

AMERICAN
ASSOCIATION FOR THE
ADVANCEMENT OF
SCIENCE

SCIENCE

4 SEPTEMBER 1992
VOL. 257 • PAGES 1317-1448

\$6.00



Micrometer-wide lines of a hydrophobic self-assembled monolayer separate square regions of a hydrophilic monolayer; drops of water (with blue and green coloration) wet the square regions but do not contact one another. The lines of separation provide new structures

with which to manipulate the shapes of liquid drops. See page 1380. The sides of each square are about 4 millimeters long. The blue drops do not completely wet the corners. [Photograph: F. Frankel]

Manipulation of the Wettability of Surfaces on the 0.1- to 1-Micrometer Scale Through Micromachining and Molecular Self-Assembly

Nicholas L. Abbott, John P. Folkers, George M. Whitesides*

Micromachining allows the formation of micrometer-sized regions of bare gold on the surface of a gold film supporting a self-assembled monolayer (SAM) of alkanethiolate. A second SAM forms on the micromachined surfaces when the entire system—the remaining undisturbed gold-supported SAM and the micromachined features of bare gold—is exposed to a solution of dialkyl disulfide. By preparing an initial hydrophilic SAM from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$, micromachining features into this SAM, and covering these features with a hydrophobic SAM formed from $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$, it is possible to construct micrometer-scale hydrophobic lines in a hydrophilic surface. These lines provide new structures with which to manipulate the shapes of liquid drops.

A combination of micromachining (1) and molecular self-assembly provides the basis for a procedure that can be used to generate micrometer-scale patterns of contrasting surface properties. This procedure has three steps: (i) formation of an initial SAM of alkanethiolate on Au (2); (ii) generation of regions of bare Au in the SAM by micromachining; and (iii) formation of a second SAM on these micromachined regions. Because the two SAMs can have different compositions and physical properties and because the shapes of the micromachined features (3) can be controlled, this process controls the characteristics of a surface with micrometer resolution without the use of photolithography. We illustrate the capability of this type of

microfabrication by forming patterns of SAMs of contrasting wettability on Au surfaces and by using these patterns to manipulate the shapes of drops of water.

The experimental procedure is summarized in Fig. 1. First, a hydrophilic SAM was formed by reaction of an Au film (4) with ω -mercaptohexadecanoic acid $[\text{HS}(\text{CH}_2)_{15}\text{COOH}]$ (5). The carboxylic acid group makes the surface hydrophilic, with wettability dependent on the pH of the water: the contact angle [measured under cyclooctane (5)] decreased from $\theta_a^{\text{H}_2\text{O}} = 30^\circ$ (pH 5) to $<5^\circ$ (pH 10). Second, 0.1- to 1- μm features of bare Au were micromachined into the surface of the Au supporting the SAM. Either a surgical scalpel blade or the cut end of a carbon fiber was used as a tool (6). We used a 3 mN load on the tip of the scalpel to machine uniform grooves with macroscopic lengths (≥ 1 cm), widths of ~ 1 μm , and

depths of ~ 0.05 μm (Fig. 2). The micromachined grooves were bordered by two lips of raised metal (~ 0.1 μm high and ~ 0.2 μm wide) formed by the plastic deformation of the Au during the machining (7). Each lip presents an inclined surface to the edge of a spreading drop of liquid and influences the wetting behavior of the surface. In contrast, much smaller lips of metal bordered the ~ 0.1 - μm -wide grooves that were formed with the tip of a carbon fiber (8). Third, a second, hydrophobic SAM was formed selectively on the bare Au features by immersion of the micromachined surface in a solution of $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$. We used a dialkyl disulfide in this step because the rate at which dialkyl disulfides replace surface thiolates in SAMs is $\sim 1/100$ of that of the corresponding alkanethiols and thus the dialkyl disulfides minimize the modification of the properties of the original hydrophilic SAM while forming the second hydrophobic SAM (9, 10).

Features on the 0.1- to 1- μm scale having contrasting wettability can pin the edges of drops of water. The extent of this pinning was influenced by the type of SAM within the micromachined groove and by the shape of the groove (11). We have used grooves 0.1 to 1 μm wide having hydrophobic SAMs to manipulate the positions and the shapes of drops: several features that can be controlled are illustrated in Fig. 3.

