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

By James L. Wilbur, Eunok Kim, Youtian Xia, and George M. Whitesides

Microcontact printing 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, 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 polydimethylsiloxane (PDMS) on this master. Although photolithography 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 lithographic 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 on a thin gold film supported on a silicon (100) wafer to form a patterned SAM; ii) etching of the gold film, using the patterned SAMs as resists; iii) anisotropic etching of silicon—which reduces the scale of certain features of the original pattern—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 photolithographic techniques normally used for the production of sub-micrometer scale features.

Figure 1 shows a schematic of the procedure for lithographic molding. Microcontact printing with a patterned elastomeric "stamp" and alkanethiol "ink" formed a patterned SAM on a thin gold film 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) for 30 minutes in an alcoholic solution of KOH (4 M KOH, 15% isopropanol alcohol, 60 °C) etched regions of the silicon wafer exposed by the selective removal of gold (Fig. 1c). The KOH 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 (Wb) were determined by the width of the features at the top of the silicon surface (Ws) and the depth of etching (D). A liquid pre-polymer of PDMS was poured over the etched master, cured by heating and peeled from the etched silicon master (Fig. 1d). The resulting 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 alkanethiolates on gold (supported on a silicon wafer) by μCP to form 3 μm-wide lines of SAMs separated by 3 μm-wide regions of bare gold (Fig. 2a). We chose features of these dimensions since they were representative of the scale of features routinely accessible by many techniques[14, 19] that use patterned SAMs for microfabrication, of which μCP[11, 31] is particularly convenient for us. Etching with CN− produced 3 μm-wide gold lines separated by 3 μm-wide regions of 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).

![Diagram](https://example.com/diagram.png)

** Fig. 1. Schematic of procedure for lithographic molding. See text for details.
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. 2e). Microcontact printing of CH₃(CH₂)₉SH 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.

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 interactions 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 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 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, 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 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 substrate 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 ~8 μm² squares. b) Microcontact printing with the same stamp as in a), with gentle pressure applied by hands, followed by etching of gold, produced ~1 μm² squares. c) Microcontact printing at three different pressures (applied by hands) 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.

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 (~500 Å) film of gold 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.124 Wet-chemical etching, using the SAMs as resists,14 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 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 CH₃(CH₂)₅SH 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.151

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 lithographic-
sub-micrometer dimensions; these elastomeric stamps can be used in microcontact printing to form patterned SAMs of alkane thiolates on gold films. Using lithographic molding, we produced elastomeric stamps that had patterns with features (the radius of curvature of the tip of V-shaped line) of 100 nm, for example as small as 10 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 micropins, 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, and studies of wetting and nucleation phenomena and protein and cellular adhesion. 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 useful applied to simple patterns; its applicability to the complex patterns required in microelectronics remains to be explored.

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Cu₂O Quantum-Dot Particles Prepared from Nanostructured Copper**

By Antje Kellerstock, Erich Knözinger,* Walter Langel, and Michael Giersig

Highly disperse copper oxide nanoparticles 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,