The Use of Self-Assembled Monolayers and a Selective Etch To Generate Patterned Gold Features

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Received April 13, 1992

The combination of aqueous, alkaline cyanide ion (1 M KOH, 0.1 M KCN) and dioxygen rapidly etches Au(0) (eq 1).\(^2\)\(^-\)\(^4\)

\[ 4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{[Au(CN)]}_2^- + 4\text{OH}^- \] (1)

on the surface of the gold block this etching. Using a number of techniques—micromachining, microwriting, electron-beam lithography, ion-beam lithography—it is possible to form patterns of SAMs on the Au surface. By combining these techniques for forming patterns with selective etching using the CN\(^-\)/O\(_2\) solution, high-resolution patterns of gold on silicon can be fabricated with dimensions as small as 1 \(\mu\)m.\(^5\)

One procedure used a pen to write patterns of hexadecanethiolate as monolayers on Au substrates. The pen, filled with hexadecanethiol, was clamped to a X-Y micrometer, and the gold sample was moved across the tip of the pen at 10-100 \(\mu\)m/s.\(^7\) This system allowed the formation of 1-100 \(\mu\)m features. Only the drop of thiol (i.e., not the tip of the pen) was in contact with the gold surface. Etching resulted in complete removal of the underivatized Au and underlying Ti.\(^8\)\(^-\)\(^9\)

Figure 1 shows a representative line. The regions of the Au surface protected by the SAM exhibited little pitting (fewer than 5 pits, approximately 1 \(\mu\)m in diameter, per \(\text{mm}^2\)): the density of pitting did not increase for exposures of an additional 12 h. The monolayer was not removed: profilometry confirmed that the thickness of the protected Au was the same before and after immersion in the etching solution. The hydrophobicity of the protected surface (measured by the contact angle of water) did not change. Two-point conductivity measurements indicated that lines having widths of 10 \(\mu\)m were electrically conducting: there were no breaks in the gold over distances of 1-2 cm. Adjacent, unconnected lines spaced apart by 1-2 mm were electrically conducting.\(^6\)

(1) This research was supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency.


(6) Hexadecanethiol is the longest chain alkanethiol that is liquid at room temperature and was the best for writing lines. The thiolate monolayer should be amphiphilic. Amphiphilic alkanethiol "ink" allowed smooth formation of continuous lines without leaving excess thiol on a line and without loss of definition through reactive spreading. We used a Staedtler pen.

(7) The gold film (2000 \(\text{Å}\) in thickness) was prepared by electron beam evaporation onto a titanium-primed (100 \(\text{Å}\) Ti) silicon wafer.

(8) The etch solution consisted of 1 M KOH and 0.1 M KCN in distilled water. The solution container was open to the ambient air and stirred vigorously. Alternatively, the solution was saturated with dioxygen using a coame.

(9) The Au and Ti in the regions not protected by the SAM dissolved completely, as determined by energy dispersive X-ray spectroscopy (EDX).
isolated from each other, with resistances between them greater than 1 MΩ.

We were also able to micromachine lines reproducibly in the monolayer, with very high spatial resolution, and subsequently to etch away the gold in the machined regions (Figure 1). As with the protected Au line, the edges of the trench exhibited excellent sharpness.

SAMs—14–20 Å, ordered, organic layers—can thus protect a surface from corrosion. This thin organic resist material, in combination with patterning and selective etching, provides a convenient method for forming structures of gold on silicon, with feature sizes as small as 1 μm. Because this procedure does not require photolithographic equipment, it is particularly suitable for use in chemical laboratories and for applications such as rapid prototyping of microelectrode arrays and other relatively simple structures.

(10) The width of the trench was dependent upon the sharpness of the mechanical probe and the pressure used in the micromachining process. We routinely formed trenches of width 0.5–2 μm. Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. Science 1992, 257, 1380.

(11) SAMs formed from alkanethiols with longer chains also exhibited excellent protection. Shorter chain thiols including perfluorinated systems provided limited protection from the etching.