A Selective Etching Solution for Use with Patterned Self-Assembled Monolayers of Alkanethiolates on Gold

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This paper describes a selective etching solution for use with patterned self-assembled monolayers (SAMs) of alkanethiolates on the surface of gold; it is also effective for SAMs on the surfaces of silver and copper. This etching solution uses thiosulfate as the ligand that coordinates to the metal ions and ferricyanide as the oxidant. This etchant has a number of advantages relative to the system of cyanide ion in oxygen-saturated, alkaline water used in previous work. First, it is less toxic, less hazardous, and has smaller environmental impact. Second, using it, complete etching of bare gold can be achieved more rapidly ( ~ 8 min versus ~ 15 min for 200 A of Au). Third, etching of bare gold occurs with fewer defects in the SAM-covered regions and generates features of gold with higher edge resolution. The influence of the composition of the etching solution on the rate of etching was studied systematically.

Introduction

Microcontact printing (μCP) is a technique that generates patterned self-assembled monolayers (SAMs) of alkanethiolates typically, hexadecanethiolate) on the surfaces of gold, silver, and copper, and of alkylsiloxanes on hydroxyl-terminated surfaces. Patterned SAMs of alkanethiolates serve as nanometer-thick resists in certain etching solutions: the one we have used most extensively when gold is the underlying substrate has been aqueous KCN solution (pH = 14, [CN] = 0.1 M) saturated with O₂. Using this etchant, the patterns in the SAMs can be transferred faithfully into the thin films of gold; the resulting patterns of gold can be used subsequently as secondary masks for the etching (isotropic or anisotropic) of underlying layers of silicon dioxide and silicon nitride or as functional elements (for example, for microelectrodes and diffraction gratings). Microcontact printing is remarkably convenient for the fabrication of structures with feature sizes of ~ 1 μm and larger; it can be used, with more difficulty and less reliability, to fabricate features with sizes down to ~ 100 nm.

The toxicity and environmental impact of an etchant that contains free cyanide ion are obviously unattractive. Here we report a more selective etching solution for use with SAMs of alkanethiolates on gold that uses thiosulfate rather than cyanide as the coordinating ligand, and ferricyanide rather than O₂ as the oxidant. Ferriferrocyanide are far less toxic than free cyanide—values of LD₅₀ (ORL-MUS) are KCN (8.5 mg/kg), K₂Fe(CN)₆ (2970 mg/kg), and K₃Fe(CN)₆ (5000 mg/kg). This ferriferrocyanide etchant is also superior to that containing CN in its selectivity: it is more rapid, generates fewer defects in the SAM-covered regions and yields microstructures of gold with higher edge resolution.

Experimental Section

Materials. Au (99.99%) (Johnson-Matthey), Ag (99.999%), Cu (99.999%), Cr (> 99.99%), Ti (> 99.99%), K₂S₂O₈, KSCN, K₂Fe(CN)₆, K₃Fe(CN)₆, and CH₃(CHOH)₂SH were obtained from Aldrich. KOH, and K₂Fe(CN)₆ were purchased from Fisher Scientific. Poly(dimethylsiloxane) (PDMS) was obtained from Dow Corning (Sylgard 184). Polished Si wafers (Cz, N phosphorus-doped, 1-30 Ω cm test grade, SEMI Std. flats) were obtained from Silicon Sense, Inc. (Nashua, NH). Hexadecanethiol was purified under nitrogen by chromatography through silica gel. Gold films (> 200 A thick) were prepared using thermal evaporation (Varian 3118) onto silicon wafers whose surfaces had been primed with thin layers of chromium (~ 50 A thick). Gold, silver and copper films (500-1200 A thick) were prepared using e-beam sputtering onto titanium-primed (~ 15 A) silicon wafers. We chose 200 A thick gold films for most of the current work for three reasons: (i) Gold films ≥ 200 A appear to behave very similarly in ferriferrocyanide etching solutions; thinner films have more defects: 200 A is therefore a "standard thin film". (ii) Gold is relatively inexpensive, and we wished to use


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Figure 1. SEMs of gold films (200 A thick) that had been patterned with SAMs of hexadecanethiolate by μCP, and etched in the standard etching solution containing S₂O₃²⁻ and ferri/ferrocyanide for different intervals of time. Note that the density of pits in the SAM-covered regions increased as etching time increased. The intensity of the secondary electrons (Iₑ, shown schematically as a line scan in arbitrary units) can be used to monitor the etching process semiquantitatively. The scans drawn on the right side were along the lines marked in the SEMs on the left side.

