Fabrication of Submicrometer Features on Curved Substrates by Microcontact Printing

Rebecca J. Jackman, James L. Wilbur, George M. Whitesides*

Microcontact printing (μCP) has been used to produce patterned self-assembled monolayers (SAMs) with submicrometer features on curved substrates with radii of curvature as small as 25 micrometers. Wet-chemical etching that uses the patterned SAMs as resists transfers the patterns formed by μCP into gold. At present, there is no comparable method for microfabrication on curved surfaces.

Microlithography is a technology practiced in flatland. Substrates are planar, and fabrication involves removing or adding material in planes. Some very ingenuous efforts notwithstanding (*1*), it has been difficult to extend current photolithographic and e-beam lithographic techniques to curved substrates. Here we describe a procedure that uses microcontact printing (*2, 3*) to generate patterns with submicrometer-scale features on curved surfaces.

In μCP, a patterned, elastomeric "stamp" (typically polydimethylsiloxane, PDMS) is "inked" with an alkanethiol [for example, hexadecanethiol, HDT, $CH_3(CH_2)_{15}SH$] and brought into contact with a gold surface. A self-assembled monolayer (SAM) of alkanethiolates forms where the stamp and surface make contact; the remainder of the gold remains underivatized. On planar substrates, μCP routinely produces patterned SAMs with features between 1 μm and several centimeters and edge definition of ~50 nm (*2, 3*). Extensions of μCP have formed patterned SAMs with features as small as 200 nm (*4*).

Use of μCP on curved substrates takes advantage of the ability of an elastomeric stamp to conform to a nonplanar substrate with minimal distortion of the pattern on its surface. In one procedure (Fig. 1), a gold-coated (*5*) cylindrical substrate is rolled across the surface of the stamp (*6*) to transfer the pattern; in another, the substrate is rocked across the stamp (*7*). After μCP, the patterned gold surface can be etched selectively (see below) to remove gold not protected by SAMs. Alternatively, further derivatization of unstamped areas is possible, either by using a second stamp or by washing the entire surface with a different alkanethiol. Gold patterns can be used as masks in further stages of fabrication.

Figure 2 shows a PDMS stamp and patterned SAMs formed by μCP with this stamp on planar and curved substrates. Microcontact printing with HDT formed CH_3-terminated SAMs; exposing this patterned surface to an ethanolic solution of mercaptohexadecanoic acid [$HO_2C(CH_2)_{15}SH$, MHA] formed COOH-terminated SAMs in regions not derivatized by μCP. Comparison of the stamp and the patterned SAMs showed that μCP transferred the pattern of the stamp to both planar and curved surfaces with similar fidelity.

Chemical etchants (*8, 9*) can be used after μCP to remove gold not protected by SAMs (*10, 11*), and to generate gold microstructures on curved substrates. Figures 3 and 4 show gold structures on cylindrical glass lenses, glass capillaries, and glass fibers. These figures illustrate four characteristics of μCP on curved surfaces. First, μCP is a general method for patterning curved substrates: It generates patterned SAMs and gold microstructures on scales from ~1 μm to several millimeters and it can produce

