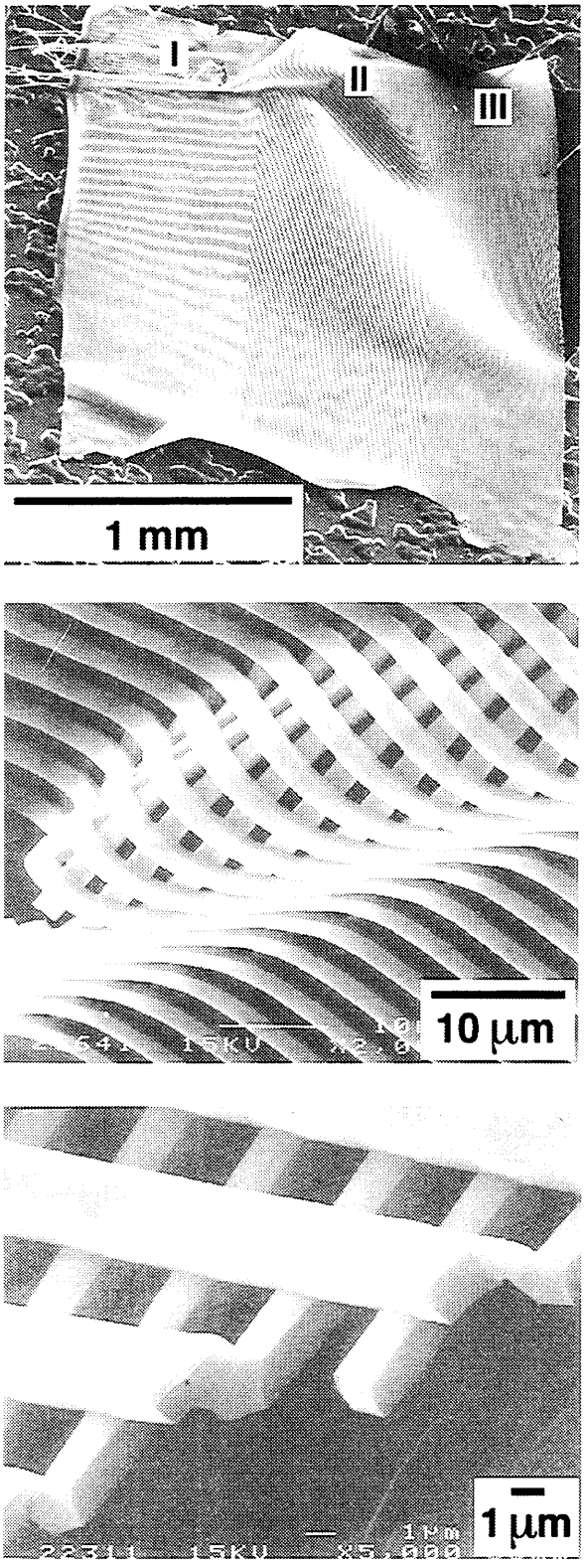

Figure 3. SEM images (at three different magnifications) of a free-standing polymeric (PU, J-91) microstructure that was formed between two PDMS molds. Each mold has a relief pattern of parallel lines in its own surface. The free-standing microstructure was placed on a piece of Scotch tape (there was a hole in the tape, just under the polymeric microstructure, to demonstrate that the microstructure had the structural stability to stand without support) using tweezers. The sizes of features in regions I, II, and III are different, as a result, the electron interference patterns (Moiré effect) from these three regions are different. The two blowups were taken from region I.