(iii) As shown in the text, 200 A gold films are thick enough to be used as substrates for forming ordered SAMs of alkanethiolates, and these gold films were also thick enough to be used as masks for the etching of underlying layers of SiO₂ and Si.

Measurements of Iₑ. The intensity of secondary electrons (Iₑ) was measured with a SEM (JEOL-6400) by setting the mode in the line scan. Samples of Figures 1 and 2a were loaded into the SEM chamber at the same time; readings of Iₑ were taken under the same conditions (spot size, accelerate voltage, filament current, contrast, and brightness).

Microcontact Printing (μCP). PDMS stamps were fabricated according to the published procedure. A solution of hexadecanethiol in ethanol (~2 mM) was used as the "ink" for μCP. Microcontact printing was carried out in a clean room (~100 particles/ft²). Gold films (200 A thick) used in this paper were also prepared in a clean room (~1000 particles/ft²) and were used as prepared immediately without any further cleaning. After application of the hexadecanethiol solution (by cotton Q-Tip) to the PDMS stamp, the stamp was dried in a stream of N₂ for ~1 min and then brought into contact with the surface of gold. After ~5 s, the stamp was separated carefully from the gold surface.

Etching of Gold. The composition of the standard ferri/ferrocyanide etchant was K₂S₂O₃ (0.1 M), KOH (1.0 M), K₃Fe(CN)_6 (0.01 M), and K₅Fe(CN)₉H₂O (0.001 M). Caution: potassium ferrocyanide is light sensitive. The photodecomposed products contain free cyanide. This etching solution should be stored in brown bottles. Potassium ferrocyanide is also incompatible with acids and liberates HCN. All components of each etchant were weighed in a chemical lab, and prepared into solution in a clean room (~100 particles/ft²) using H₂O of 18 MΩ quality.

Figure 2. (a) Dependence of the intensities of secondary electrons (Iₑ) from both bare gold regions (filled circles) and SAM-covered regions (open circles) on the duration of etching (for 200 A thick gold films). The difference between these two intensities was plotted as triangles. The quantity t₁ is defined as the time for complete etching, and t₂ - t₁ as the etching window. For the composition of the standard etching solution used (K₂S₂O₃/0.1 M, KOH 1.0 M, K₃Fe(CN)₆/0.01 M, and K₅Fe(CN)₉H₂O/0.001 M), the etching window is ~4 min. (b, c, d) Dependence of t₁ and t₂ on the concentrations of K₂S₂O₃, KOH, and K₅Fe(CN)₉H₂O, respectively. Gold films of 200 A thickness were used. When varying the concentration of each component, the concentrations of other components were kept unchanged at the values as in the standard etching solution. The curves were the best-fit.

All etchings of gold were carried out in the clean room (~100 particles/ft²) using the standard composition at room temper-
were carried out with or without visible light. The etching
ature unless mentioned in the text. Essentially no differences
in the quality of the samples were observed when etchings
were carried out with or without visible light. The etching
solution (300 mL of etching solution in a 400 mL beaker) was
stirred at ~300 rpm with a magnetic stirring bar that was ~2
cm long. Gold films (~200 Å thick) dissolved completely in
solution (300 mL of etching solution in a 400 mL beaker) was
stirred at ~300 rpm with a magnetic stirring bar that was ~2
min at room temperature. The composition of the standard
cyano etching solution was KOH (1 M) and KCN (0.1 M).

**Etching of Silicon.** Anisotropic etching of silicon was
carried in an aqueous solution of KOH and 2-propanol at 70
°C (~400 mL of H2O, 92 g of KOH, 132 mL of 2-ProH) for ~10
min. Prior to silicon etching, the native oxide on silicon was
removed by dipping in an unbuffered aqueous HF solution
(~1% w/w).

