Lithography beyond light: Microcontact printing with monolayer resists

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We describe high-resolution lithography based on transfer of a pattern from an elastomeric "stamp" to a solid substrate by conformal contact: a nanoscale interaction between substrate and stamp on macroscopic scales that allows transport of material from stamp to substrate. The stamp is first formed by curing poly(dimethyl siloxane) (PDMS) on a master with the negative of the desired surface, resulting in an elastomeric solid with a pattern of reliefs, typically a few microns deep, on its surface. The stamp provides an "ink" that forms a self-assembled monolayer (SAM) on a solid surface by a covalent, chemical reaction. Because SAMs act as highly localized and efficient barriers to some wet etches, microcontact printing forms part of a convenient lithographic system not subject to diffraction or depth of focus limitations while still providing simultaneous transfer of patterned features. Our study helps to define the strengths and limitations of microcontact printing with SAMs, a process that is necessary to assess its worth to technology. We used lithography based on scanning tunneling microscopy (STM) to demonstrate that disruption of SAMs on gold allowed the formation of etched features as small as 20 nm using a CN^-/O_2 etch. This result implied that etching occurred where damage of a few molecules in the ordered SAM allowed passage of cyanide, whereas adjacent molecules in the SAM remained unperturbed at this scale. Features as small as 30 nm etched in gold over areas greater than 1 cm^2 resulted from microcontact printing with replicas of electron-beam-formed masters, with the transfer of these printed SAMs requiring only ≈1 s. STM studies of these transferred SAMs revealed an achievable order indistinguishable from that found for SAMs prepared from solution. Facile alignment of printing steps at submicron scales may result from new designs of stamps that exploit their limited deformability and lock-and-key-type approaches to mate stamp and substrate.

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Introduction

A special *Journal* issue that examines the state of the art in optical lithography is, perhaps, an odd place for discussions of a method of pattern formation that requires no light. Stranger still, the method we describe—microcontact printing—is new but borrows from principles of printing that are centuries old. This method suggests alternatives to fabrication at ever smaller dimensions while maintaining manufacturability [1, 2]: Microcontact printing provides simultaneous transfer of patterns over areas greater than 1 cm^2 without diffraction or depth-of-focus limitations. In this paper we demonstrate that a contact between a substrate and an elastomeric stamp on macroscopic scales, together with the transfer of self-assembled monolayers (SAMs), constitutes a high-resolution lithographic system (**Figure 1**).

SAMs typically form by chemisorption of molecules from a dilute solution onto a substrate [4]. Whitesides and co-workers at Harvard University discovered in 1993 that SAMs also form on a solid surface by contact with a polymer "inked" by an alkanethiol [5, 6]. This type of self-assembly is self-passivating and forms surfaces of low interfacial tension that repel additional molecular layers so that SAMs form only in areas of conformal contact between the polymer and substrate. Stamps made with a pattern of reliefs on their surface thus allow the accurate reproduction of their area of contact with a substrate by leaving behind a patterned monolayer in a manner reminiscent of printing. We use the term *conformal contact* to describe the molecular-scale interaction that occurs between the raised regions in the elastomer and the substrate where the elastomer matches its contours on scales from nanometers to meters. No such contact occurs in regions of the elastomer where the reliefs are sufficiently deep. Printing of material onto substrates at high resolution (less than 1 μm) over areas reaching several square centimeters (or larger) provides the name for this approach to fabrication: *microcontact printing*, or μCP.

Microcontact printing is not capable *per se* of making patterns. The formation of a useful series of reliefs on the surface of a stamp typically relies on replication of a master in an elastomer (Figure 1). Microcontact printing is intrinsically parallel; that is, all of the features on the stamp transfer simultaneously, so its combination with a high-resolution master might allow the practical fabrication of meso- and nanoscale structures. Here, the time invested in forming the high-resolution master is amortized by making many replicas, each capable of parallel pattern transfer and repeated use. Microcontact printing shares some attributes with the more familiar contact printing already explored extensively by the optical lithography community: It relies on the proximity of a stamp and a substrate and transfers a pattern at a 1:1 ratio. Microcontact printing differs from its namesake, however, in two important ways. First, pattern transfer is effected directly on contact by a molecular-scale interaction between the stamp and substrate, resulting in a highly controllable chemical modification of the substrate. Chemical diffusion of the contacting ink on the surface of the stamp is, in the best cases, completely contained by the swollen elastomer-reactant phase, so reactions occur only in areas of conformal contact. Second, the stamp is formed, in all of the most convincing demonstrations to date, from an elastomer based on PDMS that accommodates the substrate topography by deformation. Microcontact printing is not subject to diffraction limitation but, instead, is restricted by the intrinsic structure-forming capability of elastomers and by the effects of distortion during the printing process [7].

Elastomer-based microcontact printing has several advantages: 1) The deformability of the stamp allows it to accommodate rough surfaces. Nanoscale asperities are readily subsumed by the μCP process [8]. More challenging topographies do not cause macroscopic alteration of the printed pattern, although local deformation (typically over a scale of a few microns) occurs. Microcontact printing works equally well on spherical substrates (such as optical fibers or lenses), even where these substrates have radii of curvatures less than 10 μm [9]. Strategies for making stamps that match, and thus compensate, the substrate topology are an obvious next step in the development of microcontact printing. 2) Elastomers based on PDMS come from an extensively studied family of polymers that are largely inert and commercially available in a wide range of molecular weights with many combinations of other polymers possible. PDMS does not adhere to novolac or poly-methyl-methacrylate (PMMA)-based polymers, allowing convenient replication of masters formed by electron-beam lithography. 3) Microcontact printing works best where the stamp acts as a dense sponge, taking up liquid in a region largely limited to the surface of the polymer. PDMS can take up alkanethiols, for example, with no apparent change in dimension on scales greater than 20 nm, so that pattern transfer remains faithful to the features present on the original master.

