Self-assembled Monolayer Films: Microcontact Printing

Microcontact printing (μ CP), one of the non-photolithographic techniques that make up "soft lithography" (Xia and Whitesides 1998), uses an elastomeric stamp to generate two-dimensional patterns by printing the molecules of an "ink" onto the surface of a solid substrate. In its most common configuration, the stamp is fabricated from an elastomeric polymer, poly(dimethylsiloxane) (PDMS), the "ink" is an alkanethiol, and the substrate on which the printing occurs is a thin, evaporated film of gold or silver. Alkylsiloxanes are also printed on Si/SiO, and glass. Microcontact printing is an experimentally simple methodology; the elastomeric stamp is easily fabricated by molding a liquid prepolymer against a master that has the desired pattern in relief on its surface. Once the master is available, multiple copies of the pattern can be produced reproducibly, using straightforward experimental procedures. The initial products of μ CP are usually patterned regions of self-assembled monolayers (SAMs). These printed SAMs can subsequently be used as ultrathin (2-3 nm) resists in selective wet etching, or as templates to control the wetting, dewetting, adsorption, nucleation, growth, and deposition of a rich variety of materials. The printing process is inherently parallel-that is, it forms the pattern over the entire area of the substrate in contact with the stamp at the same time-and thus allows for patterning over a relatively large area in a single impression. The minimum size of features that can be directly generated using µCP still has not been completely defined. It is possible to print routinely \sim 300 nm features of hexadecanethiolate SAMs over ~ 50 cm^2 areas (Xia *et al.* 1997), and it has also been demonstrated that μCP is capable of generating parallel lines of dodecanethiolate SAMs on gold that are ~ 35 nm in width and separated by ~ 350 nm (Biebuyck et al. 1997).

1. The Elastomeric Stamp

Conformal contact between the stamp and the surface of the substrate is the key to the success of microcontact printing. This conformal contact has been achieved by fabricating the stamp in an elastomeric polymer. A variety of elastomers—for example, poly(dimethylsiloxane)s and polyurethanes, as well as harder polymeric materials such as polyimides and cross-linked novolac resins (phenol formaldehyde polymers)—have been successfully used to fabricate the stamp. The elastomer commonly used in most demonstrations is PDMS. The PDMS stamp is usually fabricated by replica molding (Fig. 1); a liquid prepolymer of PDMS—for example, Sylgard 184 from

Dow Corning-is cast against a master whose surface has been patterned with a complementary relief structure using conventional microlithographic techniques such as photolithography, micromachining, or high-resolution printing. The stamp may also be cast from preformed microstructures such as optical diffraction gratings, metal grids for transmission electron microscopy (TEM), compact disks (CDs), corner cube reflectors, anti-reflection structures, and assembled structures of colloidal particles. The only requirement seems to be that the surface of a master does not react with the PDMS prepolymer to form covalent bonds. In most cases, it is necessary to treat the master with the vapor of octadecyltrichlorosilane (or a perfluorosilane such as $C_{6}F_{13}C_{2}H_{5}SiCl_{3}$ to cap any polar reactive group (e.g., -OH) on the master with a chemically inert group such as -CH₃ or -CF₃.

Several properties of PDMS are instrumental in the formation of high-quality patterns during μ CP. First, the softness of PDMS can be easily tailored by varying the amount of curing agent. The stamp can be made flexible enough to conform to the surface of the substrate over a relatively large area, with little or no applied pressure. This conformal contact can even be achieved on surfaces that are nonplanar on the scale of microns. Second, the surface properties of PDMS can be readily modified using a combination of oxygen plasma treatment and formation of alkylsiloxane SAMs. Tailoring the surface of the PDMS is necessary to accommodate ink molecules and solvents that themselves have a wide range of interfacial free energies. Third, PDMS is a durable, chemically inert elastomer: the same stamp can be used at least 100 times in µCP over a period of several months without noticeable degradation in performance. Fourth, PDMS is highly transparent down to \sim 300 nm; this optical transparency allows one to observe alignment under an optical microscope (in the transmission mode). This elastomer has also been used to construct deformable components for adaptive optics, and photomasks for phase-shift or conventional photolithography (Xia et al. 1999). Fifth, PDMS is electrically insulating; it can be directly employed to fabricate microfluidic devices for use with capillary electrophoresis (CE).

