Using Two-Stage Chemical Amplification To Determine the Density of Defects in Self-Assembled Monolayers of Alkanethiolates on Gold

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This paper describes a technique to measure the surface density of the defects in self-assembled monolayers (SAMs) of hexadecanethiolates on gold that lead to etching of the gold when the system is etched with aqueous ferricyanide solution. This technique uses two steps of amplification through chemical reaction to convert pinhole defects in SAMs into easily imaged, micron-scale pits in an underlying Si support. With this technique, it is possible to evaluate the density of defects in SAMs and in the structures prepared by using SAMs as resists under conditions that may be encountered in lithographic processing. At present, the lowest density of pits that we have measured for SAMs of hexadecanethiolates on 50 nm thick gold is ∼5 pits/mm². This density is an upper limit for the density of defects that expose bare gold to the etching solution or that comprise regions of SAM sufficiently thin that the SAM is not able to block access of the etchant to the gold.

Introduction

Self-assembled monolayers (SAMs) of alkanethiolates on gold[1,2] are candidates for resists in certain types of patterning (especially by microcontact printing, μCP) and for lithographic processing because they are thin (2 nm) yet still resist corrosion from certain wet-chemical etches.[3] A number of techniques can form patterned SAMs,[4−14] and SAMs are effective resists for the fabrication of microstructures of gold,[3−6,14] silver,[15] copper,[16] Si/SiO$_2$,[5,6,14,17] and GaAs.[11]

A number of issues will need to be addressed as SAMs become more widely used for applications in micro- and nanofabrication: among these issues is the density of defects in SAMs and in the structures that are produced from them.[18] It has been difficult to measure these defects and thus difficult to optimize the conditions for generating "low-defect SAMs".

This paper describes a technique based on chemical amplification that uses several sequential steps to convert pinhole defects in SAMs (whose sizes can, in principle, be smaller than 1 nm²) into easily imaged, micron-scale pits in an underlying Si support (Figure 1). The process consists of: (i) deposition of a gold film onto a Cr-primed silicon ⟨100⟩ wafer having a native SiO$_2$ surface layer (Cr acts as an adhesion promoter between the gold and the Si/SiO$_2$); (ii) formation of a SAM on this gold film; (iii) exposure of the SAM/Au/SiO$_2$/Si substrate to a wet-chemical etch [Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$/S$_2$O$_3^{2-}$/OH$^-$] that selectively dissolves gold (for long enough to convert nanometer- or larger-scale pinholes in the SAM into microscopic holes in the Au with areas of approximately 0.01 μm²); (iv) exposure of the system to aqueous HF to remove exposed SiO$_2$ in the regions where the gold had been removed by etching; (v) anisotropic etching of Si—a process that amplifies the holes in the Au into larger (>1 μm²), more easily imaged pits in the silicon—in the regions where removal of the gold and SiO$_2$ had exposed the underlying Si wafer; (vi) removal of the remaining gold by aqua regia; and (vii) imaging the pits in the etched silicon substrate by scanning electron microscopy (SEM).

This multistep process provides two steps of amplification of defects in the SAMs: first, converting small defects in the SAM into larger holes in the gold film; second, converting holes in the gold film into much larger (and much more easily visualized) pits in the silicon substrate. Chemical amplification has several useful characteristics as a strategy for detecting nanometer-scale defects. First, it makes it possible to count the number of defects in a gold film, obtained after etching gold using SAMs as resists, over a relatively large area (0.001−0.5 mm²), depending on the density of pits; lower densities require larger areas for statistical significance. Counting a statistically significant number of individual pits without some form of amplification would be difficult, since the density of pits may be small (<100 pits/mm²), and counting small (<1 nm² in the SAM, <0.01 μm² in the gold film