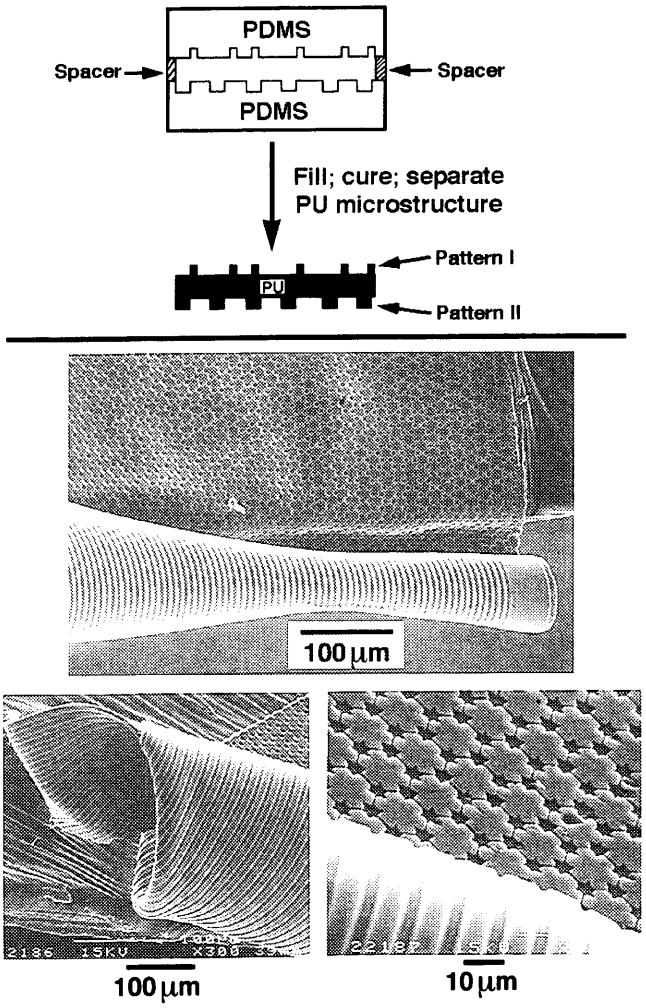

Figure 4. SEM images of a free-standing microstructure of PU that was formed between two PDMS molds that had different relief patterns in their surfaces and were separated by a certain distance using a spacer (Scotch tape) when carrying out MIMIC. After filling the channels and curing the PU prepolymer into a cross-linked polymer, the two PDMS mold were separated; the PU microstructures remained in one of the molds and could be released using tweezers.

has very low reactivity toward the organic prepolymers under the curing conditions used here—another requirement for the separation of the mold from the formed polymeric microstructures. The liquid prepolymer used in this process should be curable either thermally or photochemically; it should have low viscosity (<400 cP); it should wet the support at least partially;[1,22-24] and it should not contain compounds (such as certain organic solvents) that swell the PDMS mold.[20] The liquid prepolymer can fill the channels from all sides of the PDMS mold; the air trapped in the center seems to escape by diffusing through the PDMS mold and/or the liquid prepolymer.

Figure 2 compares a PDMS mold (with a topologically complex surface) and the complementary PU microstructure made from it using MIMIC. The PDMS mold was made by casting against a microelectronic circuit and shows the topology of that circuit. The PU microstructure is an accurate negative replica of the relief structure in the surface of the PDMS mold. MIMIC allows quasi-three-dimensional processing (that is, pat-

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(24) Meyer, D. *Surfaces, Interfaces, and Colloids*; VCH Publishers: New York, 1991; pp 87–109.

terning layers with different thicknesses) in a single step. Complex arrays of micrometer- and submicrometer-scale channels filled completely: in some regions of these structures, features are connected to one another by channels with thicknesses less than 100 nm.

The support used in MIMIC could have relief patterns in its own surface. Figure 3 shows SEM images (at three different magnifications) of a free-standing polymeric microstructure that was formed between two PDMS molds. Each PDMS mold has a relief pattern of parallel lines in its own surface. After filling with liquid prepolymer and curing it into a solid polymer, the two PDMS molds were separated. The cross-linked polymeric microstructure remained on the surface of one of the two PDMS molds and could be easily removed from the mold using tweezers. The two layers of the polymeric lines formed *one* interconnected polymeric microstructure. This type of free-standing microstructure—two layers with an independent relief structure in each—cannot be fabricated by photolithography in a single step. In carrying out MIMIC, the surfaces of the two PDMS molds could also be separated by a certain distance using a spacer (for example, Scotch tape). In this case, a free-standing polymeric film with a different patterned relief structure on each side of the film was formed (Figure 4).

We have used MIMIC to form patterned polymeric structures on a variety of substrates, including Si/SiO_2, glass, gold, silver (both bare and covered by SAMs[17]), and films of organic polymers such as Saran Wrap and the transparencies used for overhead projection. Figure 5 shows SEM images of PU microstructures that were formed on films of Saran Wrap using MIMIC; these films folded subsequently into different shapes. The polymeric microstructures roughly retained their forms during these deformations, since cross-linked polyurethane is itself modestly flexible. Figure 6 shows SEM images of PU microstructures that were formed on films of Saran Wrap using MIMIC, and were subsequently stretched uniaxially to different values of strain. As the underlying film of Saran Wrap was elongated, the PU structure deformed accordingly. The PU structures broke and became unrecognizable at an elongation of ~500%.

Polymeric Microstructures as Resists in Selective Etching. One of the applications of MIMIC is to form patterned polymeric microstructures that can subsequently be used as resists in the selective etching of underlying substrates. Figure 7 shows a series of SEM images that illustrate the procedure used in this application. Figure 7a shows the SEM image of a test structure (parallel lines) of PU that was formed on Si/SiO_2. Figure 7b shows a SEM image of this same sample, after it had been etched in an aqueous HF/NH_4F solution for ~2 min; bare regions of SiO_2 dissolved in the aqueous HF/NH_4F solution.[25] The resultant pattern of SiO_2 was then used as the secondary resist in the anisotropic etching of Si in a hot aqueous KOH/2-propanol solution.[18,25] Figure 7c shows a SEM image of the sample of Figure 7b that was subsequently etched in an aqueous KOH/2-propanol solution (400 mL of H_2O, 92 g of KOH, and 132 mL of 2-propanol) at 65 °C for ~15 min.[25] The cross-linked PU dissolved or lifted off in the KOH/2-propanol solution at elevated temperatures and could, therefore, not be used directly as the resist in the etching of Si.