PDMS also has several disadvantages that may limit its performance in certain types of applications. For example, it shrinks by a factor of ~ 1% upon thermal curing, and it can be readily swelled by nonpolar solvents such as toluene and hexane. The elastomeric character of PDMS also poses technical challenges for the use of μ CP in printing certain kinds of features. For example, the gravity, adhesion, and capillary forces exerted on the elastomeric features may cause these features to collapse or distort, and to generate defects in the printed pattern.

As shown in Fig. 1, if the aspect ratios (l/h) of the relief structures are too small, the raised portions of PDMS may fall under their own weight, or collapse



Schematic procedure for casting PDMS stamps from a master. The bottom part illustrates two possible distortions that are usually associated with an elastomer such as PDMS: the pairing of raised structures and the sagging of recessed regions during contact printing.

due to the forces involved in the inking or printing process. It has been shown that the aspect ratio (l/h)must be ≥ 0.2 in order to obtain printed patterns largely free of defects caused by mechanical distortions of the stamp (Delamarche et al. 1997). On the other hand, when the aspect ratios (d/h) are too large, the relief structures may not be able to withstand the compressive forces typical of printing and/or the adhesion between the stamp and the substrate. The result of these interactions is sagging, a process that may prevent microcontact printing from generating patterns in which features are widely separated (e.g., $d \ge 20 h$) without defects in the pattern between these features. A solution to the sagging problem that is sometimes possible is to introduce nonfunctional "posts" into the design to provide a support for the noncontact regions, or to fabricate the stamp on a rigid support. Many of the problems of mechanical distortions in the stamp can be solved by using appropriate materials, new designs, and new procedures optimized for different fabrication tasks.

2. Microcontact Printing

The concept of microcontact printing was first demonstrated using SAMs of hexadecanethiolate on thin films of gold, supported on silicon wafers (Kumar and Whitesides 1993). The printing step involves a direct contact between the raised portions of the stamp and the substrate, and can be routinely performed with one of the following three configurations: printing on a planar surface with a planar stamp; printing on a curved surface with a planar stamp; or printing on a planar surface over a large area with a rolling stamp that has been mounted on a cylindrical support. Figure 2 shows the schematic procedure for printing on a planar surface of gold with a planar stamp: the stamp is wetted with a solution of hexadecanethiol $(CH_3(CH_2)_{15}SH)$ in ethanol (~ 10mM) and is then brought into contact with the surface of gold for 5-10s. The hexadecanethiol transfers from the raised regions of the stamp to the gold, forms a species commonly represented as hexadecanethiolate [CH₃(CH₂)₁₅S⁻Au¹], and generates patterned microfeatures of SAMs on the surface of the gold. For μCP with a solution of hexadecanethiol in ethanol, a contact time of 5-10s has to be used because longer contact times may result in the destruction of the pattern, due to the transport of hexadecanethiol from the stamp to the surface of gold in noncontact regions by diffusion through the vapor phase, or by lateral movement.

The success of μCP rests on two characteristics of the system: the rapid formation of a highly ordered monolayer, and the autophobicity of the monolayer to the ethanol solution of the alkanethiol; this autophobicity blocks the spreading of the excess ink liquid across the surface. The adsorption and selforganization of alkanethiols on gold is a relatively fast process: when a gold substrate is immersed in a solution of hexadecanethiol in ethanol, an ordered SAM of hexadecanethiolate can be formed within a few minutes. The formation of highly ordered SAMs of alkanethiolates during μ CP may occur in an interval as short as a few seconds. An STM study showed that, for an ink solution of $\sim 100 \,\mathrm{mM}$ dodecanethiol in ethanol, a contact time of > 0.3 s was enough to generate highly ordered SAMs on polycrystalline gold that were indistinguishable from those formed by equilibration in solution (Larsen et al. 1997).