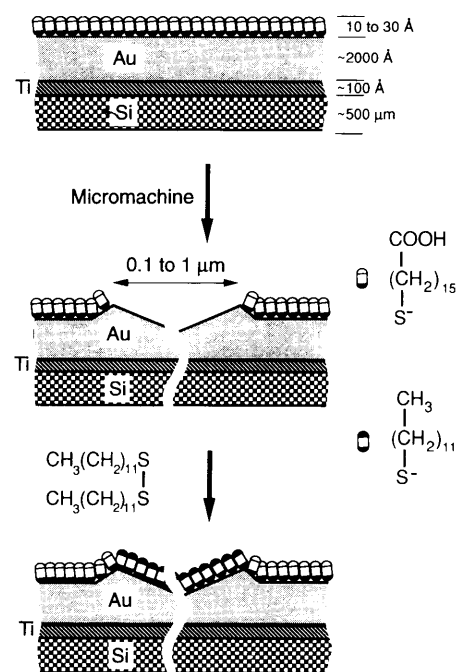


Fig. 1. Schematic illustration of the formation of 0.1- to 1- μm hydrophobic lines in a hydrophilic surface with micromachining and SAMs. We imply no asymmetry in the structure of the SAMs within the micromachined groove. Au, evaporated film of gold; Ti, evaporated film of titanium used to promote adhesion of the gold to the silicon wafer.

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

*To whom correspondence should be addressed.

Fig. 2. Scanning electron micrographs of the scalpel (**A** and **B**) and the carbon fiber (**D** and **E**). The inset in (**A**) is a low-magnification image ($\times 10$) of the tip of the scalpel. The grooves [(**C** and **F**) (marked by an arrow)] were micromachined into an Au film bearing a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$. The samples were fractured normal to the groove in liquid nitrogen for imaging. The sizes and shapes of the grooves are probably determined by local features of the tip of the scalpel and fiber.

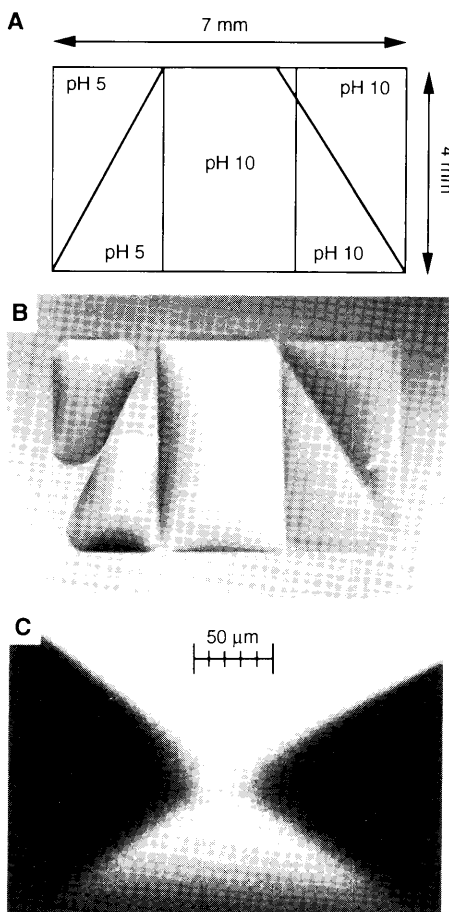
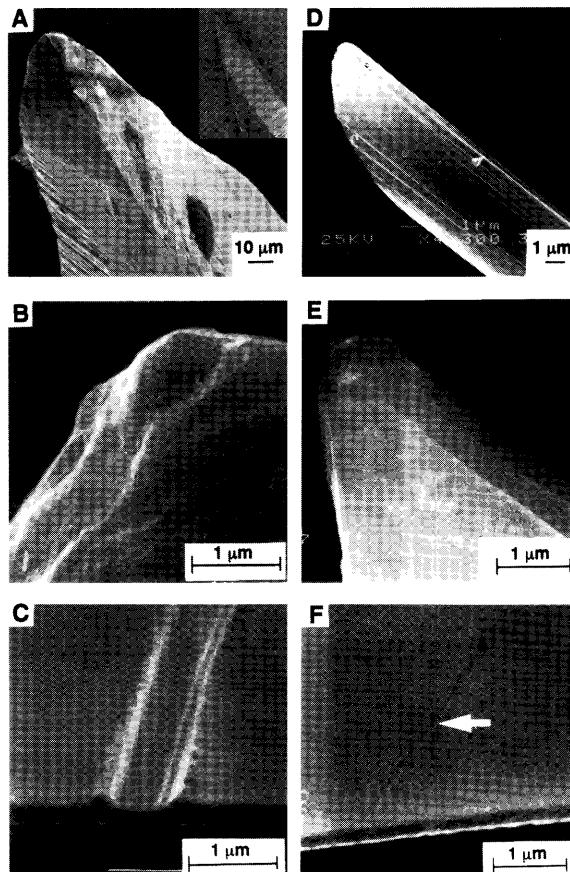