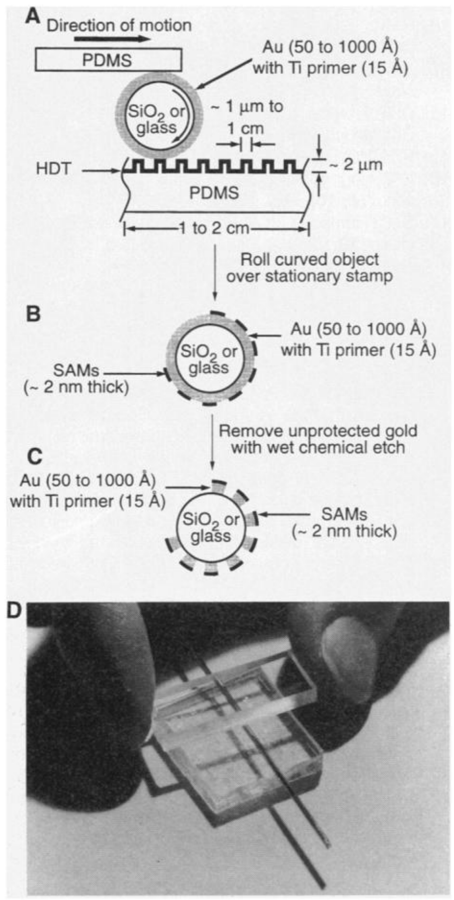

Fig. 1. Procedure for μCP on curved surfaces. (**A** to **C**) Rolling a curved substrate across an "inked," patterned stamp (in these experiments, by hand) transferred HDT from raised regions of the stamp to the surface of the substrate: patterned SAMs formed in the pattern of the stamp. Often, we used a second piece of unmolded PDMS to improve control over the motion of the substrate. Etching removed gold not protected by SAMs and produced gold microstructures in the pattern of the stamp. Features are not drawn to scale. (**D**) Photograph of elastomeric stamp, 1 mm diameter, gold-coated capillary, and unmolded PDMS used for μCP on curved substrates. Each patterned feature (1 mm^2) evident on the stamp contains many smaller (~1 μm) scale patterns that are not visible in this image.

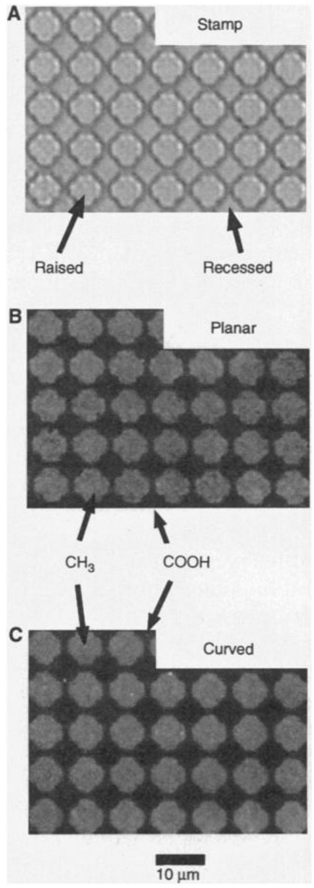

Fig. 2. Patterned SAMs formed by μCP with HDT had similar resolution on planar and curved substrates. (**A**) Optical micrograph of a PDMS stamp. The crosses (width ~8 μm) evident in the stamp were raised by ~1.5 μm relative to recessed regions. (**B**) Scanning electron microscope (SEM) image (*13*) of patterned SAMs on a planar substrate (a Ti-primed Si ⟨100⟩ wafer with a 500 Å thick film of Au) formed with the stamp shown in (A). After μCP with HDT, the substrate was washed with an ethanolic solution (~1 mM) of $HS(CH_2)_{15}COOH$ to derivatize unprotected gold. (**C**) An SEM image of patterned SAMs on a curved substrate (a gold-coated cylindrical glass lens, *r* = 5 cm) formed with the stamp shown in (A). In (B) and (C), SAMs terminated by CH_3 appear lighter than SAMs terminated by COOH.

Department of Chemistry, Harvard University, Cambridge, MA 02138, USA.

*To whom correspondence should be addressed.

complex features on substrates with radii of curvature r from 5 cm to 25 μm (*11*). There is no reason to believe that 25 μm is a lower limit for the curvature of the substrate: The limiting factor in our experiments has been our inability to manipulate (by hand) objects with smaller r. Improved mechanical control over the process should enable printing on more highly curved substrates. Second, μCP is a parallel, large-area process that can produce patterns over areas of several square centimeters in a single step requiring less than 1 min (Fig. 3). Third, it is not necessary to fabricate new stamps or masks for different substrates: a single elastomeric stamp can pattern substrates that differ significantly in r (for example, the lens in Fig. 3 and the capillary in Fig. 4) and each stamp can also be used more than 100 times. Fourth, μCP can generate submicrometer features: working by hand, we have made features as small as 800 nm (Fig. 3C). More exact control over the motion and pressure should form substantially smaller features.