Self-assembled resists

Self-assembly of molecules to more complex systems was first studied to provide fundamental understanding of its rules and consequences, with an eye toward mimicking Nature's spectacular use of these rules to form systems with high complexity at almost no cost [10–12]. Long before this understanding is reached, though, preliminary knowledge should be applicable to practical fabrication. One area where self-assembly can affect technology is the

formation of thin films of organic materials on inorganic substrates, such as the resists fundamental to optical lithography. Langmuir recognized that organic molecules, similar to those comprising the lipid part of our cells, ordered spontaneously at air–water interfaces and could be transferred to solid substrates [13]. Attempts to establish Langmuir–Blodgett monolayers as thin resists with well-defined composition and thickness failed, however, because of their generally low mechanical and chemical stability. Thin-film-forming reactions that directly attach lipid-like molecules to a substrate are similarly known (although they were discovered more recently) for a variety of materials: gold [4], silver [14], platinum [15], aluminum [16], silica [17], titanium [18], and zirconium [19]. The most extensively studied of these systems is based on organosulfurs that form SAMs on gold. Alkanethiols provide a particularly simple example of this group of compounds comprising an alkyl part terminated on one end by a nonreactive, hydrophobic methyl group, and on the other end by a moderately reactive thiol. Exposure of gold to the vapor, liquid, or a solution of an alkanethiol results in rapid self-organization of the thiol as a chemisorbed monolayer, 1–2 nm thick, on the surface of the metal. SAMs have predominantly crystalline order at room temperature, with structures that largely reflect the packing and interactions of the alkyl parts of the molecules in the film (**Figure 2**) [13]. Knowledge about order and structure in these films is continuously emerging from experimental investigations of the films' characterization using STM [20], X-ray, and He diffraction [21, 22], Fourier transfer infrared spectroscopy [23], and atomic force microscopy [24], among other techniques.

Macroscopic properties of the interface such as wetting and adhesion result directly from molecular properties of the groups present at the end of the SAM opposite the sulfur [25]. More localized properties of the interface are similarly dominated by the composition of these monolayers: Access to the underlying gold substrate by an electrochemical agent [26] or an etchant [27] is, under favorable circumstances, completely controlled by the presence of alkanethiols and their organization. SAMs might be particularly useful in eliminating or controlling the properties of surfaces that favor the accumulation of contaminants that otherwise confound pattern replication. Fluorinated SAM precursors form monolayers ≈1 nm thick with the same low wettability and resistance to adhesion characteristic of macroscopically thick films of TEFLON®. When a carboxylic-acid-terminated SAM is changed to a perfluoro-functionalized SAM, for example, the contaminant frequency decreases by several orders of magnitude because of the enormous change in the interfacial energy and reactivity of the surface [28]. Owing to their thickness and organization, SAMs are also a well-characterized alternative to organic resists based on

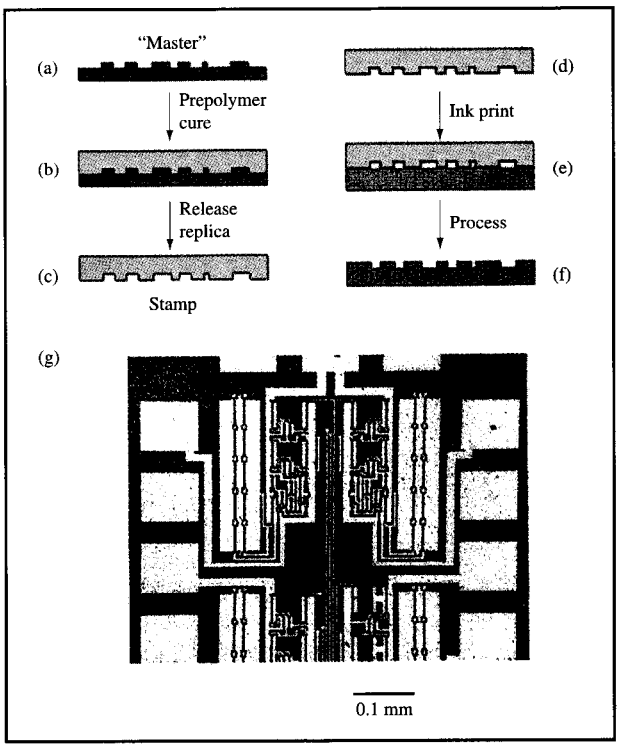

Figure 1

Scheme of microcontact printing: (a) The master is covered with a liquid prepolymer (b) cured by heat or light to form the elastomeric stamp. (c) The stamp, released (usually by a simple peel) from its mold, (d) is inked with an alkanethiol. (e) The stamp is brought into contact with a substrate, (f) where the alkanethiol self-assembles in areas of conformal contact between stamp and substrate to form a patterned SAM. Monolayer-coated areas resist subsequent etching by CN^-/O_2. (g) A scanning electron microscope image of a representative pattern of monolayers transferred by μCP (prior to etch). Image contrast results from the modulation of the secondary electron current by the presence of the 1-nm-thick monolayer [3].

polymers for applications requiring fabrication on the nanoscale. The ease of assembly of SAMs, their low cost, and their applicability to important technological substrates make this alternative interesting and possibly practical.