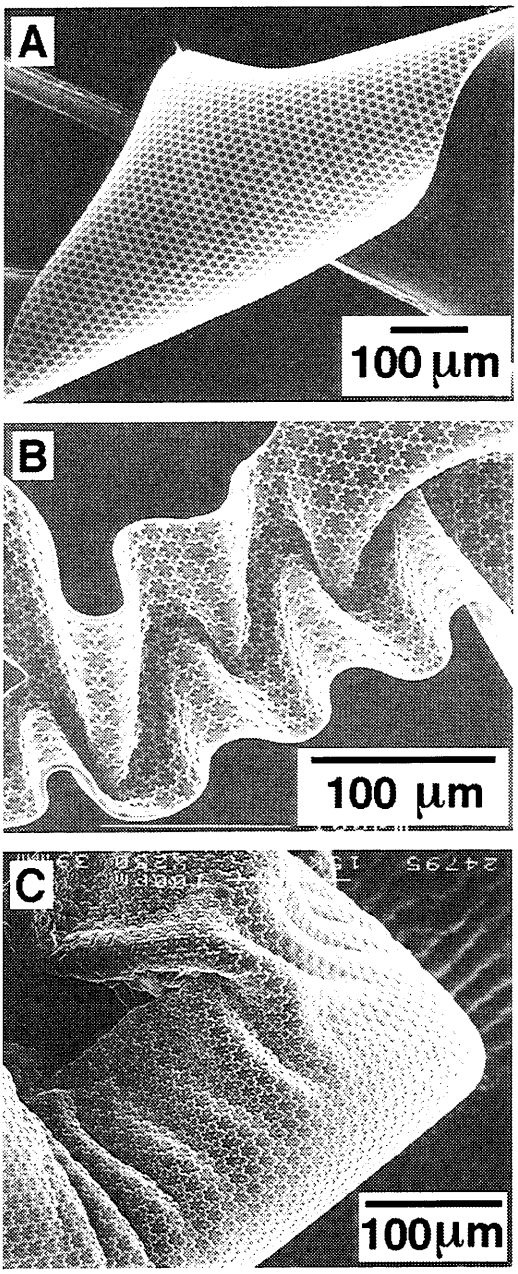

Figure 5. SEM images of patterned PU microstructures that were formed using MIMIC on films of Saran Wrap. These patterned films folded into different shapes; the PU microstructures adhere well and roughly retained their forms. The strips (A, B) were produced accidentally on certain regions of the samples when folding the films mechanically.

Patterned films of organic polymers (usually patterned using photolithography or e-beam writing) are, of course, ubiquitous as etch resists. The ability to form patterned films of organic polymers other than photoresists and to use MIMIC to form polymeric microstructures in a nonphotolithographic procedure provides a new approach to the formation of these resist structures.

Using MIMIC and Selective Etching to Fabricate Chrome Masks to be Used in Photolithography. Patterned polymeric microstructures formed using MIMIC can also be used as resists in selective chemical etching of metals such as Au, Ag, and Cr. This ability provides a new route for generating chrome masks (that is, masks made of thin films of metallic chromium supported on quartz plates) to be used in

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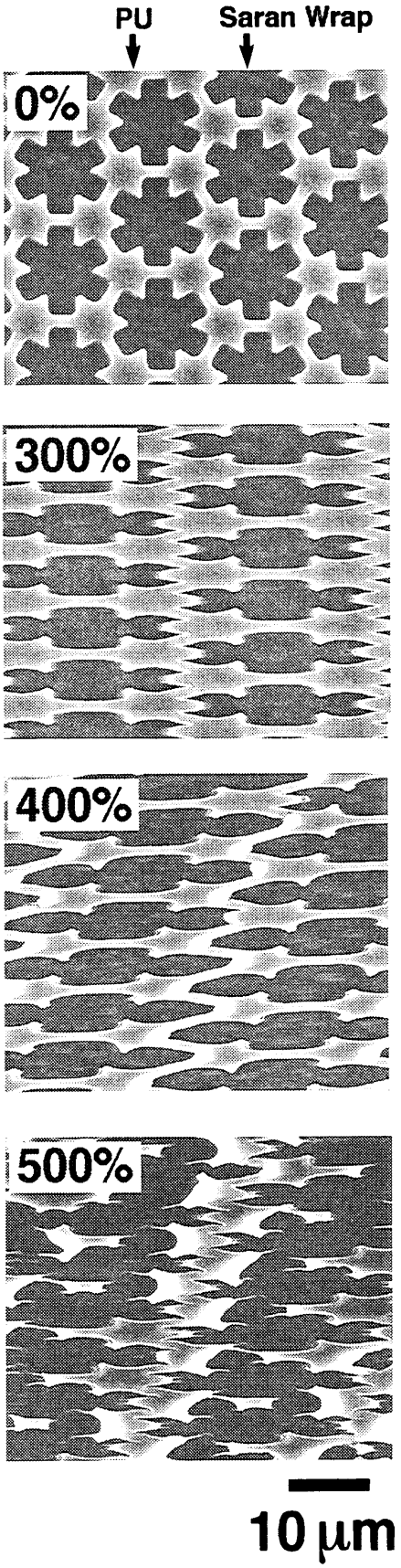

Figure 6. SEM images of a test structure of PU that was formed on films of Saran Wrap using MIMIC and then stretched along the horizontal direction. The stretched forms were fixed using Scotch tapes. As the underlying film of Saran wrap was elongated, the PU structure deformed accordingly. The PU structures broke and became unrecognizable at an elongation of ~500%.

