Microcontact Printing of SAMs

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8.1 Introduction

Self-assembled monolayers (SAMs) are used in many fields that require homogeneous surface modification, e.g., control of wetting,[1–4] control of bio-compatibility,[5–7] lubrication,[8] corrosion inhibition,[9,10] metal refining,[11] adhesion,[12,13] and passivation.[14] The utility of SAMs is based on their characteristics:[15–21]

1. They are easy to prepare and form quickly from solutions of the assembling molecules.
2. They are molecularly ordered and are robust under many conditions of use.
3. They are thermodynamic minimum structures; thus they form spontaneously and tend to reject defects.
4. They permit control of film thickness to within ~ 0.1 nm by varying the length of their constituent molecules.
5. They allow surface properties to be controlled through tailoring of exposed surface functional groups.

Many types of function, however, require *patterned* surfaces. In microelectronics, metal patterns are needed to delineate transistors and other electronic components;[22] in microelectromechanical systems (MEMS), silicon and glass patterns form free-standing microstructures sensitive to electrical or environmental actuation;[23] and in optics, relief features generate diffraction gratings, waveguides, and microlens arrays.[24] In each of these technologies, the general trend has been toward smaller devices because a microscopic device is usually less expensive, more accurate, and more sensitive than its macroscopic equivalent. Since SAMs are nanometer-sized elements in one dimension (perpendicular to the plane of the surface), patterning of SAMs and the subsequent development of these patterns into useful devices has the potential to increase the performance of certain devices. Patterning of SAMs is, then, the first step toward the realization of devices that involve this class of nanostructures in fabrication, processing, or use.

Table 1 lists the techniques for patterning SAMs currently in use and their resolutions; the most widely used are microcontact printing (μCP)[25,26] and UV lithography.[22] The latter is primarily a historical artifact, as UV lithography is the basis for photolithography and is thus widely familiar to microfabricators. In this technique, UV radiation and an amplitude photomask are used to activate,[27–29] damage,[30] or cross-link[31,32] a SAM selectively in the illuminated regions; the illumination therefore generates a pattern of SAMs that replicates that of the mask. However, patterning of SAMs with UV radiation has several drawbacks.

TABLE 1
TECHNIQUES OF PATTERNING SAMS, THEIR DEMONSTRATED LATERAL RESOLUTIONS, AND AREAS THAT CAN BE PATTERNED IN A SINGLE STEP

Technique	Lateral Resolution (nm)	Patterned Area (cm^2)
Microcontact printing[35]	500	50
UV lithography[30]	500	50
E-beam lithography[40]	10	10^{-8}
Scanning probe lithography[41]	1	10^{-12}
Focused ion beam lithography[42]	10	10^{-8}
Micromachining[43]	100	10^{-2}
Neutral metastable atom lithography[44]	70	1

First, its resolution is not high. The minimum demonstrated linewidth is 0.5 μm, and the achievable edge resolution appears to be modest. Second, this "brute force" method destroys most of the exquisite surface chemistry that SAMs introduce. The chemistry of UV photopatterning appears to be photooxidation of the sulfur (when patterning alkanethiolates) unless photolabile groups have intentionally been included in the SAM. Thus the surface that is produced is not well-defined chemically. Third, like most photolithographic procedures, it is not applicable to curved surfaces. Finally, it is relatively slow.

Microcontact printing (μCP), one of the non-photolithographic techniques that make up "soft lithography",[33–36] provides an alternative to UV photolithography that is chemically more versatile and allows certain types of patterning to be carried out more easily. In μCP, an elastomeric polydimethylsiloxane (PDMS) stamp with a surface relief pattern is "inked" with a molecular precursor of a SAM—typically an alkanethiol $HS(CH_2)_nX$—and printed to generate a SAM on the stamped regions. With this method, only the regions that come into contact with the stamp are covered with a (near) monolayer of SAM; unstamped regions remain bare. Because μCP is inherently an additive process, it is compatible with a wide range of surface functional groups, including the structurally complex and fragile groups found in biology and biochemistry.[6] Microcontact printing is a patterning technique that can be performed easily in laboratories that do not have routine access to photolithographic equipment, and because μCP is a parallel method of patterning, features are printed efficiently in a single step. Moreover, since PDMS is an elastomer, μCP can easily be adapted to curved substrates.[37] The smallest features routinely generated with μCP are 300-nm-wide lines, and 50-nm-wide lines may be achieved with careful planning of the stamp geometry.[38,39]

Alternatives to μCP and UV lithography for patterning SAMs include e-beam lithography,[40] scanning probe lithography,[41] focused ion beam lithography,[42]

micromachining,[43] and neutral metastable atom lithography.[44] While the first three of these techniques have demonstrated very high resolutions (< 50 nm), they require specialized equipment and—as with all serial lithographic techniques—are relatively slow. Micromachining (i.e., scratching the SAM with a probe) and neutral atom lithography have also been used to produce high-resolution patterns, but substantial development needs to be done before their capabilities can match that of μCP.

This chapter describes microcontact printing and its uses in microfabrication. The first section details how to carry out microcontact printing: Fabrication of PDMS stamps and the various configurations of μCP are described. The next section reviews the use of hydrophobic SAMs patterned with μCP as nm-thick resists. The final section describes the use of two-component patterned SAMs as templates for generating patterned materials such as polymers, crystals, and biological cells.

8.2 Microcontact Printing

Microcontact printing (μCP) extends conventional pattern printing to the μm-scale dimension. In conventional printing, stamping with a raised surface transfers an ink, usually a viscous suspension of a dye or carbon particles, to the printed surface; the stamp can be fabricated by a range of techniques, including polymer replica molding and manual scribing.[45] Only the raised portions of the stamp come into contact with the stamped surface; the raised pattern of the stamp is therefore replicated on the stamped surface. In μCP, stamps are molded from much more precisely patterned masters, and the ink is a SAM precursor. The key difference is that in μCP, the ink solvent is forced to evaporate before stamping; assuming a precursor concentration of ~ 1 mM and an ink volume of ~ 0.1 mL, only $\sim 10^{16}$ molecules or 10 monolayers are distributed onto the stamp. This amount is more than enough to deliver a monolayer to the surface, yet is tiny enough that excess ink does not "squirt" out the sides of the stamp when printing. Thus, with μCP, far smaller features can be generated than is possible with conventional printing. We have been able to stamp 300 nm lines and spaces of SAM over ~ 50 cm^2 areas,[46] and it is possible to print 50 nm features over ~ 10 μm^2 areas.[47]

Microcontact printing consists of two principal steps: fabrication of stamps and printing. These steps are outlined schematically in Figs. 1 and 2, respectively. Most stamps used in μCP are cast from photolithographically generated resist patterns[26] (as these provide excellent resolution) but stamps may also be cast from other types of masters, such as TEM grids,[26] commercially available diffraction gratings,[33] etched metal or silicon patterns,[48] commercially available

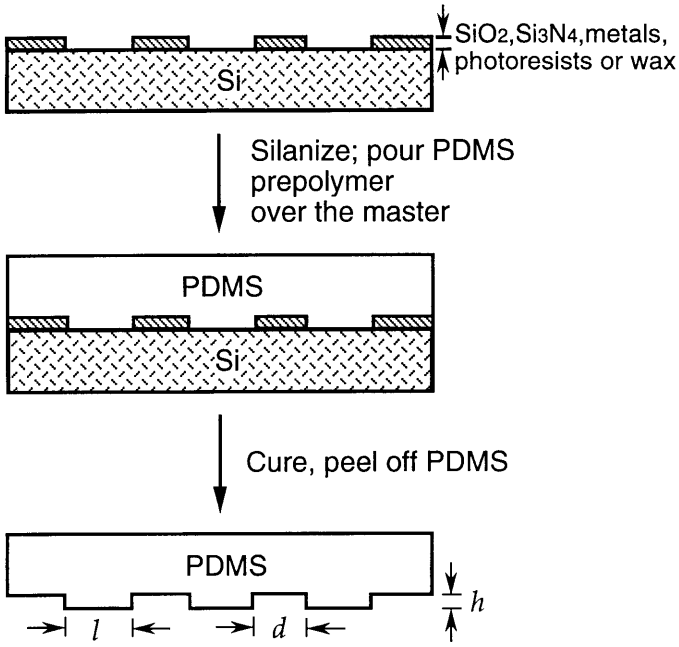

FIG. 1. Schematic diagram of fabrication of PDMS stamps.

