ADVANCED
MATERIALS

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Lithographic Molding: A Convenient Route to Structures with Sub-Micrometer Dimensions**

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Microcontact printing[1−3] uses elastomeric "stamps" and alkanethiol "ink" to form patterned self-assembled monolayers (SAMs) of alkanethiolates on gold. Microcontact printing (μCP) can routinely produce patterned SAMs with dimensions ≥ 1 μm. Although it is possible to make patterns with sub-micrometer dimensions by μCP,[2] it may be inconvenient to fabricate the necessary stamps. Typically, we have used photolithography to fabricate a master with the desired pattern; a stamp is produced by casting poly-dimethylsiloxane (PDMS) on this master. Although pho-tolithography can produce masters (and thus stamps) with sub-micrometer scale dimensions, it requires clean room conditions and careful processing to achieve reproducible results.

This paper describes a new technique, which we call litho-graphic molding, for the fabrication of elastomeric stamps for μCP. This technique provides elastomeric stamps with sub-micrometer features and does not require routine access to clean rooms; it is thus an alternative to photolithography for the fabrication of stamps for μCP. Lithographic molding combines several steps: i) microcontact printing[1−3] on a thin gold film supported on a silicon ⟨100⟩ wafer to form a patterned SAM; ii) etching of the gold film, using the pat-terned SAMs as resists;[4] iii) anisotropic etching of sili-con[3,5,6]—which reduces the scale of certain features of the original pattern[7,8]—in regions where removal of gold has exposed the underlying silicon wafer; iv) molding of a new elastomeric stamp using the etched silicon as a master, and v) μCP with this new elastomeric stamp. This demonstration is one of several[9−11] that explore alternatives to the pho-tolithographic techniques normally used for the production of sub-micrometer scale features.

Figure 1 shows a schematic of the procedure for litho-graphic molding. Microcontact printing[1−3] with a pat-terned elastomeric "stamp" and alkanethiol "ink" formed a patterned SAM on a thin film of gold supported on a silicon ⟨100⟩ wafer (Fig. 1a). Immersing the substrate in a basic, oxygenated CN⊖ solution (0.1 M KCN, 1 M NaOH, 25 C) removed the gold film in regions not protected by the pat-terned SAMs (Fig. 1b).[4] Immersing the substrate for ∼25 minutes in an alcoholic solution of KOH (4 M KOH, 15% isopropyl alcohol, 60 °C) etched regions of the silicon wafer exposed by the selective removal of gold (Fig. 1c). The KOH
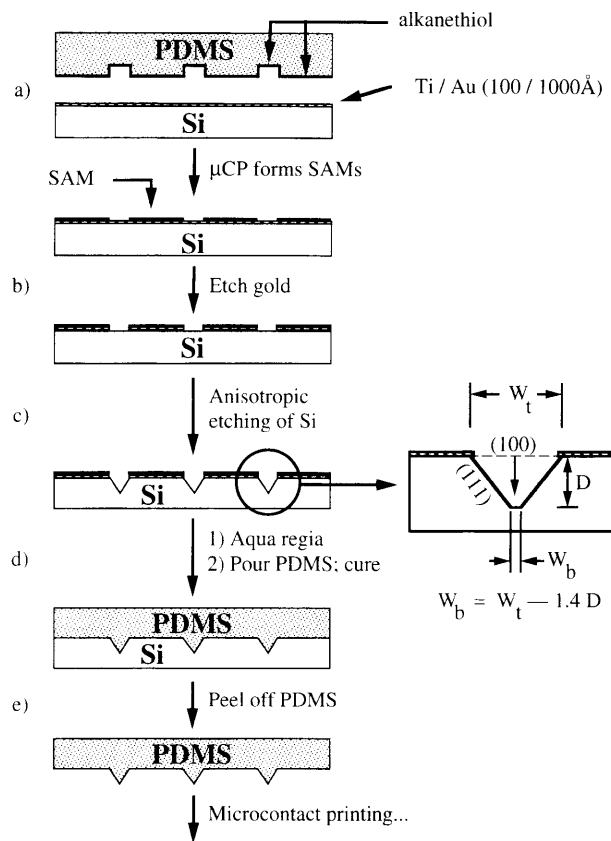
Fig. 1. Schematic of procedure for lithographic molding. See text for details.

solution etched the ⟨100⟩ surface plane of the silicon more rapidly than the ⟨111⟩ surface plane.[5,7,8] This difference in rates resulted in an anisotropic etch that reduced the size of the features in the original pattern that were not protected by the SAM (Fig. 1c, inset). The width of the features at the bottom of the etched structures (W_b) were determined by the width of the features at the top of the silicon surface (W_t) and the depth of etching (D). A liquid pre-polymer of PDMS[12] was poured over the etched master, cured by heating and peeled from the etched silicon master (Fig. 1d).[13] The re-sulting PDMS stamp had features that replicated the shape and scale of the features in the etched silicon master (Fig. 1e).