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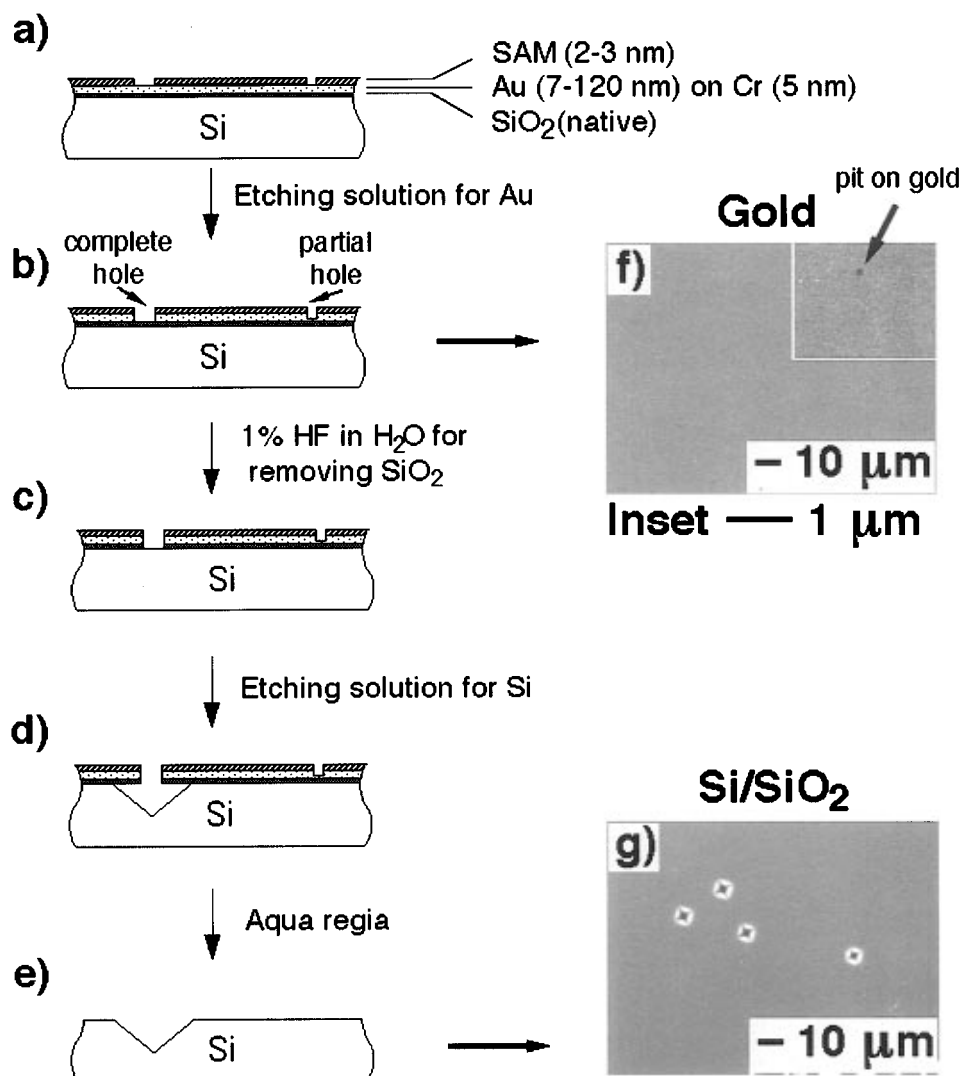(18) Wilbur, J. L.; Whitesides, G. M. In *Nanotechnology*; Timp, G., Ed.; AIP Press: New York, in press.

Figure 1. (a−e) Schematic (not to scale) of the procedure used to determine the density of etch pits on SAM-protected gold surfaces. (f) Representative SEM image of a gold film (with a SAM formed from HDT) after etching. The arrow indicates an etched pit in the gold where there was a defect in the SAM. (g) Representative image of a sample after etching Si through pinholes in the gold and subsequent removal of the gold (and the adhesion promoter) with aqua regia. As shown in part b, there are two types of holes: those that penetrate completely through the gold film and those that penetrate only partially. Chemical amplification detects only the former.

after etching) pits over large areas would require a technique with high resolution, high contrast, and high reading speed. Second, since the defects in these gold films originate from defects in the SAM that are susceptible to penetration of the wet-chemical etchants, this technique also determines the density of those types of defects in the SAM that are most directly relevant to lithography using the same type of etching step. Chemical amplification therefore provides information that is directly useful in the application of SAMs in microfabrication. Third, anisotropic etching of Si forms regular pits with pyramidal shapes that are defined by the crystal structure of the Si wafer and the anisotropy of the etch. The shape of the pits in the Si can therefore allow overlapping pits to be resolved (that is, the relatively large size of the Si pits (>1 μm^2) does not obscure pits that are separated by less than 1 μm). Fourth, it uses SEM to image the pits in the surface of the Si: SEM is convenient, fast, and capable of identifying micrometer-size pits over a large (0.5 mm^2) area.