Our initial strategy for exploring microcontact printing relied on the formation of SAMs from hexadecanethiol [$CH_3(CH_2)_{15}SH$, HDT] to provide a protective layer for thin films of polycrystalline gold on silicon wafers, although other materials (e.g., silanes on Si/SiO_2 [29]) can also be applied by μCP. SAMs of HDT are hydrophobic, with a water contact angle of 115°. These SAMs have a thickness of 2 nm, where each molecule in the monolayer occupies an area of ≈0.21 nm^2 [25]. Gold exposed to a 0.1-M solution of cyanide in 1M KOH saturated with

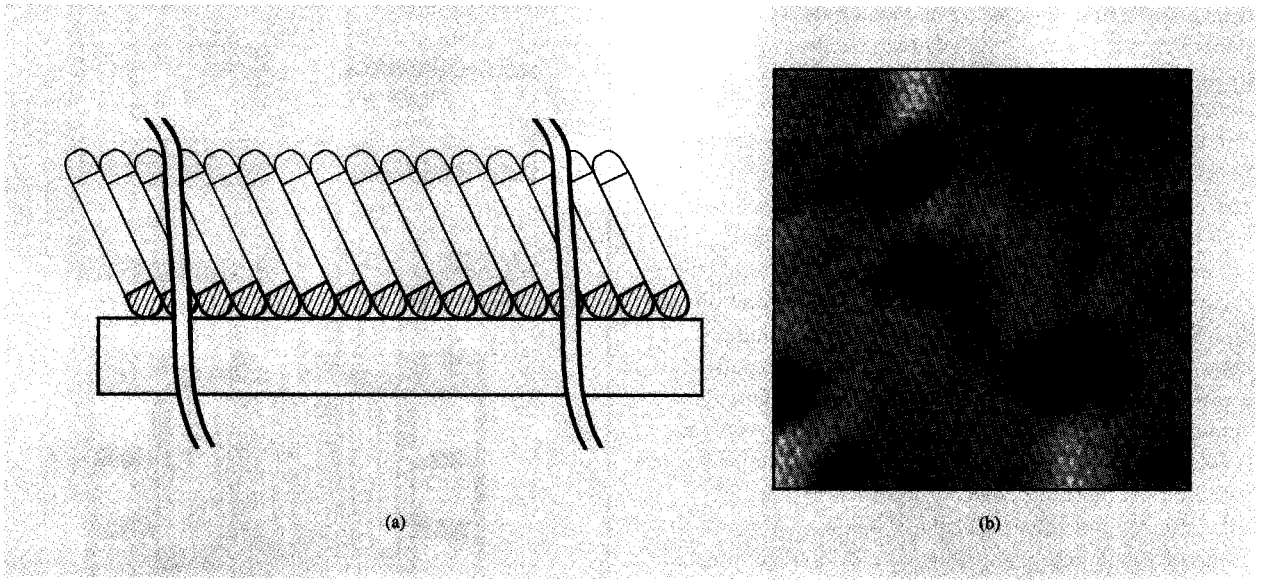

Figure 2

Structure of self-assembled monolayers: (a) Molecules order by chemisorption of their head groups on a substrate exposing their end groups to the interface. (b) STM image (21 × 21 nm^2) recorded at 0.9 V and 80 pA on dodecanethiol chemisorbed on Au(111), showing the molecular order of the end groups at the surface. This order extends into depressions of the gold surface (dark zones) and describes a basic hexagonal lattice with superstructural variations.

oxygen dissolves rapidly, reaching a rate of several angstroms per second for dissolution of its bulk [30]. Regions of gold protected by a monolayer of HDT etch 10^6 times slower in cyanide, however, allowing only marginal etching at defects distributed with densities lower than 0.01 per μm^2 in these SAMs. Few details of the relationship between the cyanide etchant and its diffusion through SAMs are known, but the poor solubility of the nonpolarizable cyanide anion in the low dielectric phase that constitutes one monolayer of HDT probably accounts for the contrast observed in etching "bare" or protected gold. Other etchants for gold, such as the polarizable I_3^- anion, show little difference in the dissolving rate of gold or SAM-protected gold.

The cyanide etch is isotropic, with no apparent preference for one particular crystallographic face of gold [31]. Thin films of polycrystalline gold, 10 nm thick, on silicon provided a useful support, because these films are flat (rms roughness <0.3 nm), easy to prepare, and similar to those already used in technology. The mean crystallite size in these films is ≈10 nm, with a predominant Au(111) texture. One significant drawback of polycrystalline substrates is that an important tool for characterization of the film, STM, no longer provides useful imaging of SAMs thus supported because the molecular structure of the SAM layer convolves with the gold topography.

Etching resolution of monolayer resists

We wanted to know more about the ultimate scale for pattern transfer into SAMs of HDT on polycrystalline gold using a cyanide etch. STM is obviously capable of nanoscale manipulation [32, 33] and thus is a convenient tool for delivering controlled, localized amounts of energy needed to activate (see below) the monolayer resist and therefore to nucleate etching in these regions [34, 35]. SAMs of HDT were formed by equilibration of polycrystalline, 10-nm-thick gold substrates in a 0.5-M solution of HDT in ethanol for at least 1 h. The samples were rinsed with ethanol and octane and dried under a stream of N_2 prior to their placement in the STM. The patterned samples were removed from the STM immediately after writing and put in a well-stirred bath of cyanide etchant held at room temperature. Removal of this sample after 100 s and rinsing with water and ethanol allowed its inspection by optical and scanning electron microscopy (SEM), as shown in **Figure 3**.

The features in Figure 3 resulted from scanning a tungsten tip mounted in our home-built STM [36] across the surface at speeds of 150–200 $\mu m/s$ while maintaining a current of 20 pA at 1 V with respect to the substrate. This level of dose corresponded to approximately 400 electrons per molecule in the SAM, or ≈100 nC/m, assuming that the tip–substrate conductance channels were localized to a

region 0.5 nm in diameter. [Note: This dose is three orders of magnitude *lower* than the dose we found for writing thin (≈2 nm thick) oxides into silicon. See also Reference [34].] Elastic tunneling is evidently not the only important process that takes place under these conditions: Irreversible damage to the barrier properties of the SAMs occurred in regions scanned by the STM tip even at moderate currents (10–100 pA).

