

Use of a Patterned Self-Assembled Monolayer To Control the Formation of a Liquid Resist Pattern on a Gold Surface

Christopher B. Gorman, Hans A. Biebuyck, and George M. Whitesides*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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Self-assembled monolayers (SAMs)^{1,2} of alkanethiolates on gold can serve as molecular resists in processes requiring either chemical etching of the gold^{3–5} or electrochemical deposition of metals and conjugated polymers on its surface.^{6–8} They have also been used to control nucleation of crystals⁴ and liquid drops⁹ and for a number of other purposes that require control of surface composition. By taking advantage of methods for patterning SAMs,^{3–5,8,10–12} features with sizes down to a few hundred nanometers can be produced using SAMs as resists. In most cases in which SAMs are used as resists, the SAMs act as physical barriers, limiting access of reagents to the underlying metal. A molecular barrier based on a SAM is thin: a monolayer of hexadecanethiol ($\text{H}_3\text{C}(\text{CH}_2)_{15}\text{SH}$, HDT) on gold is ~ 20 Å thick.^{13–15} It also contains some density of defects^{16–18} and can be damaged (for example, by exposure to light,^{19,20} by reaction with O_2 , or thermally). Although SAMs from HDT work remarkably well in some etching processes,¹¹ they eventually fail.

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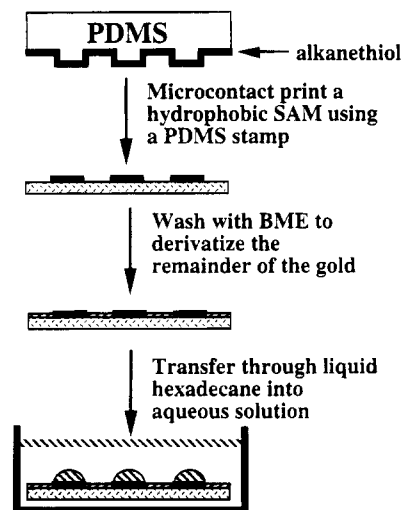


Figure 1. Schematic of the microcontact printing and liquid trapping processes. The SAM was formed using hexadecanethiol. In the third step, the slide was transferred through a thin (~ 1 mm) layer of HD into the aqueous solution. This process formed HD-covered regions with contact angles of ca. 40° on the patterned regions terminated by $-\text{CH}_3$ groups. The aqueous solution was either dilute aqua regia or an electroless deposition bath for copper.

SAMs of alkanethiolates on gold do not completely stop electron transfer from gold^{21–26} and appear to do little to prevent overgrowth of electrodeposited material from bare regions onto regions of the surface they cover: electrodeposited polypyrrole and electrolessly deposited copper metal grow only 100–300 nm thick on SAMs patterned with $10\ \mu\text{m}$ lateral features before such failure occurs.⁶ For a SAM to be effective as a resist also requires careful choice of etchants: an HDT monolayer on gold resists a basic cyanide/oxygen etch but provides no protection against aqua regia (see below).¹¹

In this communication, we show that patterned SAMs can be used to trap and hold a thin film of liquid resist on the surface and that these thicker resist systems overcome some of the problems discussed above. Previously, we showed that this liquid can be a prepolymer that is then converted to a solid via polymerization.²⁷ In the work described here, the resist remains as a liquid and is, as a result, easily removed. This liquid can be placed onto and removed from selected parts of the surface without any additional process steps (Figure 1). This process relies on the wettability of the surface²⁸ to direct liquid to patterned regions and thus to amplify the pattern into three dimensions. As before, however, properties of a small collection of molecules direct the process.