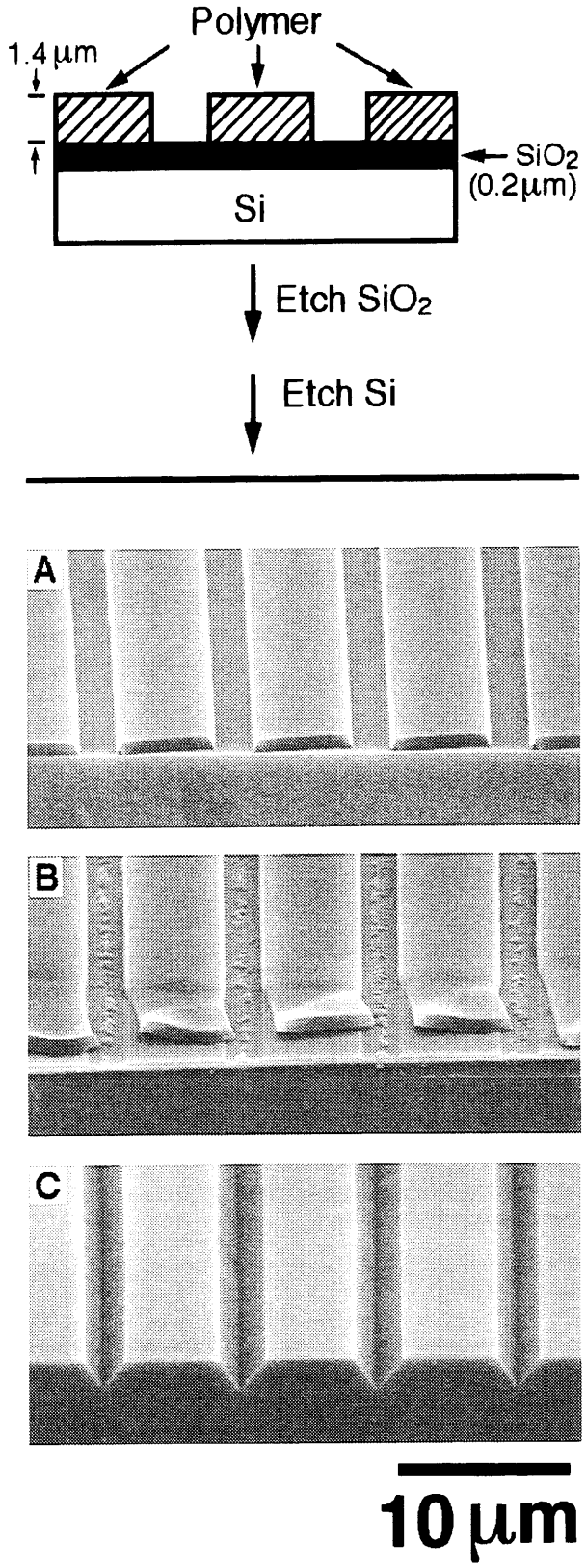

Figure 7. (A) SEM image of a test pattern of PU formed using MIMIC on a silicon wafer covered by thermally-formed SiO_2 (0.2 μm thick). (B) SEM image of this sample after etching in an aqueous HF/NH_4F solution for ~2 min. The ends of the polymer strips deadhered on fracturing the silicon substrate. (C) Same sample as (B) after further etching in an aqueous KOH/2-propanol solution for ~15 min at 65 °C. The PU structures dissolved or lifted off in the KOH/2-propanol solution at this temperature.

photolithography. Figure 8A outlines the procedure schematically. Patterned microstructures of PU were formed on chrome substrates using MIMIC; these polymeric microstructures were subsequently used as resists in the etching of chrome in an aqueous solution