Several possible processes may be involved, wholly or in part, in damaging SAMs by STM. Inelastic loss of electron energy, either nonresonant by resistive hopping or resonant by direct electron capture to form reactive radicals, is probably not favored at the fairly low energies of the electron current and given the generally nonreactive nature of SAMs derived from alkanethiols. Field-induced dissociation or disruption of the SAM cannot be ruled out by the data, although it remains unclear which chemical processes occur by these mechanisms at the intense but still moderate fields, compared to the ionization energies of molecules. Moreover, the localization of damage in the SAMs as inferred from the data does not support a simple, field-induced mechanism in which the potential decays algebraically from its source. Electrochemical processes, assisted perhaps by electromigration of adsorbates to the region between tip and SAM, may similarly play a role. The complex chemistry of the tip, its hydrophilic character, and the presence of titratable groups on its surface could all contribute to the disruption of the SAM by this mechanism. Finally, the effects of a physical interaction between surface and tip cannot be discounted. An accumulating oxide at the end of the tungsten tip could well favor this mechanism. "Scratching" techniques disrupt SAMs at scales of less than 100 nm by creating voids on the surface that are easily developed by the cyanide etch [37]. The observations of increasing feature size with current (and thus proximity to the surface) support this mechanism, provided an oxide limits the conductance between tip and surface.

The observation of 10–20-nm-wide, continuous, *etched* lines in 10-nm-thick gold suggests that the nucleation area required to initiate the cyanide etch on HDT-protected SAMs must be just a few molecules. Individual molecules in SAMs are clearly affected by the STM tip while leaving adjacent molecules in the SAM undisturbed. If more molecules were affected, wider etched features would result. In summary, the results from our STM lithography work demonstrated that HDT on polycrystalline gold allowed patterns to be formed at scales down to the crystallite size of this substrate. These data also demonstrated that intact molecules in SAMs do not diffuse at lengths of more than 10 nm over times of 1 h on polycrystalline gold and hence do not blur the pattern generated by STM lithography. A study of the resolution limits of μCP using HDT thus makes sense for thin gold substrates.

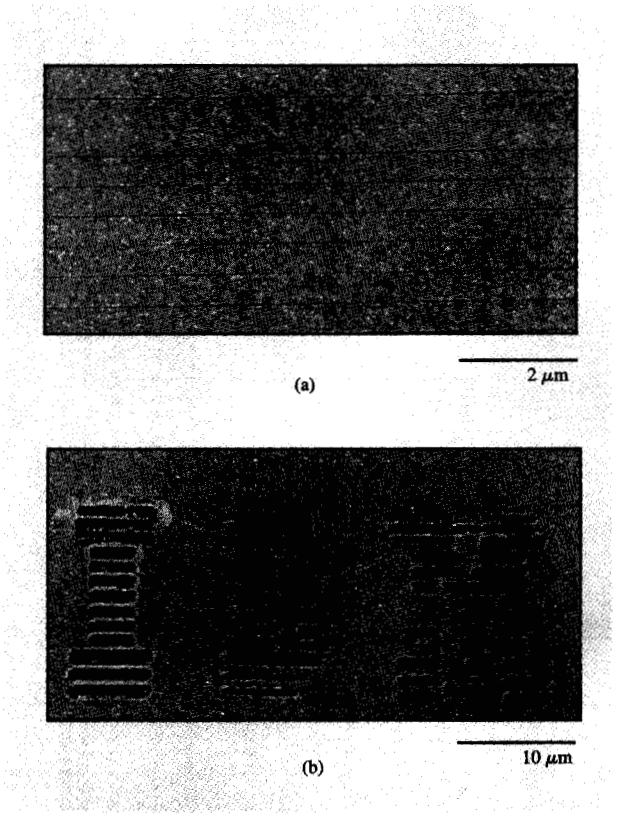

Figure 3

SEM images of polycrystalline gold surfaces on silicon patterned by STM lithography and etched by CN^-/O_2 for 100 s: (a) 20-nm-wide solid lines demonstrate smallest feature size. (b) The letters "IBM" demonstrate fast, large-area fill exposures and the ability to write controlled patterns by STM.

Transfer resolution of microcontact printing

Determination of the resolution limits of microcontact printing requires a thorough understanding of several parameters. Among the most important questions posed are, How is the replica best formed? What are the best materials for master and stamp? What pattern of reliefs can be accommodated in the surface of an elastomeric polymer? What aspect ratio is necessary? What order and structure characterize stamped SAMs? Our initial approach to these questions was to make the master for the elastomeric stamp in PMMA, so that the desired pattern of reliefs was wholly formed in the organic polymer. Development of PMMA with acetone after electron-beam writing provided the starting point.

