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 $(\mu CP)^1$ is a technique that generates patterned self-assembled monolayers (SAMs)² of alkanethiolates (typically, hexadecanethiolate) on the surfaces of gold,¹ silver,³ and copper,⁴ and of alkylsiloxanes on hydroxyl-terminated surfaces.⁵ 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 \approx 14, [CN] \approx 0.1 M) saturated with O_2 .⁶ 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^{7.8} or as functional elements (for example, for microelectrodes⁹ and diffraction gratings¹⁰). Microcontact printing is remarkably convenient for the fabrication of structures with feature sizes of $\sim 1 \, \mu m$ and larger; it can be used, with more difficulty and less reliability, to fabricate features with sizes down to ~ 100 nm.¹⁰⁻¹³

- ⁸ Abstract published in *Advance ACS Abstracts*. November 1, 1995.
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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 this ulfate rather than cyanide as the coordinating ligand, and ferricyanide rather than O_2 as the oxidant. Ferri/ferrocyanide are far less toxic than free cyanide values of LD₅₀ (ORL-MUS) are *KCN* (8.5 mg/kg),¹⁴ $K_3Fe(CN)_6$ (2970 mg/kg),¹⁴ and $K_4Fe(CN)_6$ (5000 mg/kg).¹⁵

This ferri/ferrocyanide 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 (99.999%), Ag (99.9999%), Cu(99.999%), Cr- $(>99.99\%), Ti(99.99\%), K_2S_2O_3, KSCN, K_3Fe(CN)_6, K_4Fe(CN)_6,$ and $CH_3(CH_2)_{15}SH$ were obtained from Aldrich. KI, KOH, and KCN were purchased from Fisher Scientific. Poly(dimethylsiloxane) (PDMS) was obtained from Dow Corning (Sylgard 184). Polished Si(100) wafers (Cz, N/phosphorous-doped, 1-10 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 Å thick). Gold, silver and copper films (500-1200 Å thick) were prepared using e-beam sputtering onto titanium-primed (${\sim}15$ Å) silicon wafers. We chose 200 Å thick gold films for most of the current work for three reasons: (i) Gold films ≥ 200 Å seem to behave very similarly in ferri/ferrocyanide etching solutions; thinner films have more defects: 200 Å is therefore a "standard thin film".¹⁶ (ii) Gold is relatively expensive, and we wished to use

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⁽¹³⁾ Wilbur, J. L.; Kim, E.; Xia, Y.; Whitesides, G. M. Adv. Mater. **1995**, 7, 649.

⁽¹⁴⁾ Material Safety Data Sheets (CD-ROM), Sigma-Aldrich-Fluka: Milwaukee, WI, 1994.
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results.

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Figure 1. SEMs of gold films (200 Å thick) that had been patterned with SAMs of hexadecanethiolate by μ CP, and etched in the standard etching solution containing $S_2O_3^2$ 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 (I_{se} , 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.

gold films that were as thin as possible. (iii) As shown in the text, 200 Å 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 I_{se} . The intensity of secondary electrons (I_{se}) 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 I_{se} were taken under the same conditions (spot size, accelerate voltage, filament current, contrast, and brightness).

Microcontact Printing (μ **CP**). PDMS stamps were fabricated according to the published procedure.^{1,10} A solution of hexadecanethiol in ethanol (~2 mM) was used as the "ink" for μ CP. Microcontact printing was carried out in a clean room (<100 particles/ft³). Gold films (200 Å thick) used in this paper were also prepared in a clean room (<10 000 particles/ft³) 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 $K_2S_2O_3$ (0.1 M), KOH (1.0 M), K_3Fe -(CN)₆ (0.01 M), and K_4Fe (CN)₆ (0.001 M). *Caution: potassium ferricyanide is light sensitive. The photodecomposed products contain free cyanide.*¹⁴ *This etching solution should be stored in brown bottles. Potassium ferricyanide 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/ft³) using H₂O of 18 MΩ quality.