**Results and Discussion**

**Assays Used To Follow Etching.** The etching
process was studied qualitatively and semiquantitatively
by examining scanning electron micrographs (SEMs) of gold samples whose surfaces had been patterned with
terned with lines of hexadecanethiolate by CP, and
etched under different conditions.

Figure 1 shows the progression of etching in the
standard solution containing S2O82- and ferri/ferroicy-
and nucleation and etching occurred predominantly on
the regions of bare gold; no etching was observed on
those regions derivatized with SAMs (Figure 1a). Etch-
ing on the bare regions of gold seemed to be a polishing
process: gold was homogeneously thinned and did not
roughen during etching. During the etching of the bare
regions of gold, the etchant also attacked the SAM-
covered regions; the attack was seen as pinholes (or
more generally, defects) on SEMs (Figure 1b). As etching
continued, more defects appeared in the SAM-
covered regions (Figure 1c) and, eventually, all the gold
in the SAM-covered regions also dissolved. We assayed
the etching using scanning electron microscopy (SEM):
the intensity of secondary electrons (Ie) in the SEM
image is approximately proportional to the amount of
gold left on the surface when the gold films are thinner
than the escape depth for the secondary electrons from
Au (the images shown in Figure 1 are of secondary
electrons); Ie decreased as gold was dissolving.17,18
The change of Ie with the duration of the etching can,
therefore, be used to monitor the etching process semiquan-
titatively. Figure 2a indicated that the magnitude of
Ie for bare regions of gold initially decreased as etching
proceeded, while the magnitude of Ie for SAM-
covered regions remained essentially unchanged. Ie (SAM)
started to drop only when the samples were overetched (that is, when the gold of the SAM-covered regions was dissolving in substantial quantity). The difference between these two intensities (that is, the contrast) increased at the beginning, reached a steady state (t1 to t2), and then fell (Figure 2a). In Figure 2a, t1 is defined as the time for complete etching, and t2 − t1 as the etching window. For the standard etching
solution used for most of the work described in this
paper (K2S2O8/0.1 M, KOH/1.0 M, K5Fe(CN)6/0.01 M,
and K3FeCN(b/0.001 M), t1 ≈ 7−8 min, t2 − t1 ≈ 4 min
for 200 Å thick Au.19 In practical applications, the etching window must be long enough (several minutes)
to accomplish reproducible etching of samples by com-
plete etching of the bare regions, and without unaccept-
able etching of the SAM-covered regions.

**Influence of the Composition of the Etching
Solution on the Rate of Etching.** Figure 2b,c shows
the dependence of etching time on the concentration of
each component of the ferri/ferrocyanide etching solu-
tion. All components but ferrocyanide must be present
to achieve rapid and selective etching.

Like the dissolution of many metals in aqueous solutions,20 the etching of gold is an electrochemical process with at least two primary steps:

1. Metal oxidation (dissolution):21,22

\[

cu^0 + 2S_2O_7^{2-} \rightarrow cu(S_2O_3)_{2}^{3-} + e^-
\]

or

\[
cu^0 + 2OH^- \rightarrow cu(OH)_2^- + e^-
\]

\[
cu(OH)^2^- + 2S_2O_7^{2-} \rightarrow cu(S_2O_3)_{2}^{3-} + 2OH^- + Au^{2+}
\]

(2) Reduction of an oxidizer:

\[
Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}
\]

The rate-determining step is usually one of these two
electrochemical steps. In this instance, it appears that
the oxidation of gold is rate determining since the rate
of etching is controlled by the concentrations of S2O82-
(the ligand that coordinates to Au(I)) and OH- (whose
function is not clear but which probably acts as a
coordinating ligand or by lowering the redox potential
of gold).23,24 In Figure 2b,c shows no difference in the rate of etching was
observed over the range of concentration between 0.001
and 0.1 M for potassium ferrocyanide. The addition of
ferrocyanide to the initial etching solution had little
influence on the rate of etching; its presence, somehow,
greatly reduced the density of defects that were formed in
the SAM-covered regions during the etching of gold
(see the next sections).