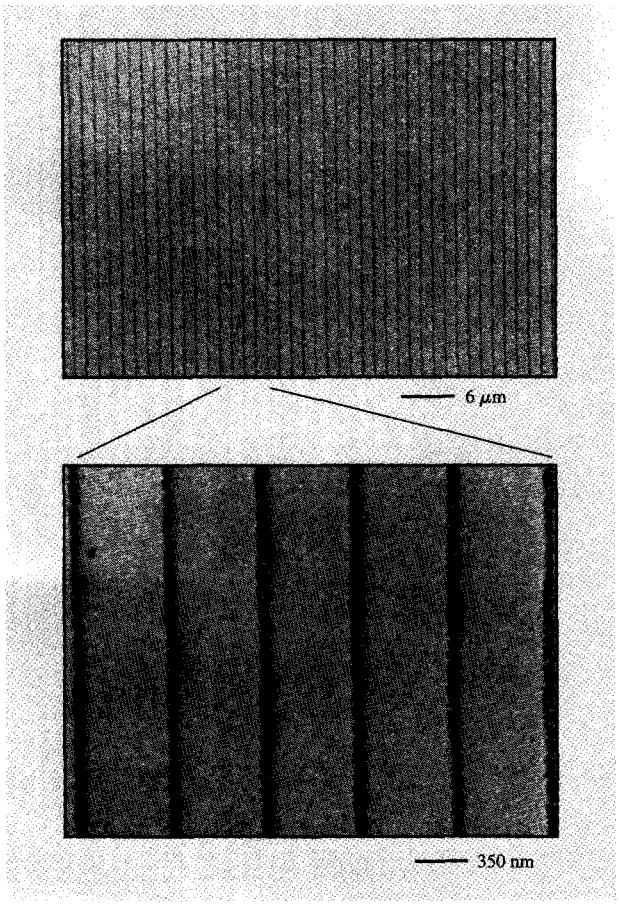

Figure 4

SEM images of gold features separated by narrow voids 35 nm wide produced by a cyanide etch using a SAM as resist. SAMs of HDT were stamped on the gold using a stamp replicated from an electron-beam-fabricated PMMA master.

High-energy electron-beam lithography is the most practical high-resolution lithography technique known [38]. Patterns written into resists with high molecular weight (such as PMMA) result from their depolymerization under moderate fluxes of electrons ($\approx$25 μC/cm^2 at 100 keV). PMMA resists provide useful barriers to a variety of liquid or gaseous etchants, allowing pattern transfer into the underlying base material. Electron-beam lithography answers all currently foreseeable needs of technology save one: Patterns are written sequentially, so mass production of devices by electron-beam lithography is not possible. The combination of electron-beam lithography and microcontact printing is thus particularly potent.

We used thin films of PMMA, 300 nm thick, supported on silicon wafers for masters. A prepolymer of PDMS, cured directly on a fluorinated PMMA master by heating at 70°C for 12 h, formed the stamp after its release from the substrate. The thickness of the stamp was typically 1 cm with a Young's modulus of $\approx 5 \times 10^6$ MPa after cure; the reliefs on its surface were $\approx$250 nm deep. "Inking" the stamp with HDT, "printing" the pattern by placing the replica by hand on top of the Au-coated substrate (like the substrates used for the STM lithography study) for $\approx$1 s, and developing the pattern using CN^-/O_2 resulted in gold features as small as 50 nm with spatial extents up to 4 cm (**Figure 4**). The stamp is not pressed onto the surface of the substrate as in conventional printing processes. Rather, it contacts the surface (gravity is not necessary to cause conformal contact between the stamp and substrate), so the only pressure experienced by the stamp is that due to interfacial forces [6].

The structures in Figure 4 depict the limit in feature size obtainable conveniently using the IBM electron-beam facility in Zurich (optimized to form large-scale features with dimensions down to 50 nm). The stamp was able to reproduce both high-curvature (radii of curvature less than 25 mm) and high-duty-cycle patterns (e.g., gratings with 100-nm features and 100-nm spacings) with no discernible loss of resolution or scale compared to the master. We noticed an increasing propensity to failure in the replication process, largely caused by the removal of PMMA from the surface of the master by the stamp as the feature scale shrank below 100 nm. We think that the wetted area between elastomer and master on high-aspect-ratio features, the poor adhesion of the PMMA film to the underlying silicon substrate, and the peel stress induced on release of the PDMS all contribute to the failure mechanism. In part, the solution to these problems lies in forming more robust masters, perhaps by a straightforward transfer of the pattern in PMMA to the underlying silicon. The high resolution of the stamped features nevertheless demonstrates the practical formation of nanometer-scale features using elastomeric stamps and alkanethiol resists.

Topography of stamps

We set up our first study of the vertical feature scale in stamps with the goal of understanding how material properties of the elastomer affect replication. Microcontact printing ideally requires a high aspect ratio (>1) between the depth of the features and their putative areas of contact so that boundaries between patterned regions remain sharp, at least to the extent allowed by intrinsic diffusion of the alkanethiols that comprise the monolayer. High-aspect-ratio features in a stamp cause loss of structural integrity of the feature, however, and are not useful in providing accurate pattern transfer. Thus, the formation of practical stamps requires a compromise between these two considerations.