In initial studies, we fabricated a patterned SAM of alka-nethiolates on gold (supported on a silicon wafer) by μCP to form 3 μm-wide lines of SAMs separated by 3 μm-wide re-gions of bare gold (Fig. 2a). We chose features of these di-mensions since they were representative of the scale of fea-tures routinely accessible by many techniques[4,14−19] that use patterned SAMs for microfabrication, of which μCP[1−3] is particularly convenient for us. Etching with CN⊖ produced 3 μm-wide gold lines separated by 3 μm-wide regions of Si/SiO₂. Anisotropic etching of silicon, in regions of the substrate exposed by etching of gold, formed a series of parallel V-shaped grooves (Fig. 2b). We estimated, by visual inspection of images obtained by scanning electron
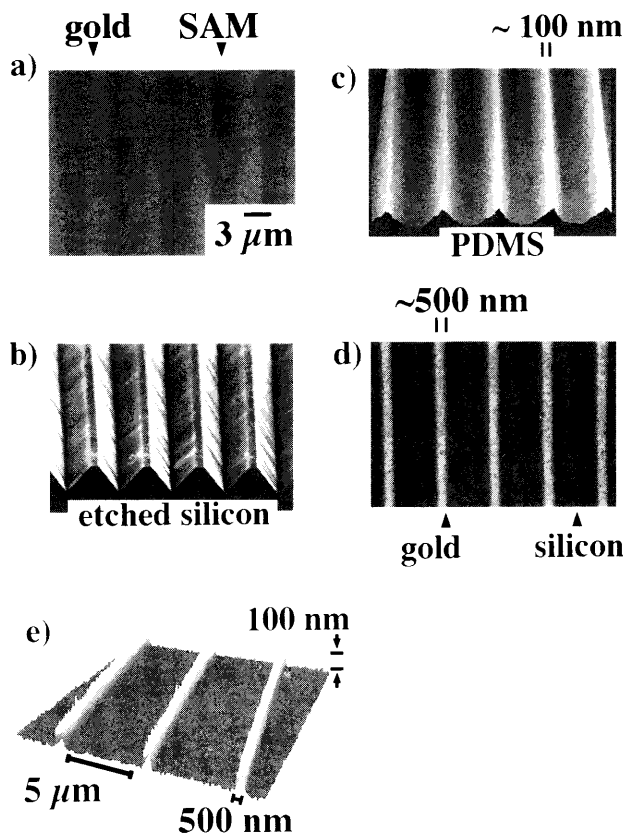
Fig. 2. a) Scanning electron micrograph of patterned SAMs formed by μCP with CH₃(CH₂)₁₅SH on a gold film. The gold film was supported on a titanium-primed silicon < 100 > wafer. The ~ 3 μm-wide lines of SAMs (dark) were separated by 3 μm-wide spaces of bare gold (light). b) SEM image of a silicon master. Etching of gold, using the patterned SAMs (shown in (a)) as resists, and anisotropic etching of silicon (where the gold was removed by etching), produced V-shaped channels with a width (at the bottom of the channel) of ~ 100 nm. c) AFM image of a PDMS stamp cast from the silicon master shown in (b)[20]. d–e) SEM (d) and atomic force microscopy (e) images of gold lines fabricated by μCP (with CH₃(CH₂)₁₅SH) using the PDMS stamp shown in (c), and etching with a basic cyanide solution. Light regions of the image corresponded to gold and dark regions are where gold was removed.
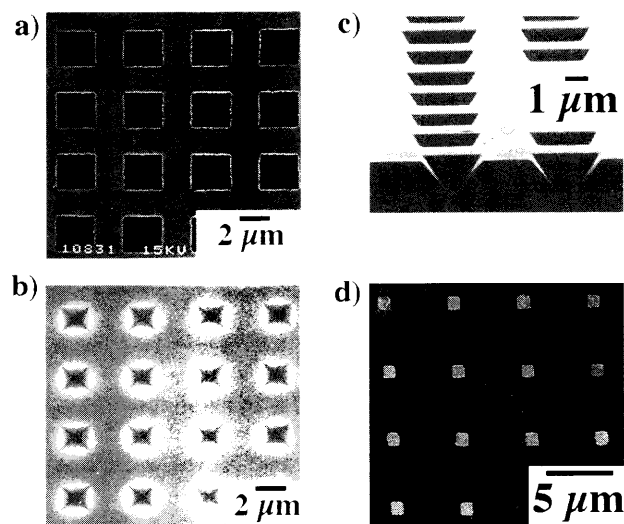