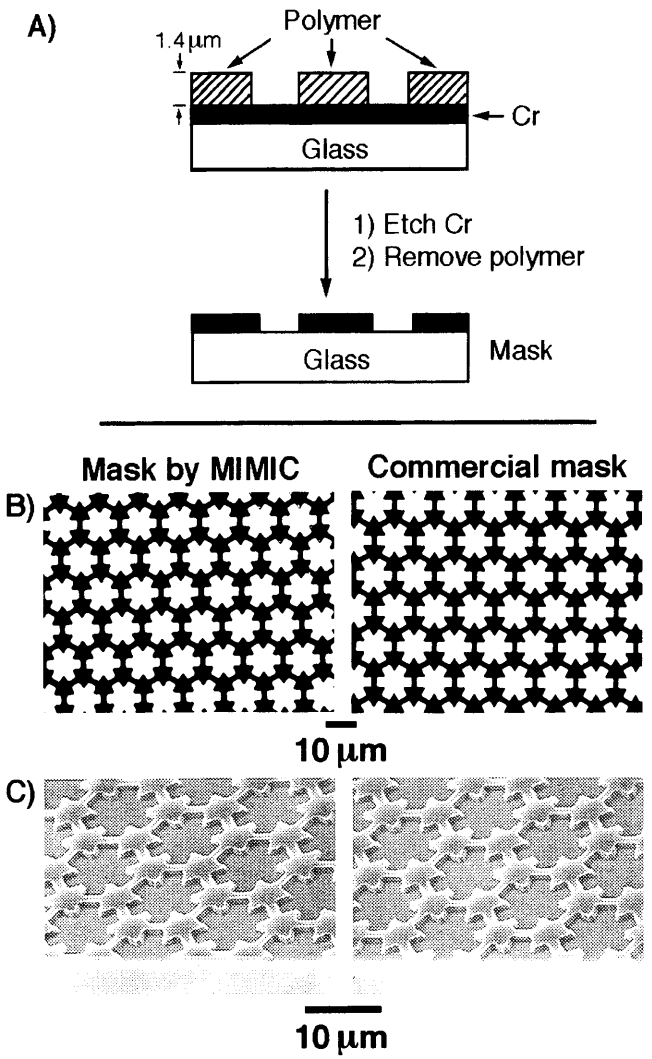

Figure 8. (A) Schematic procedure that was used to fabricate chrome-masks using MIMIC. (B) Optical micrographs of the chrome-masks that were produced using MIMIC and the conventional method, respectively. (C) SEM images of a test pattern that was generated in positive-tone photoresist films (Microposit 1813, Shipley) by photolithography using the newly fabricated mask (made using MIMIC) and the commercial chrome mask, respectively.

containing HNO_3 and $NH_4NO_3{\cdot}Ce(NO_3)_3$ (400 mL of H_2O, 24 mL of 63% HNO_3, 62 g of $NH_4NO_3{\cdot}Ce(NO_3)_3$; the etching time was ~1 min).[26] Figure 8B compares the optical micrographs (in transmission mode) of the chrome masks prepared using MIMIC and the conventional procedure[27] (obtained commercially), respectively. Figure 8C shows SEM images of the resulting microstructures in photoresists (Microposit 1813, Shipley, MA) fabricated by photolithography using the above two chrome masks, respectively. The chrome-mask fabricated using MIMIC has edge resolution as good as the commercial one.

Free-Standing Polymeric Structures as Disposable Masks in Patterning the Surfaces of Planar and Nonplanar Substrates. Free-standing polymeric microstructures can be easily fabricated using a two-stage procedure (Figure 1): (i) form patterned polymeric microstructure on a solid support (after curing, the excess polymer remained outside the PDMS mold

(26) *Thin Film Processes*; Vossen, J. L., Kern, W., Eds.; Academic Press: New York, 1978.
(27) Larrabee, G. B. *CHEMTECH* **1985**, *March*, 168.

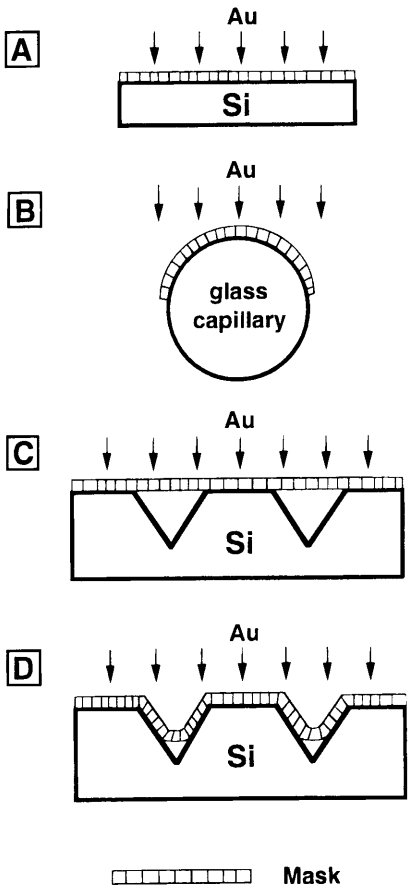

Figure 9. Schematic illustration of evaporation of gold through a patterned polymeric mask onto a planar (A), curved (B), or contoured surface (C, D). The masks used in this procedure were thin (~1.5 μm) free-standing microstructures of PU fabricated using MIMIC and lift-off.

formed a frame around the patterned polymeric microstructure, Figure 1); (ii) release the patterned polymeric microstructure by dissolving the support—for example, dissolving glass or SiO_2 films in aqueous HF/NH_4F solutions, single crystals of NaCl and KCl in water, and photoresist films in the developing solutions. Free-standing polymeric microstructures having micrometer-scale features in them and with macroscopic dimensions up to several cm^2 have been prepared. The free-standing polymeric microstructures could be transferred to the surfaces of other substrates using two different procedures: (a) polymeric microstructures with frames could be placed on the surfaces of solid substrates using tweezers (Figure 9A,C); (b) polymeric microstructures without frames (the frame could be removed using a razor blade) were allowed to float on the surface of water, and were subsequently picked up by other solid substrates from underneath (Figure 9B,D).