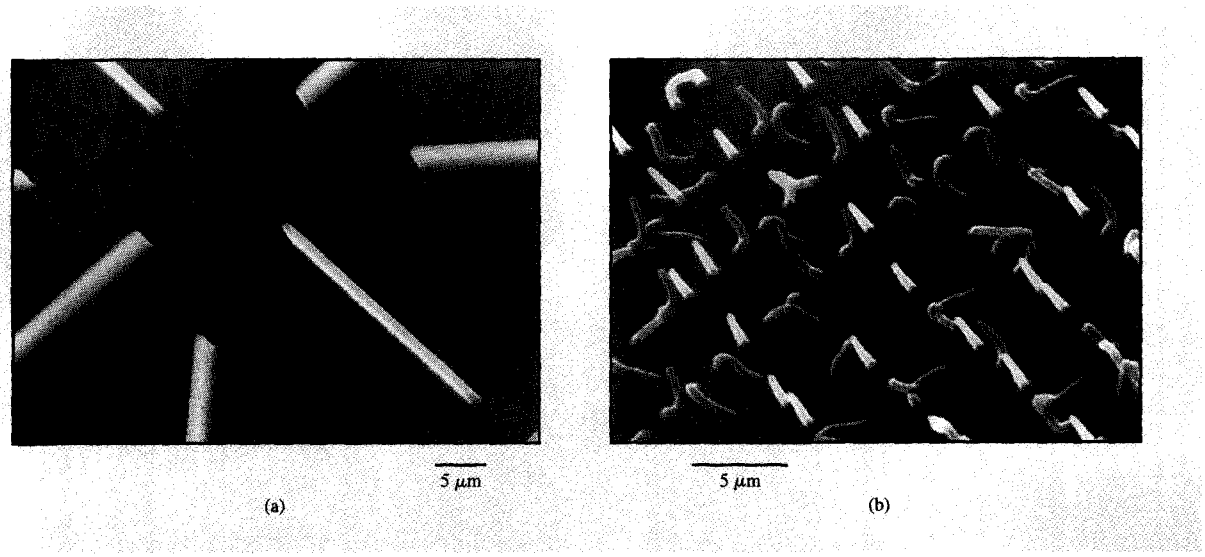

Figure 5

SEM images of gold-coated, patterned PDMS surfaces show effects of substrate topology on the structural integrity of features in the stamp: (a) Linear features 1 μm wide and 6 μm deep maintain their original structure. (b) Cylinders with a diameter of 1 μm and a height of 6 μm collapse under their own weight.

Masters formed in GaAs with patterns etched 6 μm deep into the substrate provided a survey of the effects of aspect ratio on the physical transfer of features to PDMS. **Figure 5** illustrates two outcomes for features replicated in PDMS that are at least six times deeper than their width. Figure 5(a) shows that areas supported along one dimension by continuous structures maintain their integrity even as the aspect ratio approaches 10. Figure 5(b) shows that similar features that are unsupported collapse under their own weight after their release from the material and thus clearly provide no opportunity for coherent pattern transfer. We found that the accuracy of stamped features remained good (<5%) for aspect ratios up to 1 for stamps made from PDMS with a Young's modulus of 5×10^6 MPa; beyond this ratio, features became increasingly distorted and irregular under the stresses associated with inking and interfacial contact between the PDMS stamp and gold substrate. These samples were also useful in demonstrating that relief structures with inherent aspect ratios of at least 0.3 are necessary (data not shown) to provide successful transfer of patterns at the <100-nm level. Below aspect ratios of 0.3, significant transfer of material occurred from areas *between* raised regions in the stamp, blurring the desired pattern. Well before the limit of no reliefs, at an aspect ratio of 0.05, no patterns are achievable. Whether stiffer materials or those with composite structures (i.e., materials comprising alternating elastic and brittle layers) will remove these constraints remains an open question, although several strategies toward their solution are obvious and plausible.

Structure of stamped monolayers

The monolayers that provided the object of structural study in all cases examined to date resulted from equilibration between the substrate and solutions of an alkanethiol or disulfide for long (1–48 h) times. What happens when a monolayer is formed by μCP remained unresolved. Microcontact printing of monolayers involves only transient contact between master and stamp, and, significantly, no bulk liquid phase is present that might assist formation of the film. Differences between these two methods of SAM preparation might then be reflected in measurable properties of the resulting monolayers.

We used STM to find out what happens when a monolayer is formed by μCP because STM produces real-space images of the molecular organization in stamped SAMs. We focused on characterizing monolayers of dodecanethiol [$CH_3(CH_2)_{11}SH$, DDT] stamped on epitaxial gold on mica. DDT rather than HDT was used for STM characterization of stamped monolayers because the two monolayers are similar, except that SAMs of DDT (0.6 nm thinner than SAMs of HDT) allow STM studies at more practical currents (several pA) than HDT (<1 pA). Au(111) on mica is a well-defined substrate that is particularly convenient for STM characterization because