The most important conclusion from this work is that μCP with elastomeric stamps makes it possible to fabricate micrometer-scale features on curved surfaces. The patterned SAMs, and gold microstructures formed by using them, can be used as components of electrical and optical devices and as resists for further processing (*3*, *12*). Microstructures on curved substrates should be useful in areas requiring microfabrication in three dimensions: examples include lenses and optical fibers, microelectronic devices shaped to reduce the length of interconnects, and devices that conform to space limitations. There are parts of this procedure that must be developed further for any application in sophisticated microdevices: In particular, the density of defects must be diminished, and methods must be devised to bring the pattern into registry at the beginning and end of an impression so that the pattern can be continuous around a closed surface. The current level of development is, however, sufficient for simpler structures such as diffraction gratings and interconnects.

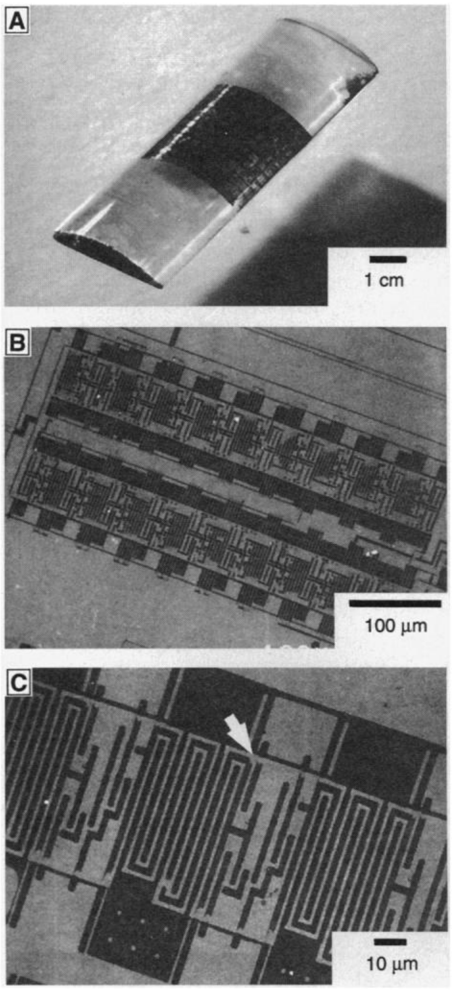

Fig. 3. Patterned SAMs formed by μCP with HDT on a gold-coated cylindrical glass lens (r = 5 cm). Etching removed gold not protected by these SAMs. (**A**) Photograph of this lens. Dark areas are gold and light areas are Ti/TiO_2/glass where the gold was removed. (**B** and **C**) SEM images of gold structures formed on this lens. The smallest features visible in these images were ~800 nm. Light regions in the SEM images correspond to gold; dark regions correspond to areas of Ti/TiO_2/glass. A number of defects were apparent in (C); one is noted by a white arrow. These defects were present in the stamp and in the master used to cast the stamp.