Figure 10a shows a SEM image of the free-standing polymeric microstructures that were subsequently transferred onto various solid substrates and then used as the disposable masks in the deposition of patterned metals and in the formation of patterned SAMs. Figure 10b shows SEM images of a planar Si surface that was covered with a free-standing polymeric mask and that had been patterned with gold using evaporation through the mask. Some portions of the mask still remained on the surface. Figure 10c shows a SEM image of patterned silver features that were formed on Si/SiO_2 using a three-stage procedure: (i) a piece of free-standing polymeric mask was placed on a Ag film (50

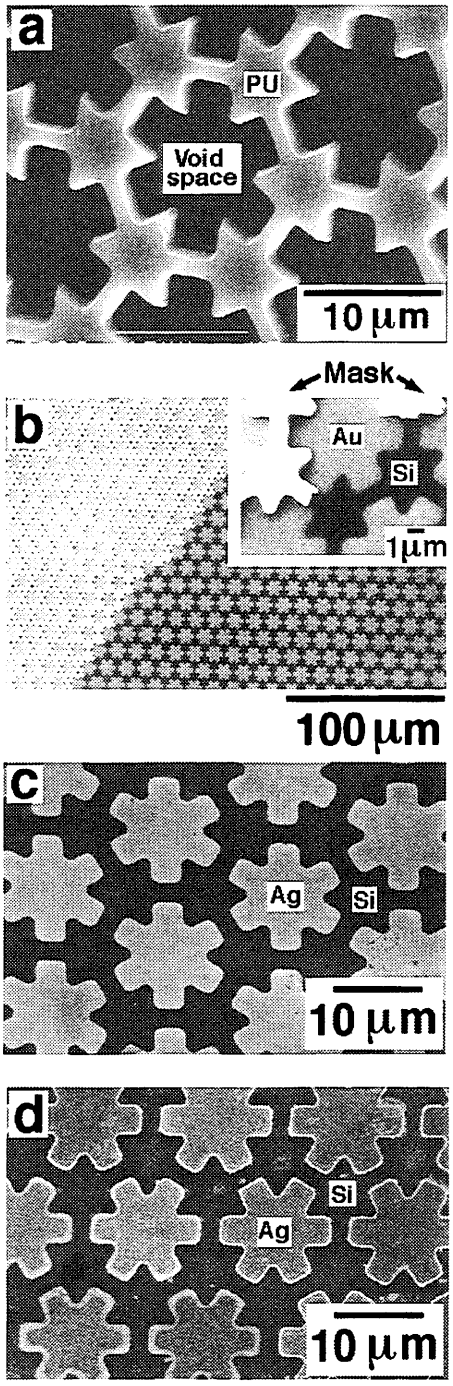

Figure 10. (a) SEM image of a free-standing PU microstructure that was used subsequently as the disposable mask for pattering different substrates using evaporation of metals or formation of SAMs. (b) SEM of a planar Si/SiO_2 surface that had been patterned with gold by evaporation through the mask. In this picture, half of the mask still remained on the surface. The inset is a blowup to show the edge resolution of this pattern. (c, d) SEMs of patterned features of silver (bright regions) that were generated on a Si/SiO_2 surface by selective etching using patterned SAMs of hexadecanethiolate as resists that were formed using free-standing PU films as the masks (see text for detail).

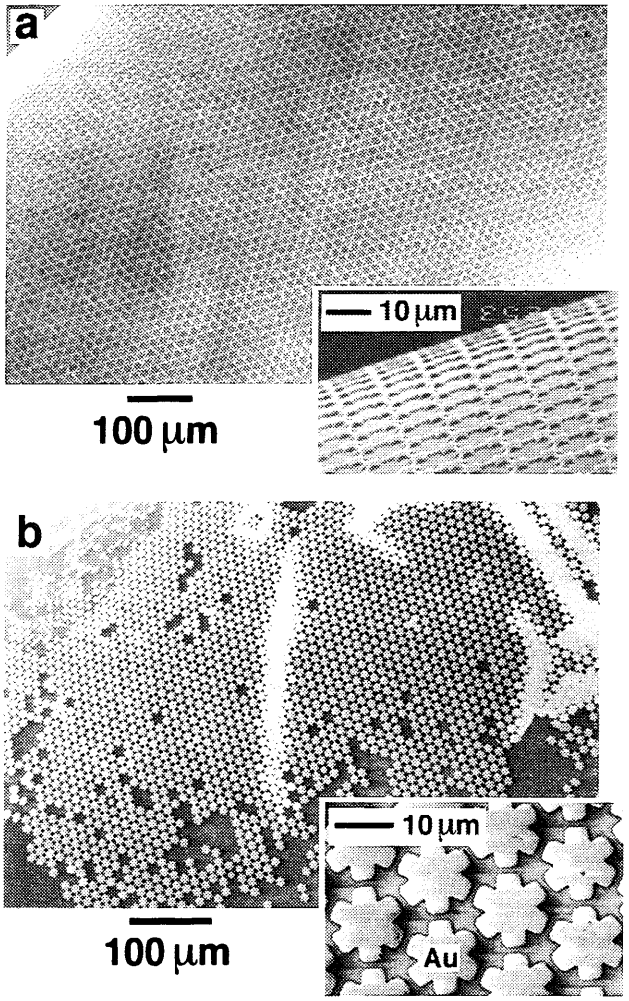

Figure 11. (a) SEM images of a glass capillary (the radius of curvature is ~400 μm) that was covered by the polymeric mask and was exposed to gold by evaporation for ~5 min. The image is of the mask resting on the capillary, with both mask and glass covered with gold. (b) SEM images of the glass capillary of (a) after removing the polymeric mask by dipping the capillary in an aqueous KOH/2-propanol solution at 65 °C for ~2 min. Gold patterns (~100 nm thick) were formed on the glass capillary. The inset is the blowup of the corresponding SEM image.