polymer relief structures (such as a polyurethane corner cube reflector),[49] and polymer bead patterns.[50] Before casting stamps from any of these masters, it is important to functionalize the master with silane vapor; any hydrophobic silane such as the fluorosilane $Cl_3Si(CH_2)_2(CF_2)_5CF_3$, octadecyltrichlorosilane, or hexamethyldisilazane will do. This treatment caps any reactive —OH groups on the master with inert $—CH_3$ or $—CF_3$ groups so that the cast polymer does not adhere to the master.

Once the master has been prepared and silanized, a stamp may be cast from it (Fig. 1). In general, a thermosetting prepolymer is poured over the master, cured, and then peeled off the master (Fig. 3). If the master contains sub-μm-sized features, or if the prepolymer is highly viscous, removal of air bubbles with vacuum before curing of the polymer may be necessary to ensure filling of the submicron-wide channels. Materials successfully used as stamps include Novolac resin,[26] polyimide, polyurethane, and polydimethylsiloxane (PDMS), and we anticipate that other polymers would be suitable as well. (Even patterned Cr on glass has been used as a stamp, although the relative softness of polymers makes conformal contact between the stamp and surface easier to obtain.[51]) For PDMS stamps, we use the two-component Sylgard 184 elastomer available from

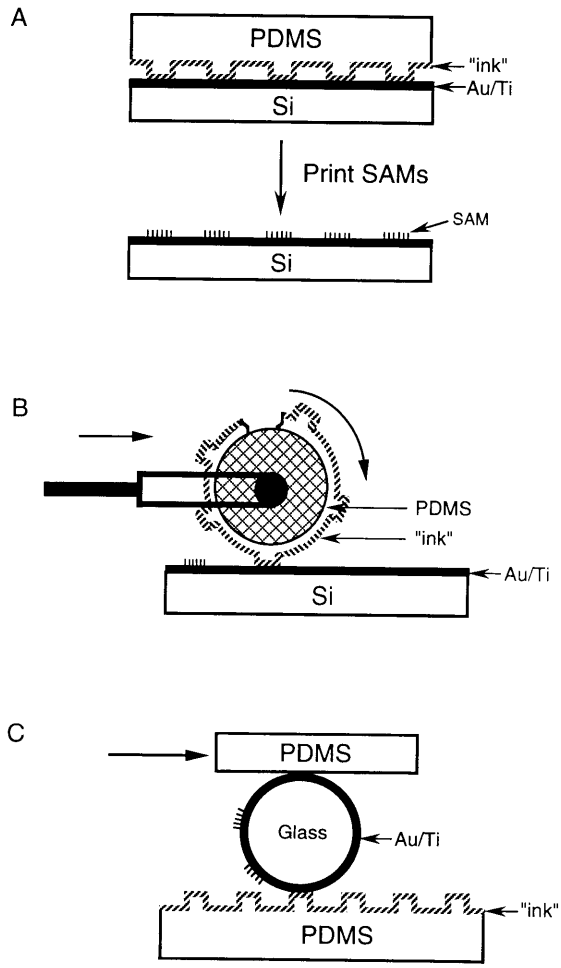

FIG. 2. Methods of carrying out microcontact printing. (a) *Planar*: The PDMS stamp is placed on the surface. (b) *Rolling*: The thin PDMS stamp is rolled over the surface. (c) *Curved*: A cylindrical substrate to be stamped is rolled in between an inked PDMS stamp and a clean flat piece of PDMS.

Dow Corning in the specified 1:10 ratio of curing agent to prepolymer and cure at 60°C for > 2 hrs. It is also possible to tailor the tackiness/softness of the stamp by varying the ratio of the two components—less curing agent results in PDMS stamps that are softer and stickier.[39]

We have focused on stamps made of PDMS for several reasons. First, in contrast to polyimide and polyurethane, PDMS is highly elastomeric, i.e., PDMS

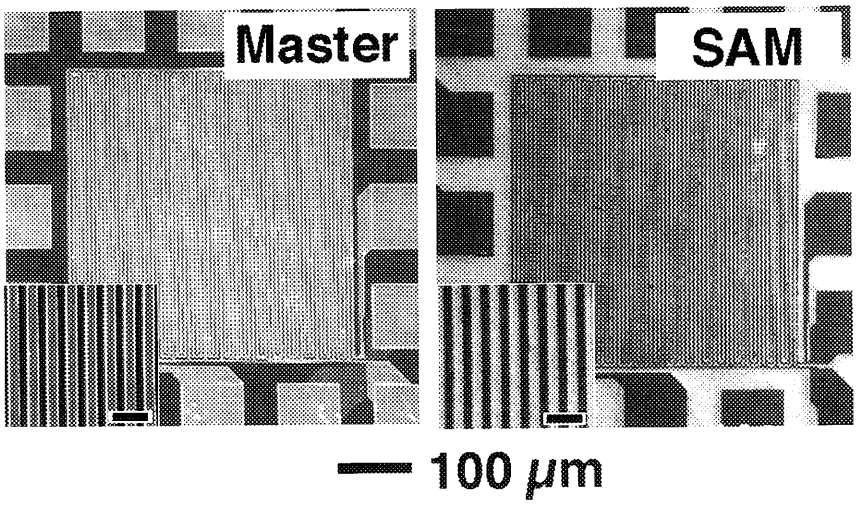

FIG. 3. SEM images of a master and patterned SAM made with a PDMS stamp cast from the master.

deforms elastically, not plastically, over a wide range of strain. The elastomeric properties of PDMS allow stamps of PDMS to achieve conformal contact with the substrate to be stamped with little or no applied pressure. This situation contrasts sharply with μCP with a rigid stamp; in the case of μCP with a hard Cr/glass "stamp," substantial pressure was needed to stamp an area of only a few μm^2.[51] Because μCP with PDMS stamps occurs with little external pressure, a stamp can be reused repeatedly without degradation of the pattern—a problem that plagues contact printing in photolithography.[22] As an elastomer, PDMS can be deformed mechanically to large ($\sim 10\%$) strains without damage to the stamp. Thus, it is possible to change feature sizes by simply squeezing the stamp; as discussed later, this idea forms the basis of *compressive stamping*.[52] Second, PDMS has desirable chemical properties: It presents an inert surface with a low surface energy of 22 dyn/cm^2. This low energy allows easy release from the substrate after stamping and results in little attraction of the stamp for dust and contaminants.[53] Dust can also be removed easily by washing or with Scotch tape. If a hydrophilic surface with the elastomeric properties of PDMS is desired, treatment with an O_2 plasma easily oxidizes the PDMS to a porous silica. PDMS resists dissolution in most solvents, is only partially swollen by hydrocarbons, and is attacked chemically only by concentrated KOH or HF/H_2O_2. Finally, for reasons not well understood, PDMS appears to be one of the few polymers into which alkanethiols can dissolve at a concentration that allows the stamp to act as

a reservoir.[54] This property allows the stamp to act as a reservoir of ink during μCP and may be one reason why μCP of alkanethiolates has been so effective at printing dense monolayers.