Fig 3. Top and side views of drops of water on a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ and patterned with micrometer-scale micromachined grooves (see Fig. 2C) supporting a SAM formed from $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$. (**A**) Diagram of grooves; (**B**) top view of drops; (**C**) side view of two drops separated by a hydrophobic groove. The pH values of the buffered drops of water are shown in (A). The hydrophobic line that forms the hypotenuse of the triangular drops of pH 10 water cuts off the top right corner of the rectangular drop; a dust particle can be seen on a triangular pH 10 drop; and the circular edge of a pH 5 drop is slightly pinned. The dark regions in (C) are the two water drops, which almost meet at the hydrophobic line in the center of the photograph. The top surface of each dark region is the air-water interface, and the apparent bottom surface is caused by the reflection and diffraction of light in the vicinity of the closely positioned edges of the two drops.

Drops can be positioned with edges straight and can be pinned close together: the resolution of a side view of two drops with edges pinned by a common, $1\text{-}\mu\text{m}$ -wide line is limited by the effects of diffraction and reflection, but the drop edges are clearly separated by less than $30\ \mu\text{m}$ (12). The drops do not appear to communicate with one another: a dye in one compartment remains localized and does not diffuse into neighboring compart-

ments. The extent of wetting of the corners of the pattern depends on the contact angle of the water on the SAM (and thus, in this system, on the pH of the water), the angle at the corner, and the volume of liquid in the drop.

Control experiments in which the initial SAM and the second SAM deposited on the surface of the micromachined features were both formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ showed little or no pinning of a drop (pH 10, 0.05 M borate) (11). Micromachined features with hydrophobic SAMs having $0.1\text{-}\mu\text{m}$ widths showed a weaker tendency to pin a drop than those with $1\text{-}\mu\text{m}$ widths. We have not quantified the importance of the width of the groove and the shape of its edge in pinning the edge of the drop (13, 14).

The combination of micromachining with molecular self-assembly offers a versatile procedure for manipulating the structure and properties of surfaces and the shapes of liquids drops on them. Micromachining provides both convenient access to small features and control over the geometry of these features. By using simple procedures, we have generated features that are already smaller ($0.1\ \mu\text{m}$) than those that can be routinely generated with optical lithography (15). With the use of improved micromachining tools (including the scanning tunneling microscope), it should be possible to extend this technique to create features as small as $10\ \text{nm}$ or less. Molecular self-assembly is particularly useful as a part of this procedure because it allows molecules to be adsorbed on very small features ($<1\ \text{nm}$) with high selectivity and because it permits sensitive control of the surface free energies (16).

The procedure illustrated in Fig. 1 is an uncomplicated one that uses an Au support, one width for the grooves, and two different SAMs. The procedure can be extended to other supports and geometries of the grooves and, through combinations of sequential pattern formation and orthogonal self-assembly (17), to multiple combinations of SAMs. We believe that this procedure can be readily generalized and widely useful in controlled patterning of surfaces. It provides an alternative to optical lithography and should be applicable to problems for which optical techniques are not (such as, nonplanar substrates) and in laboratories where optical lithography is not available. The ability to manipulate the shapes of drops should be applicable to problems in wetting and adhesion and to the characterization of surfaces (18).