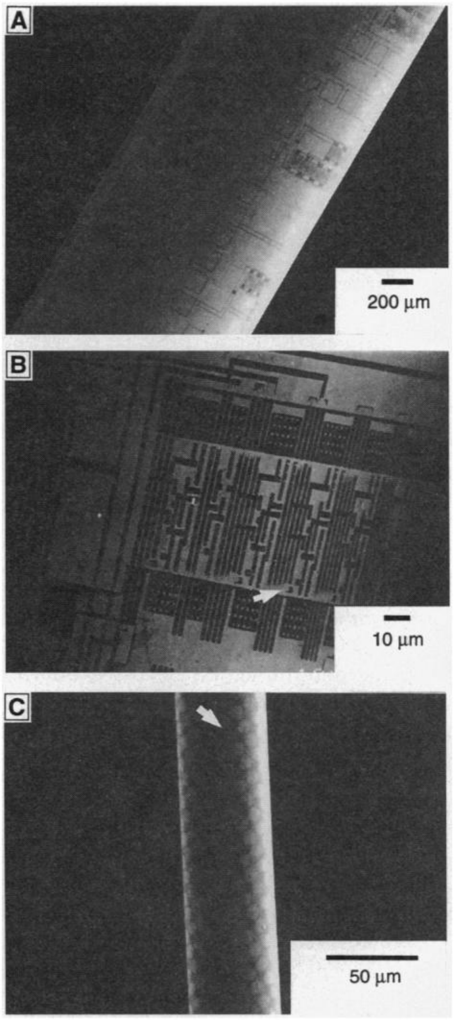

Fig. 4. (**A** and **B**) SEM image of gold microstructures formed by μCP with HDT on a gold-coated capillary (r = 500 μm), followed by etching. A number of defects are apparent in (B) (white arrow); these defects originated in the master used to cast the stamp. (**C**) SEM image of patterned gold structures formed on a 50 μm–diameter gold-coated glass fiber. There was a stripe (white arrow) where the capillary was printed twice when it rolled more than 360°. Light regions in these images correspond to gold; dark regions are Ti/TiO_2/glass where etching removed the gold.

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5. Curved substrates were coated with 15 to 200 Å of titanium (adhesion promoter), and 50 to 1000 Å of gold (99.999%) by electron-beam evaporation.
6. The elastomeric "stamp" was fabricated by casting a PDMS prepolymer onto a master that had features with three-dimensional relief. We typically prepared our masters by photolithography, although any master with suitable features can be used. The raised features of the stamp could have spacings from ~1 μm to several centimeters; sagging of the stamp limited the dimensions of the recessed areas to ~100 μm.
7. An ethanolic solution (1 to 10 mM) of HDT "ink" was applied to the surface of the stamp with a cotton swab. The stamp was subjected to a stream of dry, filtered N_2 gas until its surface appeared dry (20 to 30 s). The substrates were prepared for use by rinsing with heptane, distilled water, and ethanol. We dried the substrate after each rinsing step in a stream of dry, filtered N_2 gas. The substrates were then rolled across the surface of the stamp. We estimate that the time of contact between the stamp and the substrate was <5 s.
8. Microcontact printing with HDT on curved, gold-coated substrates formed SAMs patterned with micrometer-size features. Immersing these substrates in a basic, oxygenated CN^- solution (0.1 M KCN, 2 M NaOH, 25°C) for 15 to 30 min removed the gold in regions not protected by the patterned SAMs. An aqueous ferricyanide etch [0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.1 M $K_2S_2O_3$, and 1 M KOH] was also used as an alternative to the CN^- etch (Y. Xia, M. Zhao, G. M. Whitesides, unpublished work).
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Observation of Stable Shapes and Conformal Diffusion in Genus 2 Vesicles

Xavier Michalet* and David Bensimon

The observed equilibrium shapes of phospholipid vesicles of topological genus 2 (shapes with two holes) are found to be in agreement with theoretical predictions on the basis of a minimization of the elastic curvature energy for fluid membranes under the constraints of constant area, volume, and area difference (between the inner and outer layers of the membrane). For some particular geometrical characteristics, the shapes of the vesicles change continuously and randomly on a slow time scale (tens of seconds) and thus exhibit conformal diffusion. This phenomenon is a reflection of the conformal degeneracy of the elastic curvature energy. Its observation sets a limit (three constraints) on the number of physical constraints relevant to the determination of the shapes of vesicles.

Phospholipid vesicles are closed fluctuating bags (less than a few micrometers in size) whose surfaces are made of phospholipid molecules organized in a membrane, a fluid bilayer structure a few nanometers thick. These vesicles, also known as liposomes and used as such in a number of applications (from cosmetics to pharmacology), are often studied as a simplified model of the cell membrane. They are easily formed from a sample of phospholipids dissolved in water and can be observed by phase-contrast microscopy (*1*). Understanding the shapes of these vesicles is a crucial test for the validity of the various physical models that describe fluid membranes. This has been an active experimental field since the mid-1970s when the first models were proposed as an explanation for the various shapes of red blood cells that had been observed (*2*). These models are all based on an elastic description of the fluid (shearable) membrane, its energy being

$$E = \frac{\kappa}{2}\iint\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 dS \qquad (1)$$

where κ is the elastic modulus, R_1 and R_2 are the local principal radii of curvature of the membrane (*3*), and S is the differential surface element.

