Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric stamp and an alkanethiol "ink" followed by chemical etching

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This letter describes a technique that can be used to produce well-defined features of gold. The technique involves patterning of a self-assembled monolayer (SAM) on a gold substrate using an elastomer stamp (fabricated either from a phenol-formaldehyde polymer or polydimethylsiloxane), followed by selective etching in an aqueous, basic solution of cyanide ion and dissolved dioxygen (1M KOH, 0.1 M KCN). Electrically conductive structures of gold with dimensions as small as 1 μm have been produced using this procedure. Once a rubber stamp is fabricated, patterning and etching of gold substrates is straightforward. This method is convenient, does not require routine access to clean rooms and photolithographic equipment, and can be used to produce multiple copies of a pattern.

This report describes a simple method for the fabrication of patterns of gold, supported on silicon substrates. A rubber stamp is used to pattern a self-assembled monolayer (SAM) on a supported gold film. The patterned substrate is etched in an aqueous, basic solution of cyanide ion and dissolved dioxygen.[1-4] Features having dimensions as small as 1 μm and as large as several square cm have been produced through this technique. This process has the advantage of simplicity and convenience: the desired stamps can be fabricated either lithographically or nonlithographically, and once the stamp is available, multiple copies of the patterns can be formed using extremely straightforward experimental techniques.

The rubber stamps were made by two methods. Large features were made using standard lithographic fabrication procedures available as commercial services (Logan Stamp Works, Boston, MA). The desired pattern was photographed, and a positive slide was used as a mask. The output of a medium pressure mercury arc lamp was projected through the slide onto a Novolac resin (a phenol-formaldehyde polymer, Hercules, Wilmington, DE). Regions that were exposed to the ultraviolet radiation dissolved in a mild soap solution. The remaining, unexposed polymer was mounted on a base for stamping. Features as small as 200 μm were produced using this relatively imprecise photolithographic process. Currently, the upper limit in size is dictated by the size of the stamp that can be produced (30 cm$\times$40 cm) by the commercially available Merrigraph 1216 Photopolymer Exposure Unit (Hercules, Wilmington, DE).

Ink pads for stamping were prepared by moistening a piece of lint-free paper with a 0.1–1 mM solution of hexadecanethiol in either ethanol or diethyl ether. It was important to keep the ink pad as free of lint as possible. Alternatively, the hexadecanethiol solution was poured directly onto the stamp. Ink formulations using other solvents such as toluene or iso-octane produced features having poorer resolution. After inking and stamping, the substrate was immediately immersed in the etch solution described previously.[4]

Figure 1 depicts representative patterns formed using stamps made of the Novolac resin polymer. The versatility of this procedure—stamping followed by etching—is evident from the range in size and detail of the features that can be produced. Any feature having dimensions greater than 200 μm can be photographed, prepared as a rubber stamp using routinely available commercial services, and reproduced in gold supported on silicon.

Stamps for small (1–100 μm) features were fabricated from polydimethylsiloxane (PDMS); Fig. 2 describes the process. The masters were made lithographically or were

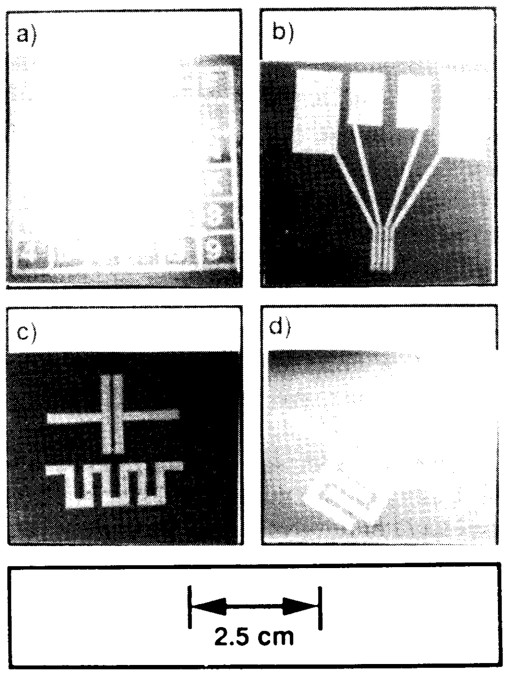

FIG. 1. Photographs of large Au features produced using the Novolac stamps. (a)–(d) Complex and simple features can be easily produced. These representative features show the degree of imperfection that results from the use of commercially prepared stamps.