Figure 2. (a) Dependence of the intensities of secondary electrons (I_{se}) from both bare gold regions (filled circles) and SAM-covered regions (open circles) on the duration of etching (for 200 Å thick gold films). The difference between these two intensities was plotted as triangles. The quantity t_1 is defined as the time for complete etching, and $(t_2 - t_1)$ as the etching window. For the composition of the standard etching solution used (K₂S₂O₃/0.1 M, KOH/1.0 M, K₃Fe(CN)₄/0.001 M), and K₄-Fe(CN)₄/0.001 M), the etching window is ~4 min. (b, c, d) Dependence of t_1 and t_2 on the concentrations of K₂S₂O₃, KOH, and K₃Fe(CN)₆, respectively. Gold films of 200 Å thickness were used. When varying the concentration of each component, 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 (\leq 100 particles/ft³) using the standard composition at room temper-

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 \sim 300 rpm with a magnetic stirring bar that was \sim 2 cm long. Gold films (\sim 200 Å thick) dissolved completely in 7–8 min at room temperature. The composition of the standard cyanide 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 lines of hexadecanethiolate by μ CP, and etched under different conditions.

Figure 1 shows the progression of etching in the standard solution containing $S_2O_3^{2-}$ and ferri/ferrocyanide. Immediately after exposure to the etching solution, nucleation and etching occurred predominantly on the regions of bare gold; no etching was observed on those regions derivatized with SAMs (Figure 1a). Etching 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 SAMcovered regions; the attack was seen as pinholes (or more generally, defects) on SEMs (Figure 1b). As etching continued, more defects appeared in the SAMcovered 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 (I_{se}) 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); $I_{
m se}$ decreased as gold was dissolving.^{17,18} The change of I_{se} with the duration of the etching can, therefore, be used to monitor the etching process semiquantitatively. Figure 2a indicated that the magnitude of $I_{\rm se}$ for bare regions of gold initially decreased as etching proceeded, while the magnitude of I_{se} for SAMcovered regions remained essentially unchanged. I_{se} - $\left(SAM\right)$ 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 $(t_1 \text{ to } t_2)$, and then fell (Figure 2a). In Figure 2a, t_1 is defined as the time for complete etching, and $(t_2 - t_1)$ t_1) as the etching window. For the standard etching solution used for most of the work described in this paper (K₂S₂O₃/0.1 M, KOH/1.0 M, K₃Fe(CN)₆/0.01 M, and K₄Fe(CN)₆/0.001 M), $t_1 \approx 7-8 \text{ min}$, $t_2 - t_1 \approx 4 \text{ min}$ (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 complete etching of the bare regions, and without unacceptable 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 solution. 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}

$$Au^{0} + 2S_{2}O_{3}^{2-} = Au(S_{2}O_{3})_{2}^{3-} + e^{-}$$

or

Α

$$Au^{0} + 2OH^{-} = Au(OH)_{2}^{-} + e^{-}$$

 $u(OH)_{2}^{-} + 2S_{2}O_{3}^{-2} = Au(S_{2}O_{3})_{2}^{-3} + 2OH$

(2) Reduction of an oxidizer:

$$Fe(CN)_{6}^{3-} + e^{-} = Fe(CN)_{6}^{4-}$$

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 $S_2O_3^{2-}$ (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}). No difference in the rate of etching was observed over the range of concentration between 0.001 and 0.1 M for potassium ferricyanide. 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, regenerating 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 ferricyanide etchant used in

⁽¹⁷⁾ The escape depth for the secondary electrons from gold is \sim 50–100 Å.¹⁸ As the roughness of a surface increases, the intensity of secondary electrons also decreases.

⁽¹⁸⁾ Goldstein, J. I.; Newbury, D. E.; Schlin, P.; Joy, D. C.; Roming, A. D. Jr.; Lyman, C. E.; Fiori, C.; Lifshin, E. Scanning Electron Microscopy and X-ray Microanalysis, 2nd ed.; Plenum Press: New York, 1994; pp 69–90.

⁽¹⁹⁾ The times $(t_1 - t_2)$ for complete etching of 1000 and 1200 Å thick gold films are 29–32 and 39–42 min, respectively.

⁽²⁰⁾ Randle, T. H. J. Chem. Educ. **1994**, 71, 261. Mattsson, E. CHEMTECH **1985**, April, 234.

⁽²¹⁾ We assume that the gold ions produced in the etching process are Au(I), since the redox potential of ferricyanide is not high enough to oxidize Au(0) to Au(III). We also assume that the coordination number for Au(I) is two, the most common coordination state for complexes of Au(I).²² The exact value of this number does not affect the discussion made in the text.