Of course, the elastomeric properties of PDMS require certain trade-offs in performance. For one, nanometer-scale registration, already difficult to achieve with rigid materials such as quartz, is presently impossible with PDMS. The difficulty in accomplishing high-resolution registration of PDMS is compounded by the sensitivity of its shape to temperature: It has a high thermal expansion coefficient. The softness of PDMS results in sagging of the stamp in areas where the stamp is suspended over the surface. If the stamp sags far enough toward the substrate, a SAM may be transferred into regions that were intended to be bare. This undesired side effect can sometimes be avoided by constructing stamps that possess relief depths that vary with feature size. However, fabricating such stamps is not trivial. Appropriate design—for example, placing "posts" in the design to prevent sagging—may be effective but may also compromise other functions of the pattern.

For now, these difficulties have not been significant. We have not attempted to achieve nanometer-scale registration, and unwanted sagging may often be avoided with careful stamping technique. The ability to achieve conformal contact over large areas with PDMS outweighs any drawbacks arising from the unwanted deformation of PDMS; this characteristic explains why our group has worked almost exclusively with stamps made of PDMS for the past several years.

Microcontact printing with a PDMS stamp has been performed with three distinct geometric configurations of the stamp: planar,[26] rolling,[46] and curved[37] (Fig. 2). In all of these arrangements, the stamp is inked, either by spin-coating or by using a Q-tip, with millimolar solutions of a SAM precursor. The inked stamp is then dried with a stream of N_2 for 30–60 sec., and the stamp is brought into contact with the appropriate surface (usually a thin gold or silver film). Upon contact of some part of the stamp with the substrate, a "wetting front" is usually seen as the rest of the PDMS stamp comes in conformal contact with the substrate. If the stamp is very large, or if the stamp is very soft (e.g., incompletely cured or cast using a 1:20 mix of curing agent to monomer), gentle tapping on the stamp may be needed to ensure that air bubbles are not trapped between the stamp and the substrate. After 5–10 sec., the stamp is removed from the substrate, and the stamped surface may be washed with another solution containing a second SAM precursor to derivatize the unstamped regions.

Where these configurations (planar, rolling, and curved) differ is in how the stamp is applied to the substrate. In the planar arrangement, the stamp is simply placed on the substrate. Planar stamping has achieved $\sim$500 nm lines/spaces over a $\sim$10 cm^2 area; larger areas tend to result in trapping of air bubbles between the stamp and the substrate. In the rolling configuration, a thin ($\sim$1 mm)

stamp mounted on a plastic rolling cylinder is rolled over the surface of the substrate. This method has the advantage of being able to pattern large areas (≥ 50 cm^2) in one printing. In the curved configuration, the stamp is brought into contact with a curved substrate, and gradually the substrate is rolled on the stamp. For simple pattern transfer, rolling by hand is sufficient,[37] but generating more complex features such as microcoils requires mounting the stamp more carefully using an alignment jig.[55] The curved configuration can also be extended to pattern the *inner* surfaces of curved shapes (e.g., the inside of a capillary) by rolling an inked stamp on the inner surface; this capability is unique to μCP.[56]

In these configurations, the stamped features have exactly the same dimensions as those in the stamp. We can, however, use the elastomeric properties of PDMS to reduce the spacing between stamped areas.[52] By compressing the stamp in a vise and stamping with such a stamp while under compression, the widths of the recessed regions of the stamp can be decreased by as much as 50% and μCP can be extended down to ~ 200 nm spaces.[39] Also, by squeezing one side of the stamp more than another side, a stamp of parallel lines can be used to produce chirped patterns of a SAM.[33] The ability to change spacings and features of a pattern by mechanical distortion is unique to these elastomeric stamps.

At first glance, it would seem unlikely that distinct features could be generated with μCP since the SAM precursor might spread reactively all over the surface.[57] However, distinct features are generated when printing with CH_3-terminated SAM precursors because CH_3-terminated SAMs are *autophobic*.[58] That is, the SAM precursor will dewet from the already formed SAM; this dewetting limits the extent to which the SAM can spread during stamping and thus generates sharp features of the SAM (Fig. 4).

This property of SAMs lends another approach to reducing feature sizes achievable with μCP by stamping under water.[59] When a hydrophobic SAM such as hexadecanethiolate on Au is stamped under water, the SAM tends to spread laterally along the edges of the stamped features. This effect is not an artifact resulting from excess material being squeezed out along the sides of the stamp, for it is only observed when stamping under water. Reactive spreading occurs because the SAM of hexadecanethiolate on gold is hydrophobic and drives the spreading of the SAM precursor across the gold surface as the high-surface-energy water retracts. In general, the speed of spreading ranges from 10–100 nm/min, depending on the concentration of the applied solution. By controlling the time in which the stamp is in contact with the substrate, one can reach dimensions for certain types of features of ~ 100 nm.

Three important aspects of μCP need to be considered. The first question concerns the structure of the PDMS stamp: What geometries are allowed in the stamp? One can imagine the extreme case of μCP with a stamp with 1 μm lines, 1 mm spacings, and 1 μm relief depth. In this case, μCP will not generate 1 μm

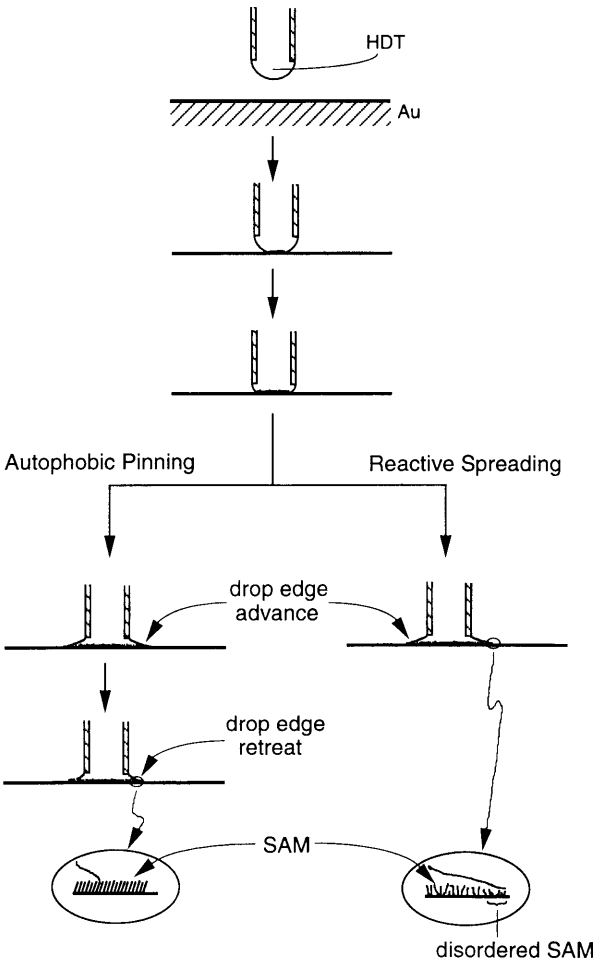

FIG. 4. Schematic diagram of formation of SAMs with μCP. The autophobicity of the already-formed SAM causes the SAM precursor to retract.

lines of SAM separated by 1 mm spacings because the PDMS will sag during stamping and make contact with the substrate between lines. Delamarche et al.[60] found that to minimize sagging an aspect ratio (height to width) of less than 1:5 in the stamp is required. By the same token, stamps with unreasonably high aspect ratio are useless in μCP. If the stamp has, say, 100 nm lines and spacings but the relief depth is 10 μm, the lines will buckle under stamping. In fact, stamps with high aspect ratio posts are inherently unstable, and the PDMS posts collapse after

removal from the master. Even if the features are mechanically stable, often the lines will "pair up" from mechanical agitation during application of the SAM solution or from capillary forces during evaporation of the solvent. This effect is equivalent to that of stiction in microelectromechanical systems (MEMS)[61] and originates in van der Waals attractions between components. Here, the attractive forces are more pronounced than in MEMS because PDMS is soft and compliant; the compliance results in a larger adhesion area and thus a larger attractive force for PDMS than for silicon dioxide.