Chemical amplification does, however, have limitations. First, it detects only those defects that allow penetration of the etch completely through the gold (for example, pits that do not extend entirely through the gold layer are not

detected). We believe that we use conditions that permit complete penetration of pits originating in pinholes through the SAM that reveal bare gold; "weak spots" in the SAMs—regions that allow nucleation of pitting in the gold, but only after some interval of exposure to the ferricyanide-containing etching solution—may not be converted into visible pits in the silicon. Second, the conditions of the etch are stringent, and the etch may itself *generate* defects in the SAMs: the number of defects in the SAMs may therefore be higher than the number that would be observed in a milder assay for defects. Third, this procedure is destructive: both the SAM and the gold film are destroyed during processing.

Several methods have been used previously to determine the density of defects in SAMs (Table 1). The type and number of defects found depend, as expected, on the

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Table 1. Techniques Used To Determine Density of Defects in SAMs

method	observable	observed density of defects	experimental considerations
electrochemistry[19]	Area of surface that allows conduction of electrons to Au electrode vs. total area of the surface	Lower limit of fractional area of defects $\sim 6 \times 10^{-6}$. Assuming defects in SAM have an average area of 1 nm^2 ^{a} corresponds to 6×10^6 defects/mm^2.	Large areas (>1 mm^2). Number of defects not available (cannot count individual defects). Detects defects that allow electrons to penetrate through SAM to Au electrode.
STM[20−24]	Molecular resolution image of SAM and substrate	Defects present in SAM (missing molecules or rows, grain boundaries) and substrate (terraces, pits) at molecular and nanometer scales	Molecular-scale imaging possible; difficult to apply to large areas ($>10^4$ μm^2). Electron beam or tip can damage SAM and generate defects. Not possible to correlate observed features with etching and other processes relevant to lithography.
SEM	Image of surface of sample; Number of pits in etched gold	2−5 pits/cm^2 (0.02−0.05 pits/mm^2) reported.[5] Current experiments indicate that this value is too low.	Density of pits may be inaccurate; limited resolution and contrast for low density of pits: difficult to count small (<0.01 mm^2) pits reliably over statistically significant areas.
chemical amplification	SEM images of etched pits in Si originating from etched pits in SAM-protected gold	Lowest density of pits^b ~ 5 pits/ mm^2	Counts defects directly over large areas. Relevant to lithographic processing. Identifies only defects that allow penetration of etchant through the gold. Stringent conditions may induce defects.

^{a} This area is an arbitrary choice. There is no direct evidence indicating the size of the defects detected electrochemically. ^{b} From present study. See text for experimental details.

technique used. Using the procedures described here, the minimum densities of pits that we have observed were ~ 5 pits/mm^2 in hexadecanethiolate-protected gold films (Au 50 nm/Cr 5 nm).

Experimental Section

Instrumentation. Scanning electron microscopy (SEM) measurements used a JEOL JSM-6400 scanning electron microscope operating at 15 keV.

Materials. Dioxygen was removed from absolute ethanol (Quantum Chemical Corp.) by bubbling dry N$_2$ through ethanol immediately before use. Hexadecanethiol (HDT, Aldrich) was purified by vacuum distillation and stored under nitrogen. Other thiols were synthesized according to literature procedures.[25,26] Lithium hexadecanethiolate was synthesized from hexadecanethiol and *tert*-butyl lithium. Potassium ferricyanide (99+%), potassium ferrocyanide trihydrate (99%), and potassium thiosulfate hydrate were used as received from Aldrich. Potassium hydroxide (87.9%) was used as received from Fisher.

Preparation of Substrates. Thermal evaporation of gold (Materials Research Corp., Orangeburg, NY; 99.99%) onto silicon ⟨100⟩ wafers (N/phosphorus-doped, prime-grade, Silicon Sense, Nashua NH) provided 7−120 nm-thick gold films. We used chromium (~ 5 nm, 99.9%) as an adhesion promoter between the gold and silicon oxide. The rate of evaporation was ~ 0.5 nm/s. The pressure during thermal evaporation was $\sim 1.5 \times 10^{-7}$ Torr, and the temperature of the stage was less than 40 °C. Silicon wafers were cleaned by sonication in trichloroethylene, acetone, and methanol immediately before use. Some experiments used titanium (~ 5 nm, 99.999%) as an adhesion promoter between the gold and Si/SiO$_2$. For these experiments, titanium and gold were deposited onto silicon wafers by electron-beam evaporation.