The shape of the vesicle can be determined by minimizing its elastic curvature energy under various physical constraints, among which its area A and volume V are the most obvious. However, these are not sufficient to account for all the vesicle shapes that have been observed, for example, the variety of red blood cell morphologies. To account for those cases, other constraints have been introduced, such as a spontaneous curvature (which might result from a bilayer asymmetry) or a constraint on the area difference ΔA between the inner and outer layers of the membrane [which could be constant as a result of a very low rate of lipid exchange (flip-flop) between the two layers], or a combination of both (*4–6*). Recently Jülicher, Seifert, and Lipowsky (JSL) pointed out that the number of relevant constraints could be determined to be three on the basis of the observation in vesicles of topological genus 2 or higher (that is, shapes with two holes or more) of a new phenomenon, which they called conformal diffusion (*7*). Here, we report the observation of this phenomenon.

To understand the possible shapes of vesicles, it is helpful to first consider the invariance properties of their elastic curvature energy (Eq. 1). This energy is obviously invariant under translations and rotations. It is also invariant under dilations. Indeed, if we scale a vesicle (if it is spherical, its radius) by a factor α, because its area increases as α^2, its overall energy and shape remain unchanged. This invariance has an important consequence: The number of relevant geometrical characteristics is reduced by one, and adimensional parameters are defined as the reduced volume v and the reduced area difference Δa (*8*). Another more subtle property of the energy is its invariance with respect to sphere inversions. A sphere inversion is defined simply by choosing an inversion center O and "inverting" the distances (*9*). In contrast with the previous symmetries, the sphere inversions, although they may preserve the energy of a vesicle, may alter its shape. All of these transformations combined—translations, rotations, dilations, and inversions—form the group of three-dimensional conformal transformations, and, as just explained, the elastic curvature energy does not change as a result (that is, it is conformally invariant).

In particular, the state of minimal elastic curvature energy (the ground state) is conformally invariant. For vesicles of spherical

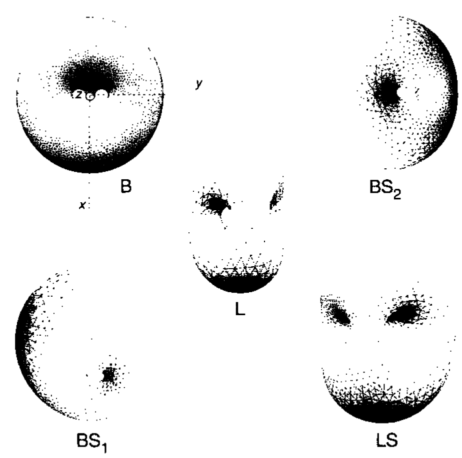

Fig. 1. Some of the absolute minimal shapes of topological genus 2 (shapes with two holes) for the elastic curvature energy (Eq. 1). These shapes can be obtained by special conformal transforms (SCTs) of the Lawson surface L; SCTs are defined by **I**∘**B**∘**I**, where **B** indicates the translation of vector **b**, and **I** is the sphere inversion with its center at the origin of coordinates (*7, 9*). For the sake of commodity, we start from the "button" surface B. With **b** parallel to the z axis, B [$(v,\Delta a)$ = (0.68, 1.068)] can be continuously transformed into L [$(v,\Delta a)$ = (0.67, 1.021)], which has a threefold symmetry axis, and finally into a sphere with two infinitesimal handles (a "genus 2 sphere") [$(v,\Delta a)$ = (1, 1)], going through surfaces of the LS kind shown here. With **b** parallel to the x axis, it is possible to continuously reach a genus 2 sphere going through surfaces of the BS$_1$ kind; the same is true for **b** parallel to the y axis and surfaces of the BS$_2$ kind. Shapes were calculated with the SURFACE EVOLVER program (*17*). This figure was inspired by a similar figure published in (*7*), which was based on a different numerical algorithm.

Laboratoire de Physique Statistique, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 5, France.

*Present address: Laboratoire de Biophysique de l'ADN, Institut Pasteur, 25, 28 rue du Dr Roux, 75724 Paris Cedex 15, France.