Fig. 3. Lithographic molding reduced the size of features of a pattern in two dimensions. a) SEM micrograph of patterned gold array formed by microcontact printing and chemical etching. Light regions corresponded to gold; dark regions are where the gold was removed by the etch. b) SEM micrograph (top view) of an etched silicon master formed from the substrate shown in (a). The outer dimensions of the etched structures were determined by microcontact printing. etching of gold and undercutting of the gold resists during etching. Irregularities in the shape of the etched features were evident: we did not determine the origin of these irregularities. c) SEM image (fracture profile) of the etched silicon substrate from (b). d) SEM image of sub-micrometer (~ 700 800 nm) gold structures formed by microcontact printing with an elastomeric stamp cast from the master shown in (b–c), and etching of gold.

teractions[22] between the stamp and the gold/SAM surface, produced features with dimensions similar to those produced by μCP in air. This observation suggested that the second mechanism was less important than the first.

In a separate experiment, μCP formed a grid of perpendicular lines[1] of alkanethiolate SAMs on Au/Si ⟨100⟩. Wet-chemical etching produced a grid of gold (Fig. 3a); anisotropic etching of silicon produced an array of pyramidal

microscopy, that the grooves were ~ 100 nm wide at the bottom of the channel. The anisotropy of the silicon etch therefore reduced ~ 3 μm-wide lines to ~ 100 nm-wide lines.

Micromolding with PDMS produced an elastomeric replica of the etched silicon substrate (Fig. 2c). Microcontact printing of CH₃(CH₂)₁₅SH on a gold film with this elastomeric "stamp", followed by wet-chemical etching, produced 500 nm-wide lines of gold (Fig. 2d). These lines of gold were wider than the features of the stamp or master (~ 100 nm). We hypothesized that the teeth of the stamps deformed during the μCP process, either as a result of the pressure on them, or as a consequence of attractive interactions between the stamp and the gold/SAM surface.[21]

The first of these mechanisms was supported by the observation that deliberately putting a load on the elastomeric stamp, either with a weight or by hand pressure, increased the width of the lines formed by μCP. We discuss this variation in the process in more detail below. Microcontact printing under water, which we expected to reduce attractive in-

pits in the silicon, with 200 nm-wide squares at the bottom (Fig. 3b–c). Micromolding with PDMS produced an elastomeric replica of the etched silicon substrate: μCP with this elastomeric stamp, followed by wet-chemical etching,[4] produced an array of gold squares (Fig. 3d). Some variation in the size and shape of the gold squares was evident: these variations may have resulted from irregularities present in the silicon master (Fig. 3b,c). Although we did not monitor the size and shape of individual gold structures for many μCP and etching steps, the variations evident in Figure 3d were present in many (> 20) samples.