Delamarche et al.[62] have shown that an aspect ratio of 2:1 or lower is necessary to eliminate the problem of line pairing. Since line pairing seems to correlate with the stickiness of the PDMS stamp—a characteristic that depends on the degree of curing—extensive (≥ 2 days) curing greatly reduces line pairing. Once damaged by line pairing, a stamp can be restored to nearly pristine condition (from 50% surface damage to $\leq 0.1\%$) by washing the stamp with 5% aqueous sodium dodecylsulfate, rinsing with heptane, and drying with supercritical CO_2. Thus, to be useful in μCP, *a PDMS stamp (Sylgard 184, formulated according to Dow Corning's instructions) should have relief aspect between 2:1 and 1:5 and be cured for* ≥ 2 *days*. Having one aspect ratio throughout the entire stamp is easy to achieve if the feature sizes are identical, but widely different feature sizes on the same stamp would necessitate different stamp depths. Fabricating masters that present such varying depths is technically difficult and may require several photolithographic steps.

The second issue facing μCP is this: What is the quality of SAMs printed by μCP compared to that of solution-grown SAMs? This question, addressed by Larsen et al., was answered by using scanning tunneling microscopy (STM) on SAMs of dodecanethiolate on single-crystal Au(111) thin films.[62,63] STM can image surfaces with atomic resolution and is thus appropriate for determining the structure of SAMs. Single-crystal Au(111) films were chosen as substrates since these films are relatively easily prepared with μm^2-sized atomically flat terraces.[64] (Polycrystalline Au is less useful for STM since the image of the SAM would then be convoluted with the disordered background image of the Au.) SAMs of dodecanethiolate were chosen for imaging since molecules of dodecanethiol are long enough to form close-packed, well-ordered SAMs on Au,[18] yet short enough to allow an appreciable tunneling current to pass from the Au surface to the probing tip.[65] Moreover, there exists a substantial background of work on STM of dodecanethiolate on gold.

Before proceeding to images of stamped gold, it is useful to review the salient features present in STM images of solution-grown SAMs of dodecanethiolate on Au (Fig. 5a). Solution-grown monolayers of thiols on gold form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer on top of the reconstructed Au(111) face, with the sulfur atoms residing on threefold coordination sites on the Au.[16] In STM, the

sulfurs are the atoms that are imaged,[65] and these appear on top of the signal given by the Au atoms. Kinetic images of solution-phase growth of the SAM shows the nucleation of the $solid_1$ phase, with the thiolate molecules lying flat on the substrate, followed by gradual coalescence of the $solid_2$ phase, where the thiolate molecules project upward with the usual 30° cant from the Au surface normal.[66,67] The thiols either etch the gold surface or cause it to reconstruct with time, and the resulting etch pits (and/or pits formed by reconstruction of the surface) are present in Fig. 5a as dark regions one atom deep.

Larsen et al. examined the effect of ink concentration, printing time, and inking "technique" on the quality of stamped SAMs (Fig. 5b).[62] For an inking concentration below 0.1 mM, a disordered SAM results; between 0.1 mM and 1 mM, the $solid_1$ phase is the product; between 1 mM and 10 mM, the $solid_1$ phase is replaced by $solid_2$; and for ink concentration above 10 mM, the stamped gold is

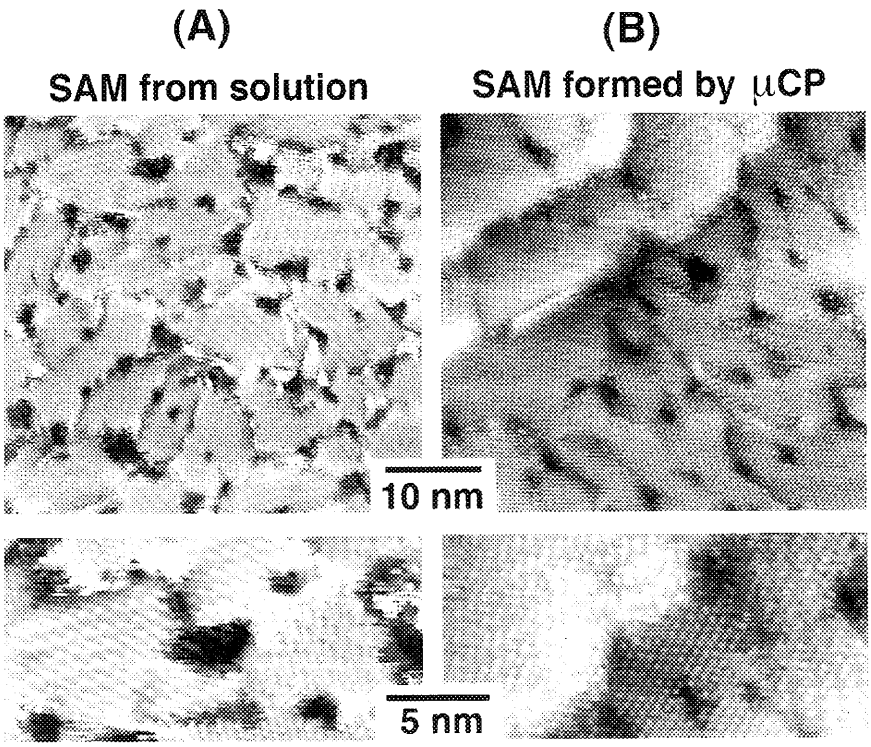

FIG. 5. STM images of SAMs of dodecanethiolate on single-crystal Au. (a) Solution-grown SAMs. (b) SAMs formed by μCP. (From ref. 60.)

indistinguishable from well-packed solution-grown SAMs on gold. Apparently the quality of stamped SAM is independent of time, provided that a printing time of ≥ 0.5 sec. is used. (When stamping a pattern, printing times of ≥ 1 min. are inadvisable because vapor transport of the thiol from the recessed areas of the stamp to the surface will eventually functionalize the unstamped areas.) To obtain reproducible stamping, the researchers adopted the standardized inking procedure of placing drops of solution directly on the stamp, letting the solution and stamp equilibrate for 30 sec., and blowing dry with N_2 for an additional 30 sec. With such an inking procedure, stamping becomes highly reproducible, and the only variable affecting stamped SAM quality is ink concentration. *Ink concentration of ≥ 10 mM in ethanol and printing time of ≥ 0.5 sec. results in stamped monolayers indistinguishable by STM with solution-grown monolayers.*

The third issue involved in μCP is the question of stamp distortion: How well can the pattern on the stamp be replicated on the substrate? The softness of PDMS is expected to cause some distortion in the stamp during μCP, and substantial distortion may lead to a limit on the ability of μCP to register submicron features. To quantify this distortion, Rogers et al. examined distortions in test grids using Moire patterns.[68] In these experiments, a stamp with a square pattern is brought into contact with a substrate with the same square pattern on its surface (made by lift-off of Au). Any distortion, whether angular or lateral, leads to the characteristic, visible features in the Moire pattern, and these features can be recorded by a CCD camera for analysis. The distortion was defined as the maximum distance between the grid square on the PDMS stamp and that on the surface, and the distortion across a 0.5×0.5 cm^2 area was found to be ~ 500 nm. The least distortion occurred with thin (~ 1 mm) stamps cast from PDMS with a 1:5 mix of curing agent to monomer.