REFERENCES AND NOTES

1. We use the term "micromachining" to mean the moving of metal by a mechanical means rather than by chemical etching.
2. R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*

- 105, 4481 (1983); C. D. Bain and G. M. Whitesides, *Angew. Chem. Int. Ed. Engl.* **28**, 506 (1989), and references therein; G. M. Whitesides and P. E. Laibinis, *Langmuir* **6**, 87 (1990), and references therein.
3. We use the term "feature" to mean a region of the surface with a property that is distinguishable from its surroundings.
 4. The Au substrates were prepared by evaporation of 100 Å of Ti (99.999%) onto a polished Si(100) wafer (Silicon Sense, Nashua, NH) followed by 2000 Å of Au (99.999%) with an electron beam evaporator operating at a pressure of approximately 10^{-6} torr.
 5. C. D. Bain and G. M. Whitesides, *Langmuir* **5**, 1370 (1989); S. R. Holmes-Farley, C. D. Bain, G. M. Whitesides, *ibid.* **4**, 921 (1988).
 6. The depth and width of the micromachined grooves could be controlled by varying the load (1.2 to 9.8 mN) on the tip of the scalpel blade (Feather Industries, Tokyo) and carbon fiber (diameter, 8 μm). By using energy-dispersive x-ray fluorescence measurements, we detected no evidence of exposed Si within the micromachined groove.
 7. The plastic deformation of the Au suggests that the machining pressure exceeded the yield strength of the Au. If we assume a scalpel tip area of 10 μm^2 in contact with the Au surface, a load of 3 mN corresponds to a tip pressure of 300 MPa. This pressure is greater than the yield strength of bulk Au (3.4 to 14 MPa, depending on thermal history) and comparable to the ultimate tensile strength of bulk Au (131 MPa) [E. M. Wise, *Gold: Recovery, Properties, and Application* (Van Nostrand, New York, 1964)].
 8. Scanning electron microscopy (SEM) images of the tip of the carbon fiber showed a morphology resembling thin parallel sheets. These tips sometimes formed distinct parallel grooves, separated by as little as 0.1 μm .
 9. By using a dialkyl disulfide to form the second SAM, the exchange with thiolates of the first SAM can be reduced to less than 0.1%. For example, a SAM formed from $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$ has been measured, by using the contact angles of water on the SAM and x-ray photoelectron spectroscopy, to exchange less than 0.1% when exposed to a 0.1 mM solution of $[\text{HO}(\text{CH}_2)_{11}\text{S}]_2$ in ethanol for 10 s at 25°C (H. A. Biebuyck and G. M. Whitesides, unpublished results).
 10. We have also formed the second SAM using a 0.1 mM solution of $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SH}$ in ethanol and very short (~ 1 s) adsorption times. The rate of reaction of $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SH}$ with the bare Au is faster by a factor of 10 than the rate of its exchange into the first SAM [C. D. Bain *et al.*, *J. Am. Chem. Soc.* **111**, 321 (1989); C. E. D. Chidsey, C. R. Bertozzi, T. M. Putvinski, A. M. Muijsce, *ibid.* **112**, 4301 (1990); D. M. Collard and M. A. Fox, *Langmuir* **7**, 1192 (1991); C. D. Bain, H. A. Biebuyck, G. M. Whitesides, *ibid.* **5**, 723 (1989)].
 11. Although grooves formed with a load of 3 mN applied to the tip of the scalpel did not pin the edges of drops, grooves formed with larger loads (≥ 10 mN) showed a weak tendency to pin drops. Because larger loads produce larger grooves, this suggests that the shapes of the grooves can influence the pinning of drops.
 12. Top views of the drops under an optical microscope indicated that the separation of the drops was ≤ 5 μm .
 13. These observations are consistent with the established influence of "surface roughness" (including grooves) on the wetting of solid surfaces with liquids [P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985), and references therein].
 14. Drops of water can also be pinned by "writing" lines of SAMs with liquid alkanethiols. In this case there is no deformation of the surface (H. A. Biebuyck and G. M. Whitesides, unpublished results).
 15. We use the term "optical lithography" to mean lithography with radiation wavelengths in the range 248 nm (KrF excimer laser) to 436 nm (mercury arc source) [J. Bruning, *Opt. Photonics News* **2**, 23 (May 1991)].
 16. The rate of lateral diffusion of molecules in the SAM is unknown but may ultimately limit the resolution of the method.
 17. P. E. Laibinis, J. J. Hickman, M. S. Wrighton, G. M. Whitesides, *Science* **245**, 845 (1989).
 18. The analysis of wetting in the corners can yield fundamental information such as the contact angle of the liquids on the SAMs.
 19. Supported by the Office of Naval Research and the Defense Advanced Research Projects Agency. SEM images were obtained at the Harvard University Materials Research Laboratory. We thank H. A. Biebuyck for helpful suggestions and insightful discussions.

17 April 1992; accepted 8 July 1992