nm thick) evaporated on Si/SiO_2; (ii) regions of the Ag surface not covered by the polymeric mask were derivatized with SAMs of hexadecanethiolate by exposing the sample to the vapor of HDT in a closed container at room temperature for ~30 min; (iii) the polymeric mask was then removed, and the sample was etched in an aqueous solution containing $K_2S_2O_3$ and $K_3Fe(CN)_6/K_4Fe(CN)_6$ (0.5 M/0.01 M/0.001 M) for ~20 s;[19] this procedure dissolved those regions of the silver film that were not covered with the SAM. Figure 10d shows a SEM image of patterned silver features that were produced on Si/SiO_2 using a procedure similar to that of Figure 10c, except that the HDT was transferred to the unmasked regions of the silver surface using a flat PDMS stamp "inked" with a solution of HDT in ethanol.[2,3] When an "inked" flat PDMS stamp was placed (in this case, for ~1 min) in contact with a polymeric mask that was in turn resting on the surface of an evaporated silver film, SAMs formed on those regions not covered by the mask by processes that probably include reactive spreading and the diffusion of HDT to the silver surface through the vapor phase.[28] Since the SAM formed by reactive spreading is more ordered than that formed by exposure to HDT vapor for the short period of time used here (<5 min), the edge of the silver pattern has a lower density of defects than the center part of the pattern (Figure 10d).

Figure 11a shows a SEM image of a glass capillary (the radius of curvature is ~400 μm) whose surface was

(28) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274.

covered with a free-standing polymeric mask and then sputtered with gold. In this procedure, a patterned free-standing PU film (without a frame) was transferred to the surface of the capillary by floating the film on the surface of water and then picking up the film carefully with the capillary from underneath. The free-standing polymeric microstructure was thin enough (~1.5 μm thick) to bend and to make conformal contact with the surface of the capillary (see the inset of Figure 11a). Gold was sputtered onto this system for ~5 min (the thickness of evaporated Au was ~100 nm). After evaporation of gold, the mask was dissolved by dipping in an aqueous KOH/2-propanol solution for ~2 min (Figure 11b). The defects seen in the pattern were probably caused by the removal of gold from the capillary surface during the stripping of the polymeric mask, since no adhesion promoter (for example, Cr or Ti)[29] was used in this demonstration. This procedure provides a new approach to forming patterns having micrometer-scale dimensions on curved surfaces.[30] Patterning curved surfaces is difficult by current photolithographic techniques.

Using a free-standing polymeric microstructure as the mask, it was also possible to form patterned features of metals on a contoured surface. Figure 12a shows a SEM image of a contoured silicon surface that was masked by a free-standing polymeric microstructure (see Figure 9C; the mask had a frame and was placed on the surface using tweezers) and was patterned by evaporation of gold through the mask for ~6 min. A small portion of the polymeric mask was removed (most of the mask remained on the surface) by blowing a stream of N_2 over the sample for ~2 min. The polymeric mask made conformal contact with the surfaces of the plateaus but remained suspended over the trenches. Evaporation of gold through this structure produced patterned features of gold only on the surfaces of the plateaus; the surfaces of the trenches were completely covered with gold as a result of the random diffusion of gold and the spread in the beam.[31] When a free-standing polymeric mask (without a frame) was placed onto the contoured surface using a different method—floating on the surface of water and picking up using the substrate from underneath—the polymeric mask folded into the trenches and made partial conformal contact with the surfaces of the trenches while retaining conformal contact with the surfaces of the plateaus (see Figure 9D). Under these conditions, patterned features of gold were formed on the surfaces of both plateaus and trenches (Figure 12b).[32]

These results illustrate the use of these free-standing polymeric microstructures as masks to fabricate patterned microfeatures on both planar and nonplanar surfaces. They represent only initial, proof-of-concept experiments and substantial development will be needed to define the full utility of this method of forming microstructures. It is, however, immediately clear that for certain applications—for example, limited areas of complex structures on nonplanar surfaces (see Figure 11 and the in-trench patterns of Figure 12b), it would be much easier to use this type of procedure than any other method currently available.