Electrochemical regeneration of Fe(III) from Fe(II) in
solutions is quite straightforward. For example, regener-
ating FeCl3(aq) (an etchant that is used widely for making
printed circuits of copper in microelectronics) from FeCl2(aq) has been demonstrated.25 It is, therefore, possible to regenerate the ferrocyanide etchant used in
this paper (i.e., convert ferrocyanide to ferricyanide) using electrochemical methods.\textsuperscript{26}

**Edge Resolution and Defects.** Figure 3 compares test patterns of gold that were fabricated by μCP of hexadecanethiol on gold, followed by selective etching in the standard etchants that contain \( \text{S}_2\text{O}_8^{2-} / \text{ferri}/\text{ferrocyanide} \) and cyanide, respectively. The etching solution containing \( \text{S}_2\text{O}_8^{2-} / \text{ferri}/\text{ferrocyanide} \) produces microfeatures of gold with fewer defects and higher edge resolution than that using cyanide and acts more rapidly. The etching behavior of gold in these two etchants also appears to be qualitatively different: SEM indicates that, in the \( \text{S}_2\text{O}_8^{2-} / \text{ferri}/\text{ferrocyanide} \) solution, etching on bare gold is a polishing process (homogeneous nucleation and etching): in the cyanide solution, etching on bare gold is a pitting process (heterogeneous nucleation and etching). The pitting of bare gold in the cyanide etchant implies an etching mechanism similar to the corrosion of iron in which part of the metal acts as an anode and part acts as a cathode, and oxygen is reduced on the gold surface. The homogeneous thinning of bare gold in the ferrocyanide etchant indicates that ferrocyanide is probably reduced in the solution rather than on the gold surface.

The addition of ferrocyanide to the initial etching solution containing \( \text{S}_2\text{O}_8^{2-} \) and ferrocyanide helped to reduce the density of defects formed in the SAM-covered regions (probably via lowering the redox potential of the ferri/ferrocyanide pair). Figure 4 compares test patterns of gold that were fabricated by etchants with and without addition of ferrocyanide to the initial etching solutions, respectively.

The defects produced in SAM-covered regions during the etching of gold seem to originate from the domain structures of the SAMs or from the intrinsic defects (such as pinholes) in the SAMs. Etching, of course, can amplify flaws in the SAMs. Although the initial density and size of defects were determined by the SAM itself, the final density and size of defects produced in SAM-covered regions after etching are influenced by the coordinating ligand probably related to the association constant of the resulting coordinating compound used in each etchant: etchants containing different coordinating ligands usually result in different etching morphologies (that is, different models for nucleation and growth of defects) in the SAM-covered regions.

**Other Coordinating Ligands.** Other anions—especially thiocyanate (KSCN), halides (KCl, KBr, KI), hypophosphate (KHPO\textsubscript{3}), and dithiocarbamate ([C\textsubscript{2}H\textsubscript{3}]\textsubscript{2}NCS\textsubscript{2})—were also tested as coordinating ligands using ferrocyanide as the oxidant.\textsuperscript{27} No etching was observed in solutions containing bromide, chloride, hypophosphate, and dithiocarbamate anions. Selective etching was observed for those etchants that...

\textsuperscript{26} Palanisamy, R.; Sozhan, G.; Narasimham, K. C. Indian J. Technol. 1993, 31(8), 597.

\textsuperscript{27} The concentration of each ligand was 0.1 M; the concentrations of other components were the same as those in the standard etching solution of ferri ferrocyanide.
Figure 5. SEMs of test patterns of gold (200 Å thick) that were fabricated by μCP with hexadecanethiol, followed by etching in solutions that use ferric ferrocyanide as the oxidant, and thiosulfate, thiocyanate, and iodide ion as the coordinating ligand (all at the same concentration, 0.1 M), respectively. The bright regions are gold covered by SAM, and the dark regions are Si/SiO₂ where underivatized gold has been removed by etching.

used thiocyanate²⁸ and iodide²⁸ to²⁹ as the coordinating ligands. Figure 5 shows test patterns of gold that were prepared by μCP of hexadecanethiol, followed by etching in the etchant that used S₂O₃²⁻, SCN⁻, and I⁻ as the coordinating ligand, respectively. Thiocyanate is not as good as S₂O₃²⁻ as a ligand as a component of a selective etchant: more defects are formed in the SAM-covered regions. Iodide is as good as S₂O₃²⁻, although the time for complete etching is ~30% longer.