⁽²²⁾ Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th ed.; John Wiley & Sons, Inc.: New York, 1988, p 940.

⁽²³⁾ $Au^+ + e = Au (E^\circ = 1.69 \text{ eV}); Au(OH)_2^+ + e = Au + 2OH^- (E^\circ = 0.40 \text{ eV}).$

⁽²⁴⁾ Antelman, M. S. The Encyclopedia of Chemical Electrode Potentials, Plenum Press: New York, 1982, p 93.

 ⁽²⁵⁾ Hillis, M. R. Trans. Inst. Met. Finish. 1979, 57(2), 73. Beyer,
 S. J.; Lukes, R. M. US 71-142065 710510.

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a) $S_2O_3^2$ /Fe(CN) $_6^8$ /Fe(CN) $_6^4$ (7 min) b) CN⁻/O₂ (15 min)

$100 \, \mu m$

100 nm

Figure 3. SEMs of test patterns of gold (200 Å thick) that were fabricated by μ CP with hexadecanethiol, followed by etching in the standard solution of $S_2O_3^{2+7}$ Fe(CN)₆²⁺⁷ /Fe(CN)₄²⁺⁷ for 7 min and of CN⁻⁷/O₂ for 15 min, respectively. The bright regions are gold covered by SAM, and the dark regions are Si SiO₂ where underivatized gold has been removed by etching. The blemishes on the dark regions are residual gold.

this paper (i.e., convert ferrocyanide to ferricyanide) using electrochemical methods. 26

Edge Resolution and Defects. Figure 3 compares test patterns of gold that were fabricated by μ CP of hexadecanethiol on gold, followed by selective etching in the standard etchants that contain $S_2O_3^2$ /ferri/ ferrocyanide and cyanide, respectively. The etching solution containing $S_2O_3^2$ /ferri/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 $S_2O_3^2$ /ferri/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 ferricyanide etchant indicates that ferricyanide is probably reduced in the solution rather than on the gold surface.

The addition of ferrocyanide to the initial etching solution containing $S_2O_3^{2-}$ and ferricyanide 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 Chem. Mater., Vol. 7, No. 12, 1995 2335

0.001 M K₄Fe(CN)₆ (7 min)



No $K_4Fe(CN)_6$ (6 min)



1μm

Figure 4. SEMs of test patterns of 2 of 2 in A thick that were fabricated by *a*CP of hexadecanethiol, the section of the infinite solutions that contain 0.001 M and not represented and for 7 and 6 min, respectively. The concentrations of other compositions were the same as in the standar test non-2 solution. The bright regions are gold covered by SAM, and the dark regions are Si/SiO₂ where underivatized collines here removed by etching. The blemishes on the dark regions are residual gold.

(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 SAMcovered 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 (KH₂PO₃), and dithiocarbamate ((C_2H_5)₂NCS₂ (C_3H_5)(N))=were also tested as coordinating ligands (using ferricyanide as the oxidant).²⁷ No etching was observed in solutions containing bromide, chloride, hypophosphate, and dithiocarbamate anions. Selective etching was observed for those etchants that

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

⁽²⁷⁾ The concentration of each ligand was $0.1~{\rm M};$ the concentrations of other components were the same as those in the standard etching solution of ferri/ferrocyanide.



100 nm

Figure 5. SEMs of test patterns of gold (200 Å thick) that were fabricated by μ CP with hexadecanethiol, followed by etching in solutions that use ferricyanide 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 thiocyanate¹⁰ and iodide^{28,29} as the coordinating ligands. Figure 5 shows test patterns of gold that were prepared by *u*CP of hexadecanethiol, followed by etching in the etchant that used $S_2O_3^{2-}$, SCN⁻, and I⁻ as the coordinating ligand, respectively. Thiocyanate is not as good as $S_2O_3^{2-}$ as a ligand as a component of a selective etchant: more defects are formed in the SAM-covered regions. Iodide is as good as $S_2O_3^{2-}$, although the time for complete etching is ~30% longer.

 $SC(NH_2)_2/H_2O_2(30 \text{ sec})$



Figure 6. SEMs of a test pattern of gold that was fabricated using thiourea etchant (pH \approx 1)with a patterned SAM of hexadecanethiolate as the resist. The edge resolution of gold structures that are fabricated using this etchant is $\sim 0.3~\mu m$. The bright regions are gold covered by SAM, and the dark regions are Si/SiO₂ where underivatized gold has been removed by etching.