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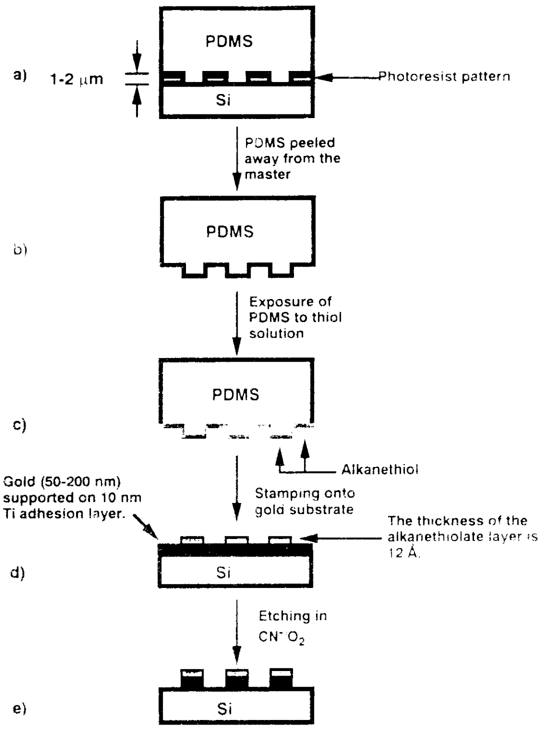

FIG. 2. Schematic description for the fabrication of Au patterns using PDMS (a) PDMS (Dow-Corning, Silicone Elastomer 184) was used to fabricate a stamp from a master template. The template was either a commercially available transmission electron microscopy grid or it was formed using conventional lithographic methods. (b) The stamp was removed from the master by peeling away the cured polymer, (c) the stamp was exposed to the alkanethiol ink. (d) After inking, the stamp was brought into contact with the Au substrate. Although the whole exposed surface of the stamp was covered with ink, only the regions that came into contact with the gold were derivatized (e) The patterned substrate was then etched in an aqueous, basic solution of cyanide ion and dissolved oxygen to produce the desired features.

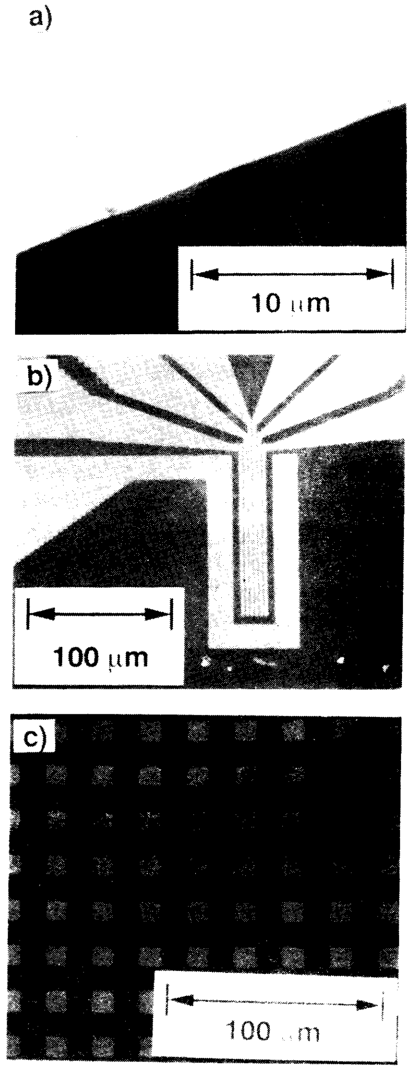

FIG. 3. SE micrographs of various types of features produced using rubber stamping and chemical etching. (a) Fracture profile of a series of gold lines supported on a silicon wafer. The width of the gold lines is 2 μm, and the thickness of the gold is 2000 Å. (b) electrodes (2.5 μm in width, separated by 1 μm spaces) in a microelectrode array. The contact pads are not visible in this frame at this magnification. (c) A regular array of squares of gold supported on silicon. The gold squares are 15 μm on a side. These arrays exhibited such regularity over several square centimeters.

commercially available templates, such as transmission electron microscopy grids. The template was placed in a plastic petri dish. A 10:1 (v:v) mixture of PDMS-Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp. Midland, MI) was poured into the petri dish. It was not necessary to put the mixture of PDMS-elastomer and curing agent under vacuum to remove dissolved dioxygen. The PDMS cured at room temperature in the laboratory ambient for 30–60 min. This cure was followed by additional curing at 65 °C for approximately 1 h or until the polymer was rigid. After cooling to room temperature, the PDMS was carefully peeled from the master.