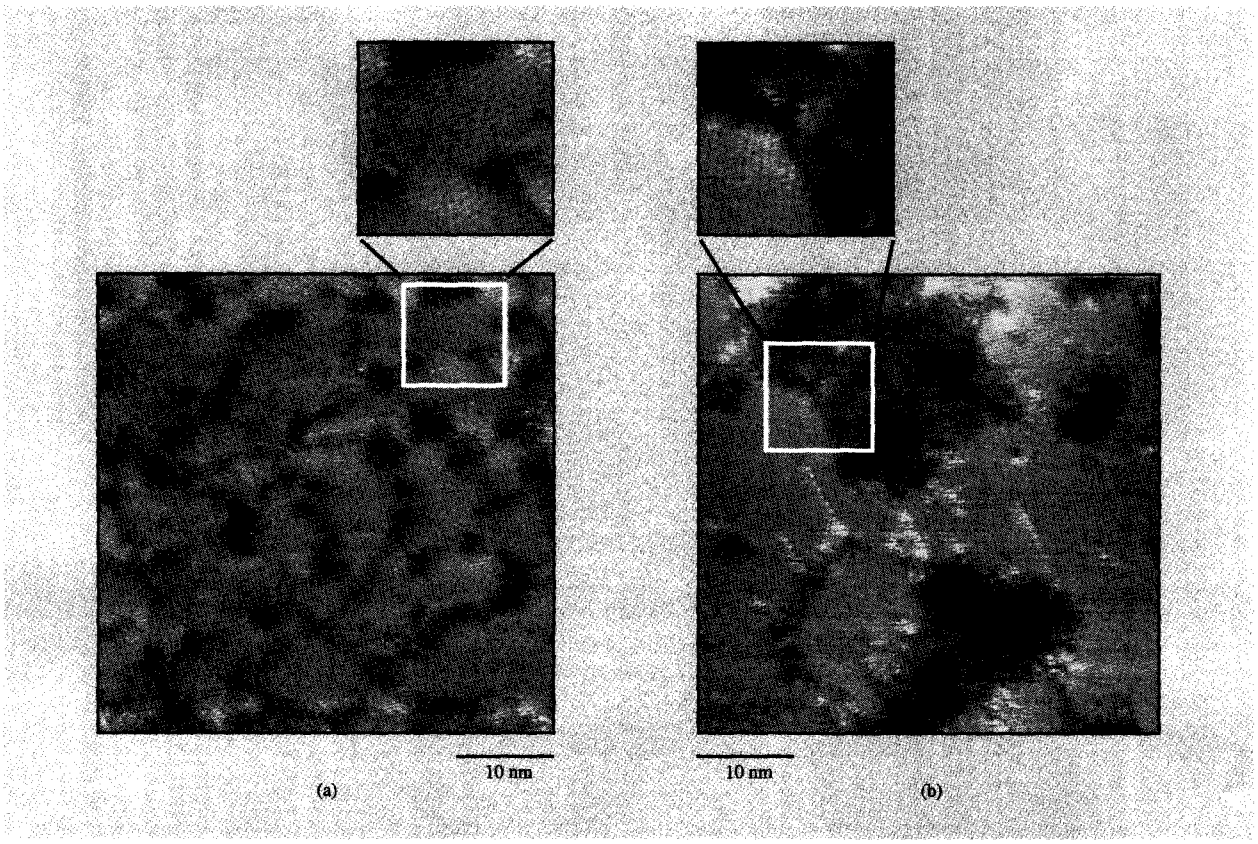

Figure 6

STM images of stamped SAMs of dodecanethiol (DDT) on Au(111) reveal that microcontact-printed monolayers are ordered and complete (images were obtained at 5 pA and 0.9 V): (a) SAM resulting from a 10-s contact between PDMS inked with a 0.1-M solution of DDT in ethanol. (b) SAM resulting from a similar procedure in which the PDMS was inked with a 0.1-mM solution of DDT.

its topography is comparatively simple and well understood; its features can be clearly differentiated from those due to the monolayer. Initial work used unpatterned PDMS stamps to transfer the DDT. The gold surface on mica was imaged *without* subsequent rinsing after its contact with the stamp for 10 s. This absence of bulk solvents excluded the possibility of reorganization of the molecules in the film due to swelling of the interfacial layer by the solvent that might thus introduce structural changes to the monolayer on drying [39].

Figure 6(a) is a striking example of the quality of SAMs attainable by μCP: In its principal and detailed organization, the stamped monolayer appears indistinguishable from similar SAMs prepared in solution for 24 h (see Figure 1) [40]. Patches of crystalline monolayer, each in one of the four known phases typical of SAMs, are connected by small (dark in the figure) lines of disorder approximately two molecules wide representing the boundary between adjacent crystalline regions in the SAM. Black holes in the figure are one gold layer deep and represent well-known corrosion features mediated by formation of the monolayer [20]. These depressions still provide sites of adsorption for DDT and do not correspond, therefore, to defects in the monolayer [see the upper part of the high-resolution extract in Figure 6(a) for an example].

Figure 6(b) demonstrates that SAMs of lower quality can result from μCP. The light patches in this image correspond to regions of high crystalline order that yield molecular resolution of the end groups by STM. The darker patches correspond to a less dense phase $\approx$0.3 nm lower than the crystalline patches. The SAM in Figure 6(b) is largely the consequence of the inking process: If this step uses a solution of alkanethiol that is too dilute,

insufficient molecules exist in the area of contact between stamp and substrate. Since only 10^{15} molecules/cm^2 form a complete, ordered monolayer, the observation in Figure 6(b) underscores the sensitivity of μCP to the detailed condition of the swollen elastomeric phase. Significantly, this figure provides direct evidence of the templated growth of ordered regions in SAMs and points to at least two different kinetic regimes in their formation. The SAM pictured in Figure 6(b) is obviously less complete than that in Figure 6(a), which, as discussed above, shares the attributes of complete SAMs formed after long times of equilibration in solution. In Figure 6(b) the order that is apparent is concentrated in a single large and irregularly shaped domain characterized by hexagonal packing. Etch pits present everywhere in Figure 6(a) are evidently "swept" out from crystalline parts of Figure 6(b), apparently because of their mode of growth. Because both types of SAM [i.e., those in Figures 6(a) and (b)] result from the same time of contact between the stamp and gold substrate, the data provide a tantalizing hint that SAMs with much longer-range order than previously thought possible might be conveniently accessed using microcontact printing. The darker areas having a less complete monolayer in Figure 6(b) are areas in which etching initiates, of course, so that strategies to complete these areas of the printed SAM are needed before the inherently higher order of μCP, as in Figure 6(b), results in better etching yields of features. These results indicate a fundamental aspect of microcontact printing and its susceptibility to defects: Reproducible features require control over the process to limit the number of sites in the SAM where etching defects might initiate, i.e., regions of lower order. SAMs allow this type of rigorous control over their composition and structure by affecting either the process of their formation or their components, as demonstrated above. Well-defined approaches to control defects in SAMs as etch barriers are therefore well within the capabilities of these remarkable systems.