With careful technique, it is possible to generate SAMs indistinguishable from solution-grown SAMs with μCP, with a registration accuracy of at least 0.5 μm over a 0.5×0.5 cm^2 area. The SAM systems used in μCP are listed in Table 2.

TABLE 2
SAM SYSTEMS USED WITH μCP[26,48,69,71,72,98]

SAM Precursor	Substrate
$CH_3(CH_2)_nSH$, $HO_2C(CH_2)_nSH$	Au, Ag, Cu, GaAs, Pd
$CH_3(CH_2)_nSiCl_3$	SiO_2, SiOH, glass, surfaces presenting —OH groups or other polar functionalities
$CH_3(CH_2)_nPO_3H_2$	Al
$CH_3(CH_2)_nCO_2H$	Al

Among the SAM precursors used in μCP, CH_3-terminated thiols on gold[26] and silver[48] have been the most widely used systems because they are the most straightforward SAMs to form with μCP. Stamping on Cu[69] leads to multilayers, although the formation of multilayers appears to be a property of SAMs of alkanethiolates on Cu rather than any particular oddity of μCP on Cu. Stamping with polar molecules such as $HS(CH_2)_nCO_2H$ leads to nonuniform stamping or stamping that results in more than a monolayer being deposited[70] since the SAM precursor tends to crystallize from solution. Stamping of alkylsiloxanes also often leads to multilayers[71] (again this appears to be characteristic of the SAM system rather than peculiarities in μCP). Stamping thiols on Pd and alkylphosphonic and carboxylic acids on Al is in development[72]: Preliminary results have shown that SAMs do form in the case of thiols on Pd and acids on Al and that these SAMs are ordered enough to act as barriers to etching. Other systems, such as hydroxamic acids on refractory metals,[73] isonitriles on Pt,[74] and alcohols on Pd,[75] have not been explored and remain targets for future development of μCP.

8.3 Patterned Hydrophobic SAMs as Ultrathin Resists

Homogeneous CH_3- and CF_3-terminated SAMs have long been known to protect the underlying substrate from corrosion and etching. The ability of these SAMs to act as a barrier stems from their inherent low defect densities, nearly crystalline packings, and hydrophobic natures; these characteristics render the films relatively impermeable to water vapor and oxygen. Thus, a film of Ag, when protected by a SAM of hexadecanethiolate, can be kept in ambient air for several months with no visible corrosion. Without the SAM, a piece of Ag tarnishes in air after only a few days. This property has naturally motivated the application of μCP toward patterning thin films by etching or gaseous CVD. In pattern delineation by etching, a surface patterned by μCP is simply placed in a wet etchant, and a patterned thin film develops due to the difference in etch rates between SAM-covered and bare regions. In regions covered with a SAM, etching proceeds slowly—probably initially at defects and grain boundaries in the SAM—while attack on underivatized substrate is unhindered and rapid. This contrast in etch rate can be used to generate a patterned thin film; this film itself can act as a resist for etching the underlying substrate in a subsequent process step. For wet etching, the most appropriate SAMs to use are the hydrophobic CH_3- and CF_3-terminated ones since hydrophobic interactions between patterned SAM and surrounding aqueous wet etch seems to enhance the barrier properties of the SAM.[76]

The use of patterned SAMs as ultrathin resists against etching has been recently reviewed by Xia et al.,[77] and we will only mention general points here.

TABLE 3
ETCHANTS AND EDGE RESOLUTIONS ACHIEVABLE BY μCP[72,77]

SAM System	Etchant	Edge Resolution (nm)
$CH_3(CH_2)_nSH/Au$	Ferricyanide	200
$CH_3(CH_2)_nSH/Ag$	Ferricyanide	50
$CH_3(CH_2)_nSH/Cu$	Ferricyanide	500
$CH_3(CH_2)_nSH/Pd$	Ferricyanide	≤ 1000
$CH_3(CH_2)_nPO_3H_2/Al$	Phosphoric acid	≤ 1000

Table 3 lists typical edge resolutions achievable with different SAM systems and etchants; typical examples of etched films are shown in Fig. 6. For patterning of coinage metals by μCP, Ag appears to be the most suitable element since its reactivity lies between that of Cu and Au. The high reactivity of Cu causes SAMs of alkanethiolates on Cu to be less ordered and more permeable to wet etchants than are SAMs on Ag; the relative inertness of Au necessitates the use of harsh etchants that tend to pit SAM-covered regions substantially.

From a purely materials point of view, Ag is preferable due to the small grain size observed in evaporated thin films. Since wet etching occurs most rapidly at grain boundaries, patterning of Ag has a higher potential edge resolution than patterning of Au. Films of Ag plated by electroless deposition can be used in place of e-beam-evaporated Ag. However, the rougher metal surface produced by electroless plating results in rapid spreading of the thiol during μCP, and stamping time must be carefully controlled in order to obtain a patterned SAM with distinct features.[56] Whether electrolessly plated or deposited by e-beam evaporation, over 200 nm of Ag can be etched before etch pits nucleate in the SAM-covered regions. The patterned Ag layer is itself thick enough to function as a etch resist for the underlying substrate, be it SiO_2 or Si, and by alternating etch steps with shadow evaporation it is possible to generate unusual Si topographies in the Si bulk[78] (Fig. 7). The underlying layers can also be etched completely to yield free-standing Ag shapes.

The key question when etching is: What is the density of defects? The density of defects after etching-stamped Au or Ag has not yet been ascertained per se, but a useful approximation—based on the similarity between STM images of stamped and solution-grown films—is the density of defects observed after etching solution-grown SAMs on Au and Ag.[79] For solution-grown SAMs, the defect density was measured by etching derivatized Au or Ag layers for various times and then etching with a KOH-based Si etchant. The hydroxide etch selectively attacked the Si layer over the Ag and amplified any defects in the etched metal into the Si layer; these defects could be counted directly by inspection with an SEM. The density of defects in SAMs of hexadecanethiolate