Since its first demonstration in 1993, μ CP has been successfully extended to pattern a wide variety of materials (Xia and Whitesides 1998). For example, this technique has been extended to different systems of SAMs, including SAMs of alkanethiolates on silver, SAMs of alkanethiolates on copper, SAMs of alkanethiolates on palladium, SAMs of alkanethiolates on gallium arsenide, SAMs of alkylsiloxanes on HOterminated surfaces, SAMs of alkylphosphoric acids on aluminum/aluminum oxide, and SAMs of alkylamines on carboxylic anhydride-terminated surfaces.



The schematic procedure for μCP on Au with an alkanethiol ink.

Currently, μ CP of hexadecanethiol on evaporated thin films (20–100 nm thick) of gold or silver appears to be the most reproducible process: both systems give patterns of highly ordered SAMs with relatively low densities of defects. Printing of other systems is often less tractable: these systems may yield disordered structures, and in some cases, submonolayers and multilayers. Microcontact printing has also been applied to the patterning of colloidal palladium particles (as catalysts for electroless deposition of metals) or proteins on silicon or polymeric substrates, although the formation of uniform monolayers of such materials usually cannot be achieved (and often is not required).

3. Printed SAMs as Resists in Selective Wet Etching

Although SAMs of alkanthiolates are usually 2–3 nm thick, they are robust enough to protect the underlying substrates from corrosion and dissolution. This protection mainly stems from the inherent structure of a SAM: a nearly crystalline packing with a low defect density. When a SAM-printed substrate is placed in an appropriate etching solution, a pattern develops in the underlying substrate, due to the difference in dissolution rates between SAM-covered and bare regions. Because SAMs are extremely thin, there is little loss in edge definition due to the thickness of the resist. The major determinants of edge resolution seem to be the fidelity of the contact printing and the anisotropy in the etching of the underlying substrate (especially at the boundaries between grains). Examination of a number of wet etchants in conjunction with printed SAMs demonstrated that aqueous solutions containing $K_2S_2O_3/K_3Fe(CN)_6/K_4Fe(CN)_6$ are effective for use with printed SAMs of alkanethiolates on gold or silver; that aqueous solutions containing FeCl₂ and HCl (or NH,Cl) are effective for use with patterned SAMs of alkanethiolates on copper; and that aqueous solutions containing HCl/HNO₃ are effective for patterned SAMs of alkanethiolates on gallium arsenide or palladium (Xia and Whitesides 1996). Selfassembled monolayers themselves usually do not have the durability to serve as resists for pattern transfer in conventional reactive ion etching (RIE), although polymer films built on patterned alkanthiolate SAMs do serve as RIE resists.

When patterning coinage metals by uCP, silver appears to be the most suitable element, due to the small grain size observed in evaporated thin films of silver and its moderate reactivity towards wet etchants (Xia and Whitesides 1996). Figure 3 shows SEM images of several test patterns of silver that were fabricated using μ CP with hexadecanethiol, followed by selective etching in aqueous ferricyanide solutions. These test patterns represent the level of complexity, perfection, and feature size that can be produced routinely by this approach. The smallest features fabricated to date with a combination of μ CP of SAMs and wet etching are trenches etched in gold that are \sim 35 nm in width, \sim 350 nm in separation, and over an area of $\sim 10 \mu m^2$ (Biebuvck *et al.* 1997). The minimum feature size that can be achieved by this patterning technique remains to be defined. Adsorbates on the surface of the substrate, the roughness of the surface, and the material properties (especially, the deformation and distortion) of the elastomeric stamp may influence the resolution and feature size of patterns formed by µCP. Some tailoring of the properties of the PDMS stamp or development of new elastomeric materials optimized for the regime $< 100 \,\mathrm{nm}$ will be useful.