Outlook

Production and transfer of ultimately small structures is just one aspect of a lithographic scheme. A major challenge in fabrication is the alignment of features: Most devices result from a large number of sequentially administered chemical steps, each defined spatially by accurate masking using a resist. Overlay accuracy usually requires the mask and substrate to be as mechanically rigid and stable as possible, formed from materials with similar properties. Another approach to the alignment of patterns exploits the deformability of stamps. We suggest hybrid stamps comprising a rigid support (quartz) and a thin film (100 μm–1 mm) of patterned elastomer that use lock-and-key-type approaches to adapt to the substrate (**Figure 7**). Coarse positioning is achieved conventionally

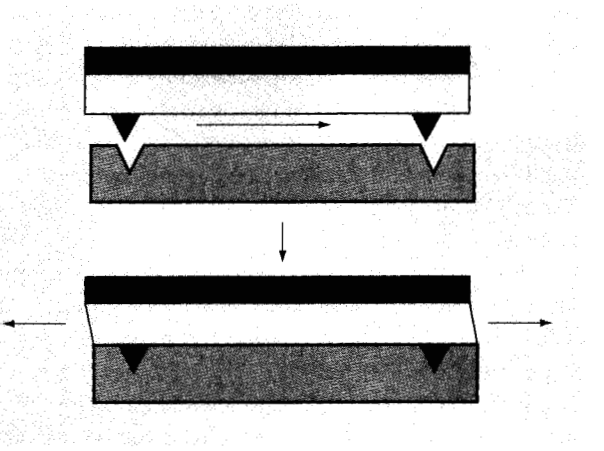

Figure 7

Scheme demonstrating self-alignment by a lock-and-key mechanism that shifts and deforms the stamp to correct alignment error.

with a mask aligner. Fine adjustment of the stamp's position involves mating to matching posts (or holes) existing on the substrate that cause small compensating shifts and deformation of its elastomeric part. A degree of self-alignment thus results that corrects thermal drifts and mechanical errors between stamp and substrate. More active processes using interfacial forces to direct alignment (i.e., self-assembly of stamp and substrate) are also plausible. Lock-and-key types of alignment might be conveniently accessed via existing topological structures that already result from processing. Our suggestion is that adding topology to a substrate (i.e., not planarizing it after each process step) can actually provide an advantage in some alignment schemes.

The ability of stamps to compensate for topography provides several useful features. The elastomer accommodates microscale roughness of a substrate. Dust particles, normally catastrophic to contact printing methods, cause only local defects because the stamp readily subsumes such entities into its bulk by deformation. Printing onto macroscopically curved surfaces [9] is possible and offers capabilities not obviously accessible by other techniques at any resolution. Alignment of features in stamps uses their limited compressibility to steer regions raised from the elastomer's surface toward their targeted destinations without substantial compromise of the high-resolution pattern.

Microcontact printing to form SAMs is most clearly useful now as a method of providing high-resolution patterning in a single step. The presence of SAMs alters many chemical processes with high contrast compared to regions with either no, or different, monolayers. Chemical

vapor deposition [41], electrochemical and electroless deposition [42, 43], etches [44], and nucleation and growth of liquids or solids [45, 46] are successful examples of the direct use of SAMs to add, alter, or selectively destroy material on a surface. SAMs are not infinitely resistive, of course. Some of the familiar processes of modern lithography are not suited to designs that utilize SAMs, particularly those requiring very high temperatures or otherwise harsh conditions. It is difficult to imagine the direct application of monolayers as barriers to reactive ion etches, for example. Nevertheless, such processes are not entirely ruled out in SAM-based schemes; methods that used patterned areas in SAMs to amplify the chemical or mechanical properties of the patterned areas [47], perhaps by one of the methods above, suggest other, more indirect ways to use SAMs for fabrication.

Microcontact printing and its use of elastomeric stamps is not restricted to the formation of monolayers. A fascinating example of these elastomers as micromolds appeared recently [48, 49]. A network of openings between a stamp and a solid substrate, filled with a liquid prepolymer by capillary action, provided a template for the structure resulting from polymerization of this liquid. Release of the polymer from this new type of mold yielded 1-μm-thick, freestanding, patterned films of the organic polymer. Structures of this complexity had not been made before, much less with the ease suggested by Kim et al. Microcontact printing may also find increasing application to systems that do not form SAMs [50]. Demonstrations involving the printing of colloids appeared recently [43] and are but the first of similar examples that rely on the exceptional characteristics of elastomer-based stamps.

A related alternative to microcontact printing is called nanoimprinting [51]. Nanoimprinting-raised regions of a SiO_2 master into a thin PMMA layer allowed fabrication of arrays of holes in PMMA with diameters of 25 nm. The master conforms to the surface at high pressure (600 kg/cm^2), and the pattern is accurately reproduced into the material above its glass transition temperature (200°C). Minimum feature sizes of this micromolding process were $\approx$10 nm, illustrating the potential of this method of fabrication. Owing to thermal expansion, the use of higher temperatures is probably a disadvantage for lithography, however. Lower temperatures and pressures would be advantageous, suggesting other combinations of masters and organic polymers. Nanoimprinting has appeared in other contexts as well. Rugar showed that scanning probe microscopy (SPM) provided convenient read/write capabilities on polymers using a method related conceptually to compact disk technology, albeit with information stored at much higher densities ($\approx$1000×) [52]. This approach, although inherently sequential, highlights ways of wedding SPM techniques with microcontact fabrication.

These examples illustrate some of the salient features of emerging ideas in materials preparation based on self-assembly [53] and microcontact, and suggest alternative approaches to problems in fabrication and manufacturing. The total investment in microcontact printing is currently just a few million dollars, directed primarily toward basic research; nonetheless, the demonstrated performance of this technique is astonishing. The engineering effort necessary to prove its ultimate utility remains to be seen. We think that sufficient information already exists to warrant speculation that these approaches will prove important in the fabrication of structures not accessible by optical lithography. Could a more distant future bring manufacture of complex circuits by processes as simple as printing and molding? We plan to seek an answer.

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