Other Oxidants. Other oxidants (KClO₂, KClO₃, 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 \sim 30 min.

An Acidic and Selective Etchant for Gold. The etchants for gold described so far are all strongly alkaline solutions (pH \approx 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 μ CP of hexadecanethiol, followed by etching in an acidic etching solution $(pH \approx 1)$ 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 \sim 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 $\sim 0.1 \ \mu m$).

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

⁽²⁸⁾ The aqueous solution of Kl/l_2 has been used to selectively etch gold with thin films of photoresists as the masks.²⁹ This etchant, however, had no selectivity when patterned SAMs of alkanethiolates were used as the masks.

⁽²⁹⁾ Eidelloth, W.; Sandstrom, R. L. Appl. Phys. Lett. 1991, 59, 1632.

⁽³⁰⁾ The concentration of each oxidant was 0.01 M; the concentrations of other components were the same as those in the standard etching solution containing thiosulfate.

⁽³¹⁾ The composition of this etchant was 1 mL of HCl (6 N), 1 mL of H₂O₂ (15%, w/w), and 20 mL of thiourea (5%, w/v), with water as the solvent.-

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10 µm

Figure 7. (a) SEMs of microstructures of gold that were fabricated by μ CP of hexadecanethiol on gold, followed by etching of gold in the standard ferricyanide 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.

structures of gold, and of etched silicon, that were fabricated by a three-stage process: (i) μ CP of hexadecanethiolate on gold; (ii) etching of gold and chromium in S₂O₃²⁻/ferri/ferrocyanide solution; and (iii) anisotropic etching of silicon in aqueous solutions of KOH/*i*-PrOH.^{7.8} The smoothness of the silicon surface (Figure 6b) indicated that few defects were formed in the SAM-covered regions during the etching of gold.¹⁶

Selective Etching of Copper and Silver. The ferricyanide etchant described here can also be used for selective etching of copper and silver with patterned SAM of hexadecanethiolate as the resist.³² Figure 8 shows, respectively, SEMs of microstructures of copper and silver that were fabricated by μ CP of hexadecanethiol, followed by etching in the ferri/ferrocyanide solutions. The rate of etching increases in the order Au < Ag < Cu. The times for complete etching of bare regions of these metals (500 Å thick) are ~17 min, ~17 s, and ~12 s, respectively. The selectivity and edge resolution for Ag/C₁₆SH are as good as those for Au/C₁₆SH; while for Cu/C₁₆SH, they are much lower.

Conclusions

This work describes a more selective etchant for use with patterned SAMs of alkanethiolates on gold than the combination of CN^{-}/O_{2} that was used previously; this $S_{2}O_{3}^{2-}$ /ferri/ferrocyanide-based etching solution is also less toxic and hence more convenient to use.^{33,34}

Cu etching



Figure 8. SEMs of test patterns of copper and silver that were fabricated using the ferricyanide etchant with patterned SAMs of hexedecanethiolate (by μ CP) as the resists. The bright regions are metals covered by SAM, and the dark regions are Si/SiO₂ where underivatized 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^-/O_2 ; this etch also yields microstructures of gold with higher edge resolution than the CN^-/O_2 system. The microstructures of gold fabricated by μ CP 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 $S_2O_3^2$ and ferri/ferrocyanide can also be used for selective etching of copper and silver with patterned SAMs of hexadecanethiolates (by μ CP) 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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⁽³²⁾ Copper and silver were etched in neutral aqueous solutions $(K_2S_2O_3/0.1~M,~K_3Fe(CN)_6/0.01~M,~K_4Fe(CN)_6/0.001~M)$. The etching window for Ag and Cu is ${\sim}15$ and ${\sim}5$ s, respectively.

⁽³³⁾ Ferri- and ferrocyanides have very high association constants $(K = 10^{37}, 10^{44}, \text{ respectively});^{34}$ 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. (34) Douglas, B.; McDaniel D. H.; Alexander, J. J. Concepts and

⁽³⁴⁾ Douglas, B.; McDaniel D. H.; Alexander, J. J. Concepts and Models of Inorganic Chemistry, 2nd ed.; John Wiley & Sons, Inc.: New York, 1983, p 333.