Microcontact printing with an elastomeric stamp provides an immediately useful route to patterning curved surfaces (Jackman et al. 1995). This type of patterning is not practical by photolithography. It has been demonstrated that μCP of alkanethiols on gold or silver can generate micropatterns on both planar and nonplanar substrates with virtually the same edge resolution. This printing technique has been further developed by introducing a monitoring and registration system into the experimental procedure. It has also been possible to form patterned microstructures on the *inside* surface of a glass capillary by using electroless deposition, rather than metal evaporation, to prepare the substrate (in this case, a thin coating of silver on the inside surface of the capillary), and an appropriately configured rolling stamp. These demonstrations microstructures suggest with potential applications in optical communication, microelectromechnical systems (MEMS), and microanalysis.

4. Printed SAMs as Templates in Selective Deposition

Although the initial products of μCP are patterned SAMs, the materials that can be patterned using μCP are not limited to SAMs. SAMs generated by μCP have been extensively explored as templates to pattern a wide variety of other materials—for example, liquid



Scanning electron microscopy (SEM) images of test patterns of silver that were fabricated by μ CP with hexadecanethiol, followed by selective wet etching in an aqueous ferricyanide solution.



Figure 4

SEM images of patterned microstructures that were fabricated with printed SAMs as templates: (a) an SEM image of microstructures of polyurethane generated by selective dewetting; (b) an SEM image of $CuSO_4$ particles (indicated by the arrow) formed by selective dewetting and crystallization. The dark squares are SAMs terminated in -COOH groups; the light grids are SAMs terminated in -CH₃ groups; (c) an SEM image of microstructures (light) of Cu fabricated in Si microtrenches using selective CVD; (d) an SEM image of microstructures (light) of LiNbO₃ on Si/SiO₂ (dark) produced using selective CVD.

prepolymers, conducting polymers, inorganic salts, metals, ceramics, proteins, and cells. Most of these processes involve the use of self-assembly at two scales: the formation of patterned SAMs by μ CP at the molecular scale, and the selective deposition of other materials on the patterned SAMs at the mesoscopic scale.

Figure 4 shows SEM images of several examples of patterned microstructures that were fabricated with printed SAMs as templates. Figure 4(a) shows the SEM image of an ordered array of isolated stars of polyure than egenerated using a combination of μCP and selective dewetting. When the liquid prepolymer of polyurethane was placed on a surface patterned with SAMs, it selectively dewetted the hydrophobic regions terminating in methyl groups, and formed patterned microstructures on the hydrophilic regions terminating in carboxylic acid groups. The liquid prepolymer selectively trapped in the hydrophilic regions was then cross-linked by exposure to UV light. Figure 4(b) shows the SEM image of a two-dimensional array of submicrometer-sized dots of CuSO₄, formed by selectively wetting a SAM-patterned surface of gold with an aqueous solution containing CuSO₄, followed by controlled evaporation of water. Using this simple approach, it has been possible to form highly ordered arrays of particles of CuSO₄ with lateral dimensions as small as ~ 50 nm.

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Printed SAMs on Si/SiO₂ can also serve as templates to selectively control the nucleation, growth, and deposition of ceramics or metals during chemical vapor deposition (CVD) or sol-gel dip-coating (Jeon et al. 1997). Two examples are shown in Fig. 4(c) and Fig. 4(d): selective CVD of copper and sol-gel deposition of lithium niobate. The patterned SAMs of CH₃-terminated alkylsiloxanes defined and directed CVD by inhibiting nucleation, because the materials to be deposited only nucleated and grew on the bare regions (SiO₂) that were not covered by CH₃terminated SAMs. As a result, the nucleation, growth, and deposition on the polar regions generated a patterned array of microstructures. These demonstrations suggest that μ CP of SAMs, in combination with other processes, has the capability of forming patterned microstructures of a rich variety of materials.