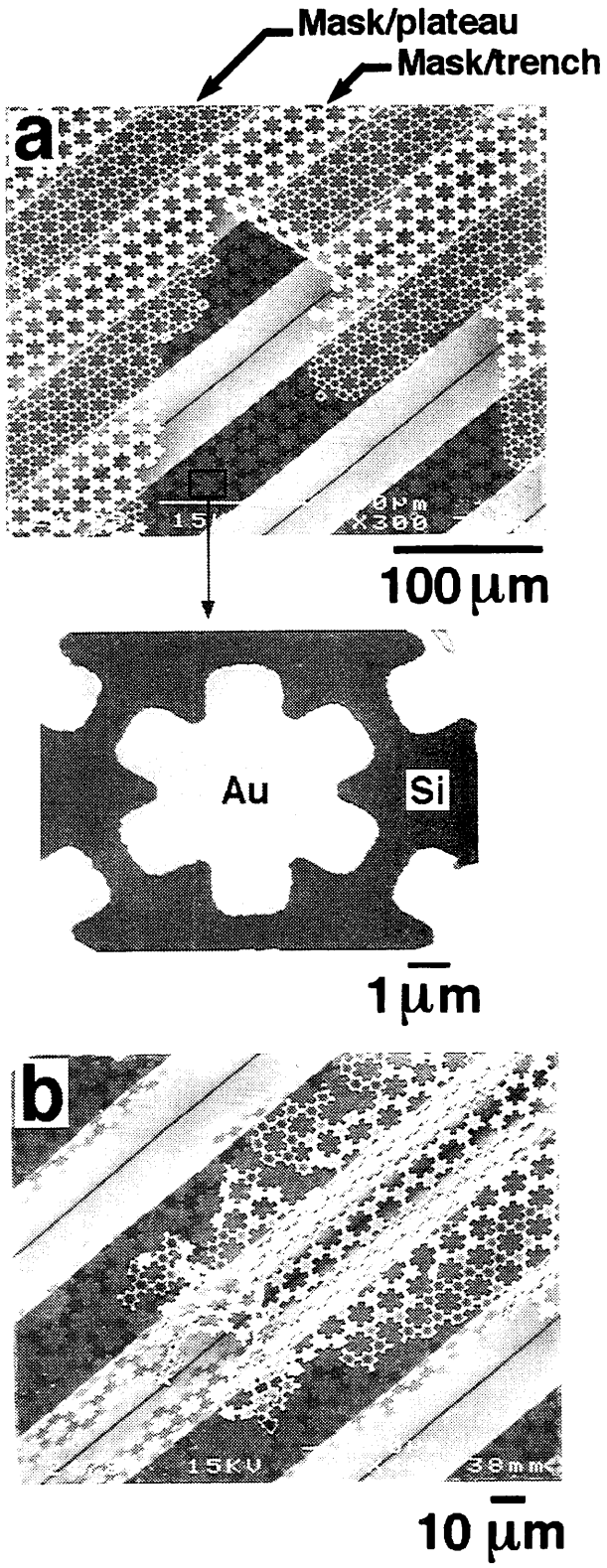

Figure 12. SEM images of contoured surfaces anisotropically etched in Si that were patterned with microfeatures of gold (~120 nm thick) by evaporation using free-standing polymeric structures as the masks. (a) Mask with a fame was placed on the surface using tweezers; (b) mask without a frame was placed on the surface by floating the mask on water and picking up by the substrate from underneath.

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(30) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *269*, 664.

(31) The mean-free-path (λ) of gold atoms is ~0.3 μm under the conditions used for gold evaporation. The mean free path of gold was estimated using the expression: $\lambda = (1/\sqrt{2}\sigma)kT/P$; here σ is the collision section (~10^{-18} m^2), and P is the pressure (~80 mTorr). The distance between the mask and the substrate must be less than 0.3 μm in order to form patterned features of gold using this procedure.

(32) Note that forming patterned features on recessed regions having dimensions of < 100 μm can not be achieved by photolithography and microcontact printing (μCP).

Conclusions

Micromolding in capillaries (MIMIC) is a remarkably versatile technique for fabricating patterned microstructures of various organic polymers on a variety of solid substrates. The smallest features that we have produced using this procedure were parallel lines with cross-sectional dimensions of $\sim 1 \times 1\ \mu m$. These dimensions were set by the PDMS molds that were available for use with this work; we have not tried molds with smaller features, and the lower limit to the definition that can be achieved by this technique is not established by the present work. The liquid prepolymer used in this process should have low viscosity (<400 cP) and should be curable either thermally or photochemically;[6,33,34] it could be a structural or functional polymer[35] or a precursor polymer to a ceramic material.[7,36] The substrate used in this procedure could be any solid material (planar or nonplanar, rigid or flexible) as long as it provides a reasonably flat surface and this surface can be partially wet by the liquid prepolymer.

The patterned polymeric microstructures formed using MIMIC could be used as resists in the wet etching of underlying substrates (for example, SiO_2, Au, Ag, and Cr). The patterned polymeric microstructures formed using MIMIC could also be released by dissolving the supporting substrates to produce free-standing microstructures. These free-standing polymeric microstructures could be transferred to the surfaces of other solid substrates (both planar and nonplanar) and subsequently used as disposable masks for the evaporation of patterned metals and the formation of patterned SAMs.

Microfabrication based on the present procedure has at least three advantages over conventional photolithographic techniques: (a) MIMIC allows a wider range of organic polymers to be patterned; (b) metal evaporation through flexible polymeric masks provides an easier way to form patterned features on curved surfaces; (c) MIMIC is less expensive and capital intensive than photolithography. At its current stage of development, it also has a range of disadvantage and undefined characteristics in important areas such as dimensional stability and registration in multilevel fabrication.

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