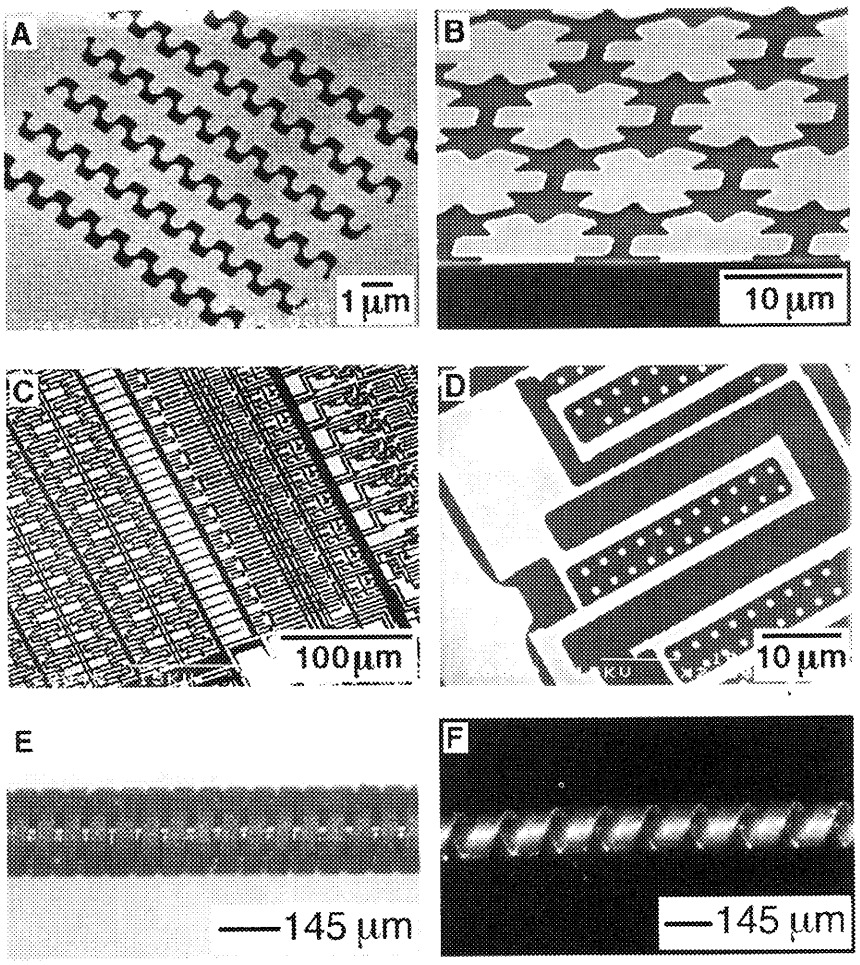

FIG. 6. SEM images of films of Ag etched using SAMs printed with μCP as resists. (a, b) 50-nm-thick patterns, stamped in a rolling configuration. (c) 50-nm-thick patterns, stamped in a planar configuration. (d) 200-nm-thick patterns, stamped in a planar configuration. (e) 100-nm-thick patterns, stamped on a capillary. (f) 100-nm-thick free-standing patterns, fabricated by patterning the Ag and dissolving the underlying capillary with HF. (From refs. 54 and 55.)

on Ag has been found to be much lower than that in SAMs on Au: $\sim 0.1/\text{mm}^2$ versus $\sim 100/\text{mm}^2$. Although these values may still be too high for certain applications (e.g., in microelectronics), often all that is required is a conducting metal film, and for these types of applications, the defect density of $\sim 0.1/\text{mm}^2$ of

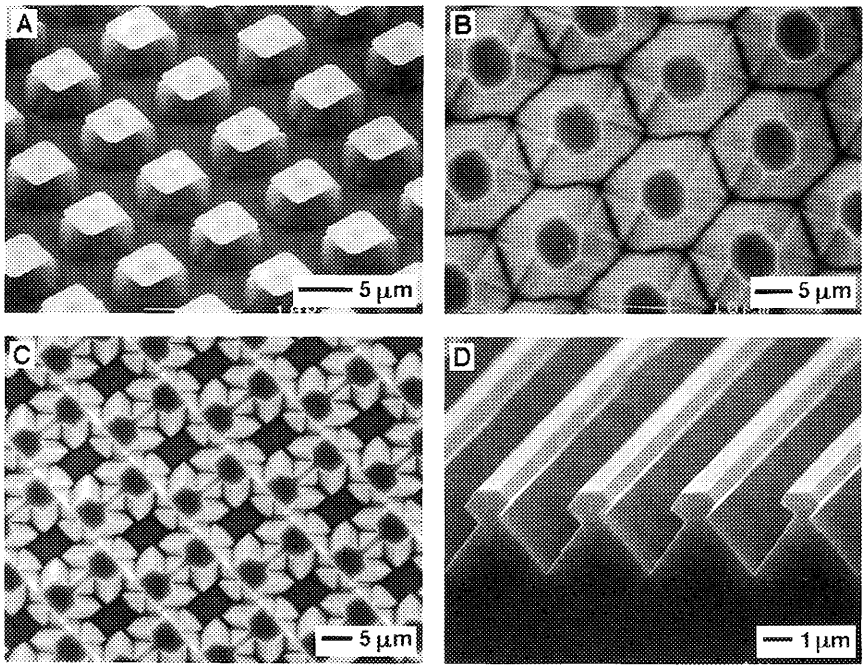

FIG. 7. SEM images of shapes etched into Si using a combination of μCP, selective etching, and shadow evaporation of gold. Gold was selectively etched using a ferricyanide etch. Silicon was selectively and anisotropically etched using a mixture of KOH, isopropanol, and water. (From ref. 52.)

SAMs on Ag is small enough to be useful. We also believe the defect density can be lowered with a judicious choice of components for the SAM—perhaps a branched thiol would be more protective than the straight-chain $HS(CH_2)_nCH_3$—along with more careful metal film preparation. Both approaches are currently under investigation.

While wet etching has been successful at producing fine features of Au, Ag, and Cu, sometimes it is desirable to pattern a film for which there is no known SAM chemistry (e.g., tungsten and ceramics) or for which the SAM system is not sufficiently robust to withstand wet etching (e.g., HF attack on alkylsiloxanes). In these cases, the ability of CH_3-terminated SAMs to resist nucleation of metal and dielectrics in chemical vapor deposition (CVD) can be used to pattern thin films by μCP.[80,81] In this application, SAMs of alkylsiloxanes are printed on oxidized surfaces, and nucleation via CVD occurs most rapidly on surfaces that are not covered with a SAM. In CVD, the driving force for nucleation is the temperature-controlled decomposition of a metastable gaseous precursor onto a heated

substrate; bonds form between the decomposing organometallic precursors and the surface during nucleation of a thin film.[82] Hydrophobic SAMs have no reactive functionalities, so the likelihood of nucleation onto those surfaces is limited to the probability that the gas penetrates through the SAM and nucleates a film directly onto the underlying substrate. Such penetration is unlikely with a well-ordered and dense SAM, and there is a substantial difference in deposition rates on SAM-covered and bare regions; this difference allows patterned thin-film deposition. Among the materials that have been patterned are Cu, Pt, and ceramics such as $LiNbO_3$; representative examples of deposited films are shown in Fig. 8. Nevertheless, the sticking probability on SAM-covered regions, while small, is nonzero, so the passivating properties of the CH_3-terminated SAM slowly erode with time. In general, ~ 0.2 μm of material can be deposited onto unpassivated regions before islands nucleate beneath the hydrophobic SAM. This thickness is sufficient for using these patterned films as wet etch resists for the underlying material. Selective thin-film deposition through μCP and CVD thus provides a complementary alternative to wet etching for the generation of patterned microstructures.

8.4 Two-Component Patterned SAMs as Templates

Hydrophobic SAMs patterned with μCP may be convenient resists against wet etchants and gaseous attack but do not take full advantage of the unmatched control over surface chemistry that μCP offers. In this section, we review the use of *two*-component SAMs—those containing not only CH_3-terminated SAMs but also SAMs with other functionalities—as templates for patterning of polymers, crystals, and biological cells. Two-component SAMs are made by printing one SAM (typically the most hydrophobic) followed by solution-phase derivatization of the unstamped regions with another SAM. The versatility of this approach allows different functional groups to be localized on a surface and enables interesting applications not accessible with other techniques.