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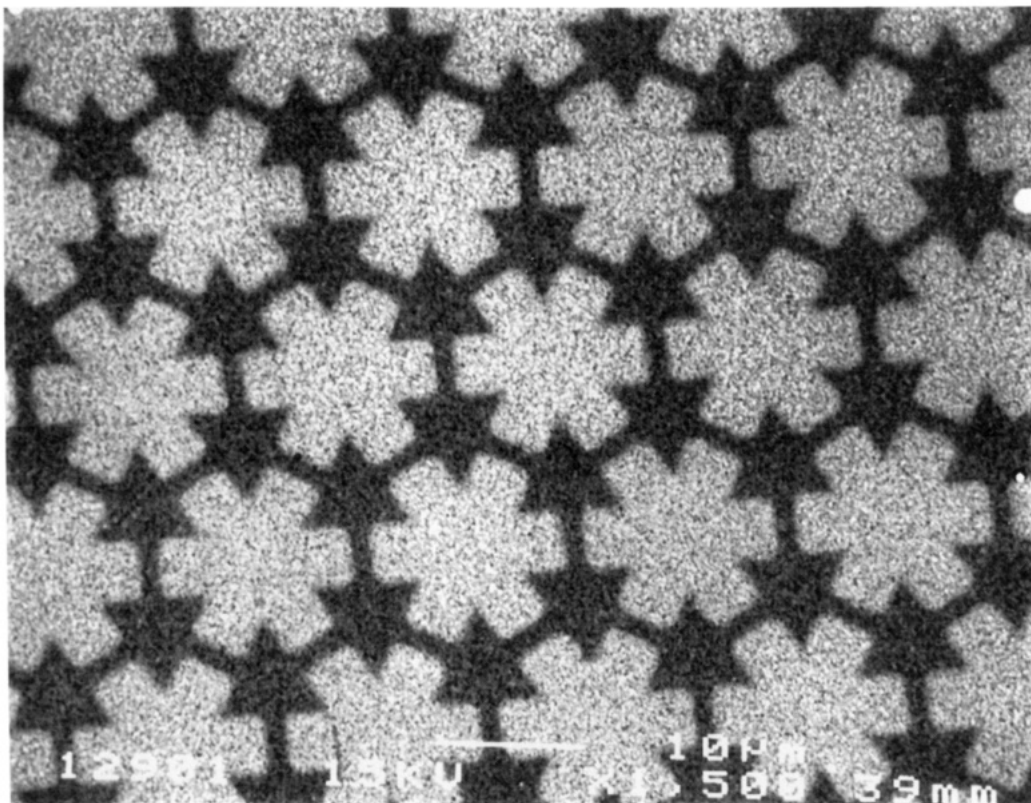


Figure 2. Scanning electron micrograph of a gold and silicon surface patterned and etched using a dilute aqua regia bath. The light areas in this image are gold regions that had been protected by HD. The dark regions in the image are the underlying silicon where the gold was dissolved away. Edge resolution is similar to that observed using a basic cyanide etch bath.¹¹

A monolayer of HDT was patterned by microcontact printing on a surface of 200 Å of gold on silicon primed with 5–10 Å of titanium as an adhesion promoter.^{3–5} Gold that remained bare after this step was derivatized using β -mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$, βME), a thiol that renders the gold hydrophilic and does not shield the gold surface from chemical etchants. This gold slide was passed through a thin (~ 1 mm) layer of hexadecane ($\text{H}_3\text{C}(\text{CH}_2)_{14}\text{CH}_3$, HD) floating on a diluted solution of aqua regia (80 mL of concentrated hydrochloric acid, 10 mL of concentrated nitric acid, 100 mL of water). HD adhered to the hydrophobic, HDT-covered regions of the SAM but not the hydrophilic, βME -covered regions.²⁹ The adherence of the HD to the hydrophobic regions of the SAM was such that the hexadecane-covered slide could be agitated in the solution without dislodging the liquid from the surface. Agitation, however, was not required to produce a good coverage of the surface with HD. A visible pattern developed rapidly (ca. 2–3 s) after a short period (ca. 30 s) as oxidation removed gold underlying the βME -covered regions. The slide was quickly withdrawn, rinsed with water and ethanol, and dried in a stream of nitrogen. The pattern (Figure 2) is similar to that produced by microcontact printing and etching in a basic cyanide solution. This process, however, avoids cyanide and requires less time (ca. 30 s versus ca. 10 min). Both processes are equally convenient. Alternatively, the gold could be removed potentiostatically by holding the slide at 2 V (vs SCE using a Mo counter electrode) in 1 M aqueous hydrochloric acid for approximately 30 s. Assembly of a HD

protecting layer by the patterned HDT/ βME monolayer is necessary for these etches to work selectively. Omission of the HD in this process resulted in rapid removal of all the gold without differentiation between the HDT-covered and βME -covered regions.