Figure 3 shows some representative scale features formed using stamps made of PDMS. We have fabricated several types of features having dimensions ranging from 1 μm to several hundred μm. Figure 3(a) shows a fracture profile of 2 μm wide lines of gold on silicon. Figure 3(b) shows a microelectrode array. The gold microelectrodes are 2.5 μm wide. Figure 3(c) shows a regular array of gold squares on silicon. The squares are 15 μm on a side. Such arrays with squares and rectangles having dimensions from 10 to 80 μm have been fabricated. The regularity of the array was maintained over several centimeters. The micrographs in Fig. 3 illustrate that many types of features can be produced using this technique.

Figure 4 illustrates one method for increasing the versatility of the stamping method. One stamp consisting of parallel lines was used to stamp the same pattern twice: for the second pattern, the stamp was rotated through some angle relative to the first. By multiple impressions, one stamp can be used to produce several types of features. This procedure is analogous to a procedure used in photolithography, where a photoresist is exposed multiple times through the same mask in different orientations.[5]

Rubber stamping followed by chemical etching, at its current state, is a method for rapid prototyping of μm–cm scale features. Lithography using rubber stamps has several advantages over conventional lithographic techniques that require extensive instrumentation and/or clean rooms. The primary advantage is the ease with which features can be produced. Once a substrate is available, a stamp can be prepared for use, and multiple impressions can be made without requiring additional photolithography.

One of the problems with this method is the relatively inefficient method of delivery of the thiol to the surface of the substrate. Since the delivery of thiol to the surface requires physical contact between the stamp and the surface, some regions become blurred due to the unevenness of the surface topology and due to mechanical movement of the stamp during the stamping procedure. Some regions do not become derivatized if contact is not made between stamp and surface. Subsequent etching produces blurred features or etch pits. The number density of these defects, however, is small enough that lines extending several cm are conductive and parallel unconnected lines are electrically isolated.

We have demonstrated a lithographic method for rapid prototyping of simple structures on a scale comparable to UV photolithography. The method incorporates the use of a selective chemical etch in combination with a technique to pattern surfaces with a SAM on a micrometer scale. The primary advantage of this method is the ease of preparation of the stamp and the desired features, and its capability for producing multiple copies of the desired pattern with only one, initial lithographic step.

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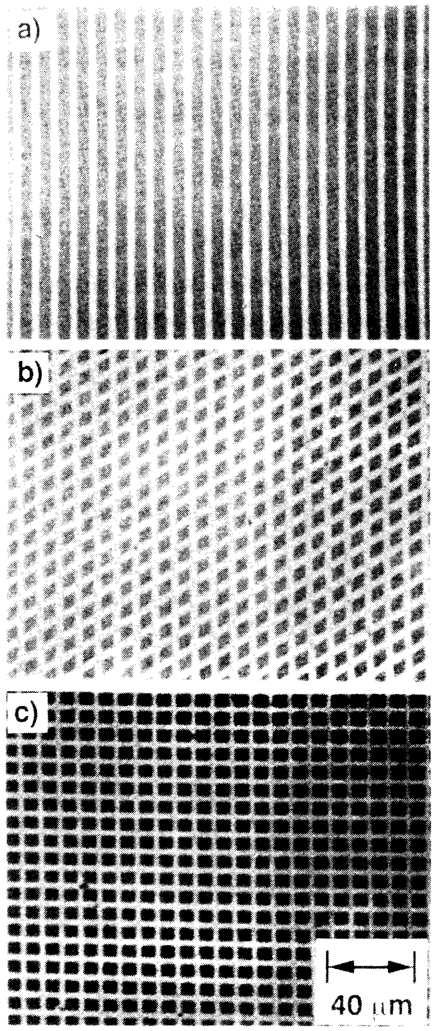

FIG. 4. SE micrographs of features produced through multiple stamping. (a) These features were produced using a stamp consisting of parallel lines of 2 μm width. To obtain the features in (b) and (c) one stamp was used to stamp the same pattern twice. To prepare the patterns in (b) and (c) the stamp in (a) was used twice, with the second impression at an angle of 45° (b) and 90° (c) relative to the first.

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