Applying pressure to a single lithographically molded stamp during μCP produced patterns having features with a range of sizes. Figures 4a–b show gold squares produced by pressure-assisted μCP (using a stamp[12,23] cast from the master shown in Fig. 3) and wet-chemical etching. Increasing the pressure (by hand) on the stamp, while the stamp was in contact with the gold surface, increased the size of features
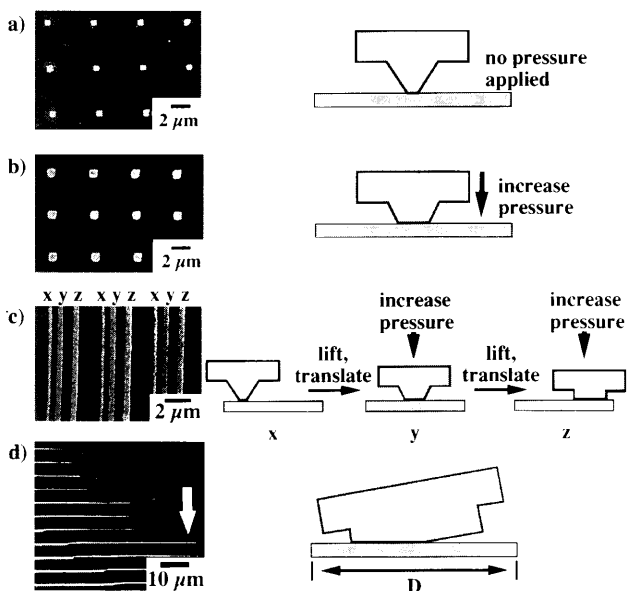
Fig. 4. The scale and shape of patterns formed by microcontact printing (μCP) with an elastomeric stamp fabricated by lithographic molding varied with the pressure on the stamp (while the stamp was in contact with the gold surface). All images in this figure are scanning electron micrographs of etched gold structures: light regions correspond to gold and dark regions are Si/SiO₂ where gold was removed by etching. a) Microcontact printing with no pressure (other than the weight of the stamp), followed by etching of gold, produced ~ 0.4 μm² squares. b) Microcontact printing with the same stamp as in (a), using gentle pressure (applied by hand), followed by etching of gold, produced ~ 1 μm² squares. c) Microcontact printing at three different pressures (applied by hand) produced three sets of parallel lines with different widths. See text for details. d) Microcontact printing, using a gradient in pressure across the stamp, formed an array of lines with a gradient in width. The gradient in pressure was established by μCP with the stamp held off-parallel from the plane of the gold surface (diagram). The stamp (shown in profile in the diagram) was similar to the stamp in Figure 2c.

formed by μCP: no distortion in the shape of the features was observed.

The lines of gold in Figure 4c were prepared using several steps: i) μCP with $CH_3(CH_2)_{15}SH$ at the point of contact between the stamp and the gold surface (estimated by eye) formed 250 nm-wide, parallel lines of SAMs separated by ~6 μm spaces of underivatized gold (x, Fig. 4c); ii) the stamp was pulled away from the sample and the sample was translated in the horizontal plane; iii) μCP with increased pressure formed 500 nm-wide lines of SAMs; (y, Fig. 4c); repeating this process, with still increased pressure formed 700 nm-wide lines of SAMs (z, Fig. 4c), and iv) gold not protected by these SAMs was removed with a wet-chemical etch.[4]

Using a gradient in the pressure applied to the stamp, we produced lines with a gradient in width (Fig. 4d). The gradient in pressure was created by μCP with the stamp tilted off-parallel from the plane of the substrate. Over a 150 μm length, the width of a line (marked by white arrow) changed from 200 nm to ~ 1 μm.

Lithographically molded stamps provided an array of "micropens" to write patterned SAMs. A PDMS stamp with an array of pyramidal features was fabricated by lithograph-

ic molding (Fig. 5a). The stamp was inked with hexadecanethiol, dried in a stream of N_2 and brought into contact with a 200 Å-thick film of gold (supported on a silicon wafer). The stamp was then translated by hand in the plane parallel to the plane of the gold film. Each pyramidal structure acted as a micropen—that is, it delivered alkanethiol to the gold surface, printing patterned SAMs where the "pen" contacted the gold. To limit reactive spreading of the alkanethiol on the gold film, the printing was conducted under water.[2-4] Wet-chemical etching, using the SAMs as resists,[4] produced a patterned array of gold structures with μm-scale dimensions (Fig. 5b). With further development, arrays of elastomeric "micropens" may be an alternative to other more complicated devices (STM tips, e-beams, for example) that are under exploration for large-scale, parallel lithography.

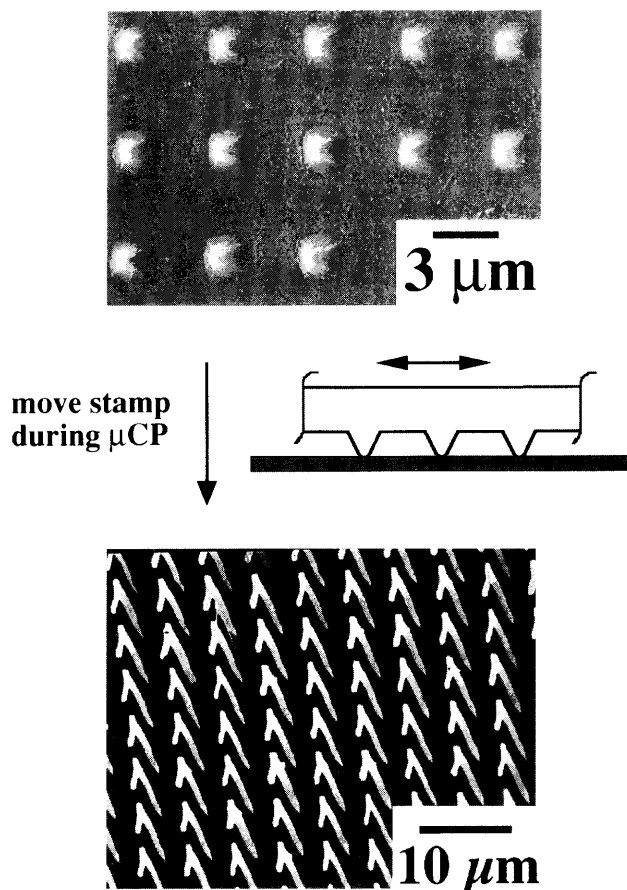This paper demonstrates a new technique–lithographic molding for the fabrication of elastomeric stamps with