When a HDT/ βME -patterned slide was transferred through HD into an aqueous electroless copper deposition bath,³⁰ copper plated onto the βME -covered regions, and avoided the HDT-covered regions of the gold. The copper-covered features in the resulting structure (Figure 3) were $0.7 \pm 0.2 \mu\text{m}$ thick, as determined by atomic force microscopy.³¹ This thickness of copper was higher than that that could be cleanly obtained without the HD coverage. The HD layer protected against unwanted overgrowth even though the size of the copper grains was large. The HD protecting layer was removed easily by washing with water and then with ethanol and then drying in a nitrogen stream.

These processes illustrate a new role for SAMs in lithographic processes that supplements their role as molecule-thick resists. A hydrophobic surface generated as one component of a patterned SAM can trap a liquid

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(30) The bath consisted of 25 g of copper(II) sulfate, 12.5 g of ethylenediamine tetraacetic acid (EDTA), 25 g of sodium hydroxide, 400 mg of potassium cyanide, and 10 mL of 37% aqueous formaldehyde solution in 500 mL of water. This bath is slightly modified from that of: Cho, J. S. H.; Kang, H. K.; Wong, S. S.; Shachamdamand, Y. *MRS Bull.* **1993**, *18*, 31–38.

(31) AFM was performed using a Topometrix TMX-2010 atomic force microscope, cantilever force constant ~ 1 N/M, scan rate $100 \mu\text{m}/\text{s}$. Variation in the thickness was determined by scanning three $50 \mu\text{m} \times 50 \mu\text{m}$ regions on the sample and averaging.

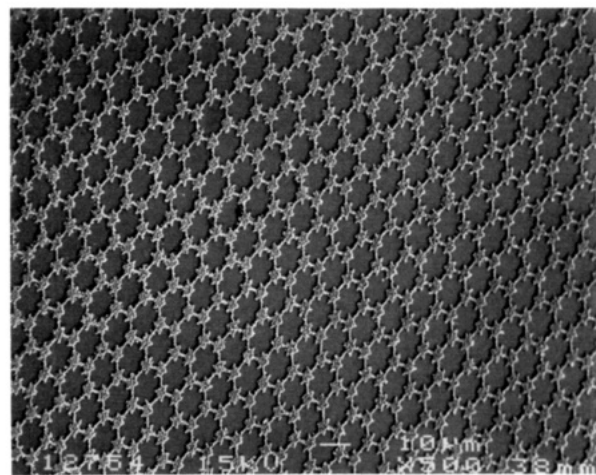
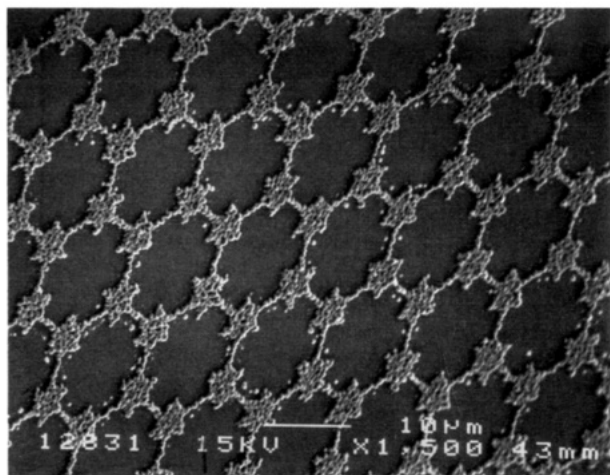


Figure 3. Scanning electron micrographs of the surface resulting from immersion of a gold surface patterned with HDT and β ME through a thin film of liquid HD into a copper metal deposition bath. Tilting the sample $\sim 15^\circ$ toward the secondary electron detector provided a qualitative indication of the thickness of the copper layer on the surface. The pattern used here is the same as that shown in Figure 2.

hydrocarbon under water, and a hydrophilic surface generated by a monolayer with a polar terminus will resist being wet by a hydrocarbon placed on it when under water. Liquids are conveniently patterned and removed on such surfaces and their barrier properties are sufficient to regard them as good resist materials. Particularly on the 1–100 μm length scale, they are robust and resist mechanical removal due to shear caused by agitation or vibration. We will describe

additional applications of three-dimensional structures prepared by self-assembly in the future.

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