Other Oxidants. Other oxidants (KClO₃, KClO₄, and KIO₃; all have approximately the same redox potential as ferri/ferrocyanide) were also tested as the oxidant in the etching solution, with thiosulfate or iodide as the coordinating ligand.³⁰ No etching of gold was observed within ~30 min.

An Acidic and Selective Etchant for Gold. The etchants for gold described so far are all strongly alkaline solutions (pH ~ 14). In some applications (for example, when the underlying substrate is GaAs), we require etchants that can function in neutral and acidic solutions. We found that thiourea could be used for this purpose. Figure 6 shows SEMs of test patterns of gold that were fabricated by μCP of hexadecanethiol, followed by etching in an acidic etching solution (pH ~ 1) that used thiourea as the coordinating ligand and hydrogen peroxide as the oxidant.³¹ The etching of gold in this etchant was extremely rapid: bare regions of gold films of 500 Å thick were completely etched in ~30 s. The etching window was also narrow: ~5–10 s. The edge resolution of this etchant is lower than that of ferri/ferrocyanide solution (~0.3 versus ~0.1 μm).

Microstructures of Gold as Masks. One of the applications of μCP on gold is preparing gold microstructures to be used as masks for the etching of underlying substrates. Figure 7 shows SEMs of micro-

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²⁸ The aqueous solution of KI/I₂ has been used to selectively etch gold with thin films of photoresists as the masks.²⁷ This etchant, however, had no selectivity when patterned SAMs of alkanethiolates were used as the masks.

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Figure 7. (a) SEMs of microstructures of gold that were fabricated by μCP of hexadecanethiol on gold, followed by etching of gold in the standard ferri/ferrocyanide solution for 7 min: (b) SEMs of microstructures of silicon prepared by anisotropic etching of silicon in an aqueous solution of KOH/i-PrOH with the above structures of gold as masks. After silicon etching, the gold masks were removed by dipping in aqua regia for ~1 min. The scale bar applies to all pictures.

Figure 8. SEMs of test patterns of copper and silver that were fabricated using the ferri/ferrocyanide etchant with patterned SAMs of alkane-thiolates (by μCP) as the resists. The bright regions are metals covered by SAMs, and the dark regions are Si/SiO₂ where undervatized metals have been removed by etching.

Using this etchant, complete removal of bare gold can be achieved within a shorter interval of time with fewer defects in the SAM-covered regions than with CN⁻/O₂; this etch also yields microstructures of gold with higher edge resolution than the CN⁻/O₂ system. The microstructures of gold fabricated by μCP followed by selective etching in the present etchant served as masks for the etching of underlying layers of silicon dioxide and silicon. The combination of S₂O₃²⁻ and ferri/ferrocyanide can also be used for selective etching of copper and silver with patterned SAMs of hexadecanethiolates (by μCP) as the resists. Thiosulfate contained in this etchant can be replaced by iodide ion without loss in the quality of the generated microstructures of gold.

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Conclusions

This work describes a more selective etchant for use with patterned SAMs of alkane-thiolates on gold than the combination of CN⁻/O₂ that was used previously; this S₂O₃²⁻/ferri/ferrocyanide-based etching solution is also less toxic and hence more convenient to use.³²,³³

³² Copper and silver were etched in neutral aqueous solutions (K₂S₂O₃/0.1 M, K₂Fe(CN)₆/0.01 M, K₃Fe(CN)₆/0.001 M). The etching window for Ag and Cu is ~15 and ~5 s, respectively.

³³ Ferris- and ferrocyanides have very high association constants (K ≈ 10⁷⁻, 10⁴⁻ respectively, but the concentration of free CN⁻ formed from the dissociation of ferri/ferrocyanide in the ferri/ferrocyanide etching solution is very low, and we believe its contribution to the etching of gold can be neglected.