5. Printed SAMs as Templates in Biological Applications

Microcontact printing has also been used to form patterned SAMs that are capable of promoting (or resisting) biospecific adsorption. The ability to form micro-scale patterns of bioactive species on the surfaces of solid substrates makes μ CP especially useful for studying a variety of fundamental phenomena in biosurfaces and biomaterials. Functional SAMs patterned by μ CP, for example, have been employed as templates to define and direct the adsorption of extracellular matrix proteins, and consequently the attachment of anchorage-dependent cells to solid substrates (Mrksich *et al.* 1996). Using this simple patterning procedure, it is possible to place cells in



SEM images of proteins and cells that were patterned with printed SAMs as templates: (a) the SEM image of fibrinogen selectively adsorbed on a SAM-patterned surface of gold: the dark regions are methyl-terminated SAMs that have been covered by proteins, and the light regions are bare SAMs terminated in oligo(ethylene glycol) units; (b) optical micrographs of hepatocytes placed on SAM-patterned (left) and bare (right) surfaces of gold to show the ability to control the size and shape of cells; (c) the SEM image of mammalian cells selectively attached to the plateaus of a contoured surface. The substrate was derivatized by μCP in such a way that the surfaces of the plateaus were terminated in methyl groups, while the remaining regions were terminated in oligo(ethylene glycol) groups. The matrix protein (fibronectin) only adsorbed to the methyl-terminated regions, and cells only attached to those regions where the matrix proteins had been deposited.

predetermined locations in an array with well-defined shapes, sizes, and distances of separation. Figure 5(a) shows the SEM image of fibrinogen adsorbed on a gold surface that has been patterned into regions of

Self-assembled Monolayer Films: Microcontact Printing

thiolate SAMs terminated in methyl groups and oligo(ethylene glycol) moieties. Because the oligo(ethylene glycol) units have the ability to resist the adsorption of protein, the fibrinogen adsorbed preferentially from the aqueous solution onto the hydrophobic region, presumably through interactions between the hydrophobic groups on the gold surface and the recessed, hydrophobic patches on the protein. This patterning procedure seems to be very general, and has been succesfully demonstrated for proteins such as fibronectin and laminin.

These patterned features of proteins can be further used to spatially control the attachment and spreading of cells. Figure 5(b) shows optical micrographs of cells that have been selectively attached to a planar surface. By using different test patterns, it is possible to dictate the shape assumed by a cell that attaches to a surface, and thus to control certain aspects of cell growth such as protein synthesis and secretion. Because this technique allows one to examine the influence of cell morphology on cell metabolism, it should find applications in biotechnology that require analysis of individual cells cultured at high density, and/or repeated access to cells placed in specified locations. The results of these fundamental studies may eventually shed light on complex phenomena such as contact inhibition of cell proliferation, and lead to new types of analytical systems or biosensors based on ordered arrays of cells.

6. Conclusions

Self-assembled monolayers and patterning by μCP illustrate a largely unexplored approach to microfabrication. Microcontact printing is attractive because it is simple, straightforward, inexpensive, and flexible. The elastomeric PDMS stamp and the surface chemistry for the formation of SAMs can also be manipulated in a number of ways to modify the features generated using μ CP. Routine access to clean room facilities is not required, although occasional use of these facilities is convenient for making masters. When carried out in an ordinary laboratory, µCP also does not requiring a stringent control over the environment. At present, μCP is best considered as an intermediate-resolution (feature size $\ge 1 \,\mu m$) technique for routine use in microfabrication; below 1 µm, each pattern becomes a technical challenge.

The authors believe that μ CP will form the basis for many fabrication tasks involved in miniaturization of sensors, microelectromechanical systems (MEMS), microfluidics, microanalytical systems, and microoptical systems. The patterned structures of metals formed by μ CP, for example, can be used directly as arrays of microelectrodes and diffractive optical components, or as secondary masks to etch channels or relief structures in the underlying substrates (e.g., SiO₂, Si, and GaAs) using wet etches or RIE. A wide range of functional devices and systems have already been successfully fabricated by μ CP, including in-fiber notch filters and Bragg gratings, microtransformers, microcoils for high-resolution NMR spectroscopy, micro-springs, and intravascular stents.

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