Fig. 5. An elastomeric stamp fabricated by lithographic molding was used as an array of "micropens". a) Scanning electron micrograph (SEM) of a PDMS stamp fabricated by lithographic molding. The stamp was coated with a thin (<400 Å) film of gold to allow imaging by SEM. b) SEM image of an array of gold structures fabricated using the stamp shown in (a): i) the stamp was inked with hexadecanethiol and allowed to dry; ii) the stamp was brought into contact with a film of gold supported on a titanium-primed silicon ⟨100⟩ wafer and translated by hand in a plane parallel to the plane of the surface. iii) the stamp was removed from the surface of the gold; iv) wet-chemical etching removed gold in regions of the surface not protected by patterned SAMs.

sub-micrometer dimensions: these elastomeric stamps can be used in microcontact printing to form patterned SAMs of alkanethiolates on gold films. Using lithographic molding, we produced elastomeric stamps that had patterns with features (the radius of curvature of the tip a of V-shaped line, for example) as small as 100 nm. Microcontact printing with these elastomeric stamps, followed by wet-chemical etching, produced patterns of gold with dimensions as small as 200 nm.

Lithographic molding brings several new capabilities to microfabrication: i) it can produce elastomeric stamps with features as small as 100 nm; the current limit for the size of features that can be produced by standard photolithographic processing is approximately 300 nm (several stamps can be produced from a single etched silicon master, and we have used a single stamp more than 100 times); ii) using pressure-assisted μCP, or by using the stamp as an array of micropens, a single stamp fabricated by lithographic molding can produce features with a range of sizes and shapes and, iii) lithographic molding does not require routine use of photolithography, and is therefore a route to micrometer scale structures for laboratories that do not have routine access to the equipment and facilities normally used for micro- and nanofabrication.

This technique has obvious limitations in the type of the patterns it can produce. In particular, although it reduces the size of the features printed from the original stamp to those of the secondary, lithographically molded stamp, it does not change the separation *between* features. Thus, for example, the width of lines decrease, but separations between them do not.

Patterned SAMs formed by μCP have many applications, including microfabrication,[1, 2, 6, 25] studies of wetting and nucleation phenomena,[24 – 26] and protein[27] and cellular adhesion.[28] Lithographic molding is a convenient new route to patterned elastomeric stamps, and thus patterned SAMs, with sub-micrometer scale features, for use in these and other applications. It is presently most usefully applied to simple patterns; its applicability to the complex patterns required in microelectronics remains to be explored.

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[12] The PDMS was SYLGARD silicone elastomer 184 (Dow-Corning Corporation).
[13] Substrates of etched silicon were washed with aqua regia (HCl:HNO₃, 1:1 by volume) and 1% HF to remove gold and TiO₂. To prevent adhesion between the silicon and the PDMS, the master was soaked for 12 h in a solution of octadecyltrichlorosilane in mineral oil (~5% by volume), this procedure formed a hydrophobic monolayer on the surface of the silicon.[11, 12] After removal from the solution of alkyltrichlorosilane, the sample was washed repeatedly with heptane, deionized water and ethanol, then dried in a stream of N₂ gas. PDMS was poured over the master, degassed under vacuum for 45 min, and cured at 60 C for 2 h. After curing, the elastomer was peeled gently from the surface of the silicon. The silicon master could be used again to mold another PDMS stamp.
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Cu₂O Quantum-Dot Particles Prepared from Nanostructured Copper**

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Highly disperse copper oxides are widely used as catalysts for industrial processes, e.g., for the methanol synthesis or for the water gas shift reaction. In all cases reported so far,

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