The simplest application involves the idea of selective wetting and dewetting on surfaces patterned with CH_3- and CO_2H-terminated SAMs (Fig. 9). In this approach, a drop of hydrophilic prepolymer is placed on top of the patterned wafer, and the excess liquid is removed either by tilting the substrate and slowly decanting the prepolymer from the surface or by blowing gently on the substrate with a stream of N_2. If the surface free energy of the prepolymer is higher than the surface free energy of a CH_3-terminated surface, the liquid will retract from the hydrophobic regions and wet only the hydrophilic parts. Many prepolymers have sufficiently high surface tensions to be used in this procedure, and among the polymers successfully patterned are polyurethane and polymethylmethacrylate

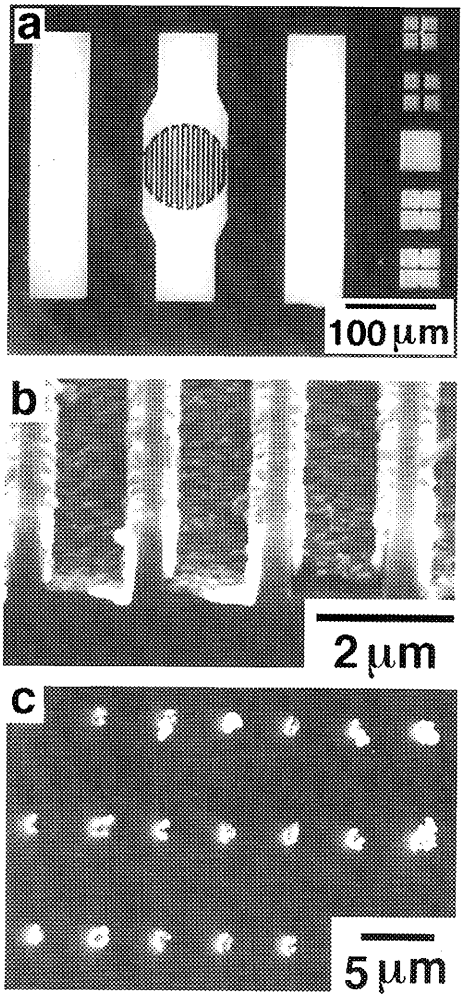

FIG. 8. SEM images of patterned thin films grown by selective CVD on surfaces patterned with alkylsiloxanes. (From ref. 80.)

(PMMA). These prepolymers can then be cured to make the pattern permanent. Among the structures made with this technique are waveguides,[83] microcrystals, diffraction gratings, and microlenses.[84] By performing the dewetting under water, it is possible to invert the roles of the CH_3- and CO_2H-terminated SAMs so that the polymer remains only on the hydrophobic patches. In this way, it is

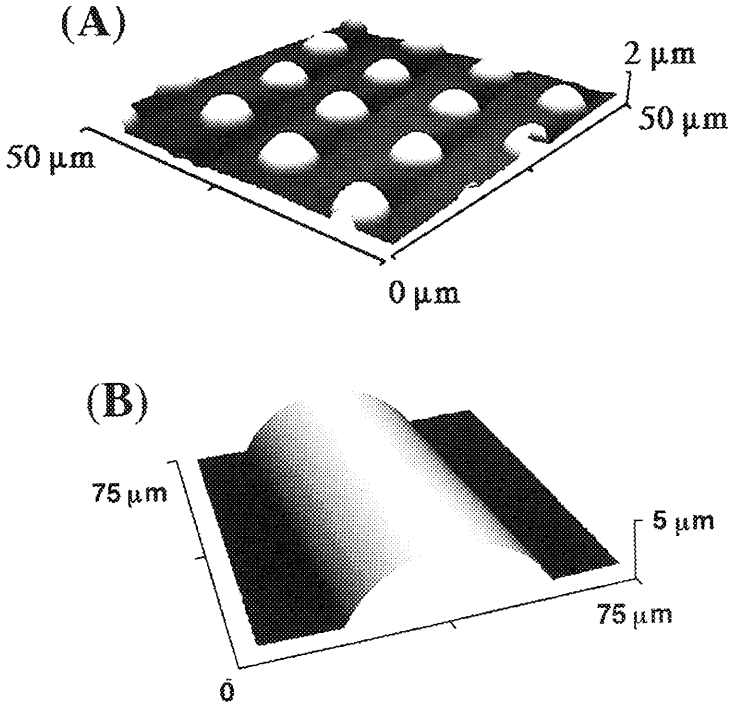

FIG. 9. Atomic force microscope images of patterned polyurethane fabricated by dewetting off a surface with hydrophobic and hydrophilic regions. (a) An array of squares. (b) A waveguide. (From ref. 83.)

possible to make PDMS shapes with constant Gaussian curvature,[85] as well as patterned films of hydrocarbon.[84]

A representative application of polymer dewetting with μCP is in the fabrication of waveguides. Although we now prefer to make waveguides by other soft lithographic techniques such as micromolding in capillaries (MIMIC)[34,86] and microtransfer molding (μTM),[36] dewetting and μCP still remain a viable technique for waveguide fabrication. Waveguides channel light; the one prerequisite for waveguide operation is that the index of refraction of the waveguide is larger than that of the surrounding material (often another transparent material, known as *cladding*). The waveguide shown in Fig. 9b was pulled from a polyurethane-based prepolymer and measures ~ 5 μm high and ~ 45 μm wide. When a He-Ne laser with rotationally symmetric Gaussian output was coupled into the end of one of these waveguides, a multimode asymmetric

output was emitted from the other end of the polymer. This asymmetry results because the waveguide used was itself highly asymmetric. By using slightly more hydrophobic prepolymers for the waveguide, it is possible to change the cross-sectional shape of the waveguide and thus tailor its waveguiding properties.

Another application of selective wetting with μCP is in the use of condensation figures, the array of water drops that appear when water vapor is passed over a cooled substrate.[87] Since water vapor condenses on hydrophilic substrates at a lower humidity than on hydrophobic regions, it is possible to use a surface patterned with CH_3- and CO_2H-terminated SAMs as a humidity sensor. At low humidities, there is no condensation, and at near-saturation, water condenses regardless of surface termination. But at intermediate humidities, a condensation figure forms that replicates the hydrophilic regions. If a periodic pattern is used, then the array of water drops form a diffraction grating, and the diffracting intensity of this grating is highly sensitive to the amount of water nucleated. Thus the patterned SAM can act as a simple humidity sensor.

Surfaces patterned with hydrophobic and hydrophilic SAMs can, however, be used for more than dewetting. In particular, selective nucleation on the hydrophilic regions can be applied to obtain patterned growth of organic and inorganic crystals. Here, we take a cue from studies of ice nucleation under Langmuir-Blodgett films of long-chained carboxylic acids: The hydrophilic areas act as "seeds" to nucleate crystal growth, with crystal orientation determined primarily by the conformation of the hydrophilic end group. In our work with inorganic crystals, we have focused on the growth of $CaCO_3$ on CO_2H-terminated SAMs. Single crystals grown on CO_2H-terminated SAMs are tilted with respect to the surface normal. This finding indicates that crystals of $CaCO_3$ nucleate in a specific conformation with respect to the templating acid groups, and has enabled the prediction of the cant angles for SAMs of alkanethiolates on other materials such as Pd and Au/Ag alloys. As a result, crystal growth on SAMs has emerged as a convenient tool for obtaining molecular-scale information about the conformation of a SAM using simple "macroscopic" techniques. We can also change the polymorphism of the grown crystals by varying pattern sizes.

As for organic crystals, diketopiperazine will selectively crystallize from solution on regions with the same termination when presented with a surface patterned with Me-terminated and diketopiperazine-terminated alkanethiolates. Similar results are obtained for crystallization of benzonitrile on similarly terminated SAMs.[88] The original intention was to use patterned SAMs to assist in the growth of large organic crystals for X-ray diffraction studies. This goal has proven elusive; the organic crystals appear under SEM to be amorphous with no apparent crystal faces. Nevertheless, μCP provides a convenient route for patterning organic compounds, which is a capability not readily obtained with other techniques for patterning SAMs.

In most of these examples, the templated material grows on the hydrophilic surface; the hydrophobic surface is inert toward chemical reaction and generally resists attachment of materials from vapor or organic solution. The opposite is true in the case of protein adsorption from water; in these adsorptions, hydrophobic interactions dominate. Proteins adsorb from aqueous solution onto any surface with a moderate hydrophobicity, presumably through interactions between recessed hydrophobic patches on the protein and hydrophobic moieties on the surface. The surfaces that best resist protein adsorption expose oligo(ethylene glycol) moieties; the mechanism of this inertness to adsorption is still controversial. When the initial μCP of Me-terminated thiols is combined with a subsequent wash with oligo(ethylene glycol)-terminated thiols, the adsorption of proteins can be directed onto only the CH_3-terminated regions[89,90]

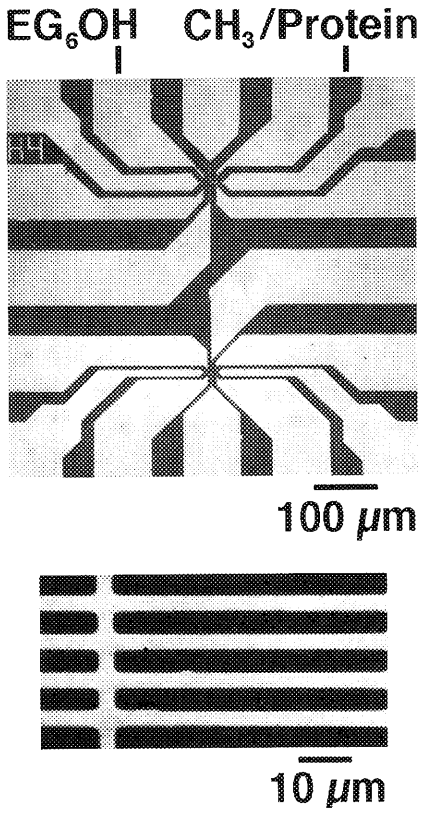

FIG. 10. SEM images of adsorption of fibronectin on surfaces patterned with hydrophobic and oligo(ethylene glycol)-terminated ($-(EG)_6OH$) SAMs. (From ref. 91.)

(Fig. 10). This procedure is very general and has been demonstrated for fibronectin[91,92] and laminin.[6] Other hydrophilic SAMs, such as the oligo(propylene sulfoxide)-terminated ones, also resist protein adsorption.[93] With patterned proteins, one can direct the growth of cells (Fig. 11)[91,94,95]; this ability to control cell growth has afforded investigations into basic questions about cell spreading and apoptosis.[91,92,96]

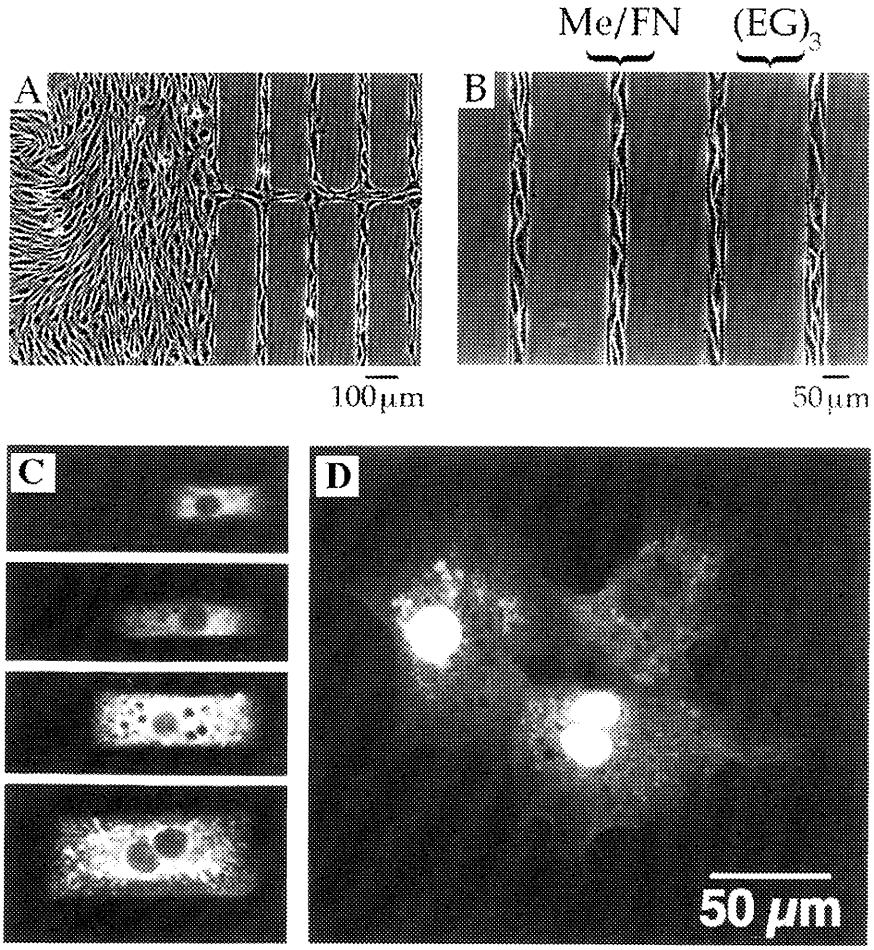

FIG. 11. Optical micrographs of cells grown on surfaces patterned with adsorbed protein. (a, b) Bovine endothelial cells plated on patterned fibronectin. (Me = CH_3-terminated SAM, FN = fibronectin, $(EG)_3$ = $HO(CH_2CH_2O)_3$-terminated SAM) (c) Primary rat hepatocytes plated on patterned laminin. (d) Hepatocytes plated on unpatterned laminin. (From refs. 6 and 91.)

8.5 Conclusions

Microcontact printing has emerged as the technique of choice for patterning self-assembled monolayers. Its ability to pattern SAMs with μm-scale linewidths and nm-resolution perpendicular to the plane over an entire 3-inch wafer in one imprint, its ability to pattern curved surfaces, its ease of use, its unique control over surface chemistry—all these qualities make μCP a powerful new technique for micro- and nanolithography, and highly complementary to photographic, lithographic, and mechanical patterning. We believe that μCP will form the basis for many applications in biology and biochemistry that use functional groups more complex than the usual CH_3 or CO_2H terminations. SAMs formed by μCP are indistinguishable by STM from SAMs adsorbed from solution; their high degree of order makes it possible to use μCP to pattern thin metal films and to use these films as resists for wet etching. Indeed, if the defect density could be reduced by one or two more orders of magnitude, μCP would immediately become a serious contender for fabrication of sensors, SAW devices, and similar simple microstructures in a relatively low-resolution single-layer fab. The capital cost of μCP is also low. All that is required is PDMS (commercially available in quantity) and alkanethiol ($50 buys $\sim$ 100 mL of alkanethiol, which is enough to make $\sim$0.5 L of inking solution). The disadvantages of μCP—problems with registration, deformation of the stamp, sagging, and defects—become significant only for feature sizes less than 1 μm and for certain types of patterns that encourage sagging and buckling; we have not come close to reaching the "theoretical" limit of this technique. Our experience with μCP has relied mainly on one system—PDMS and alkanethiols—and optimization of each component will surely lead to even greater capabilities for μCP.

In the cutting edge of microelectronics, where linewidths are approaching 100 nm and future fabrication facilities may require in excess of a billion dollars in capital investment, it would be presumptuous to believe that μCP will be competitive with photolithography. Even if μCP were able to pattern 100 nm lines and spaces over large areas with ease (and we believe this will be achieved in the next few years), the existing lithographic technology is so well-established it is doubtful μCP will ever be adopted there. However, for systems requiring features substantially smaller than 100 nm, which projection photolithography (as it is currently practiced) cannot reach, there may be a role for μCP or for other forms of soft lithography.

In the fledgling arena of microelectromechanical and microfluidic systems, however, alternatives to microlithography such as embossing and μCP are seriously being considered. Here, it is not so crucial to have ever-smaller features; in fact, most feature sizes range between 10 μm and 100 μm, well within the capabilities of μCP. Using a silicon-based fab for making such devices is a bit of