Preparation of Monolayers. SAMs of alkanethiolates on gold were prepared by immersing the Au/Cr/SiO$_2$/Si or Au/Ti/SiO$_2$/Si substrates in freshly prepared solutions of alkanethiol. The details of the preparation (the age of the gold, the time of immersion, and the composition, concentration, and solvent used in the solutions) are presented in the Results and Discussion section. All monolayers were prepared using glass vials. These vials were cleaned with "pirhana solution" (3:1 mixture of

H$_2$SO$_4$/30% H$_2$O$_2$), rinsed with deionized water, rinsed with absolute ethanol, and dried in an oven (>100 °C).[27]

Etching of Gold. After formation of SAMs was complete, the substrates were removed from solution, rinsed with absolute ethanol, and dried with a stream of filtered N$_2$ gas. Submerging the substrates in an aqueous solution of K$_3$Fe(CN)$_6$, K$_4$Fe(CN)$_6$, K$_2$S$_2$O$_3$, and KOH etched the gold in regions where SAMs had defects.[28] The etching was conducted under air. The temperature, time of etching, and relative concentration of each component in the etching solution for specific experiments are described in the Results and Discussion section. After etching was complete, substrates were removed from the solution, rinsed with deionized water, rinsed with absolute ethanol, and dried with a stream of N$_2$ gas.

Etching of Silicon. Substrates were placed in an aqueous solution of HF (1%, 2 min) to remove the SiO$_2$ that was exposed where gold had been removed by the ferricyanide-containing etching solution. Substrates were then rinsed with deionized water and immediately immersed for 30−120 min in a solution (KOH (52 g)/H$_2$O (226 mL)/*i*-PrOH (74 mL), 70 °C) that etched the Si anisotropically where the gold and SiO$_2$ had been removed.[5,6,17] After etching, the substrates were washed with deionized water, rinsed with absolute ethanol, and dried with a stream of filtered N$_2$ gas. Residual Au and Cr was removed from the etched substrates with aqua regia (3:1 mixture of HCl/HNO$_3$, 20−120 s). The substrates were then rinsed with deionized water, rinsed with absolute ethanol, and dried with a stream of filtered N$_2$ gas.

Environment. Thermally evaporated metal films were prepared in a class-10000 clean room. Electron-beam evaporations were conducted in an apparatus located outside of the clean room. (Samples from e-beam evaporation were transferred immediately to the clean room after removal from the evaporator.) Preparation of monolayers, etching of Au, etching of SiO$_2$, and etching of Si were conducted in a class-100 clean room. The temperature was 20 °C unless otherwise indicated.

Results and Discussion

I. Optimization of the Assay System. *Choice of Monolayer.* Our assay focuses on SAMs of alkanethiolate on gold. SAMs of alkanethiolates on gold are the best-developed system of SAMs and were thus a logical starting point for the development of our assay.[2] They have also

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Table 2. Densities of Pits in HDT-Protected Gold Surfaces (20 nm Thick) as a Function of the Composition of the Ferricyanide Solution Used to Etch These Surfaces[a]

$[Fe^{III}]/[Fe^{II}]$	$[Fe(CN)_6^{3-}]$ (M)	$[Fe(CN)_6^{4-}]$ (M)	$[K_2S_2O_3]$ (M)	$[KOH]$ (M)	etching time (min)
∞	0.01	0	0.1	1	7
50/1	0.01	0.0002	0.1	1	7
10/1	0.01	0.001	0.1	1	7
1/1	0.01	0.01	0.1	1	7
1/10	0.01	0.1	0.1	1	7
10/1	0.001	0.0001	0.1	1	7
10/1	0.1	0.01	0.1	1	7
10/1	0.01	0.001	0.01	1	10
10/1	0.01	0.001	0.1	0.5	9.5

[a] SAMs were prepared by immersing fresh gold substrates (Au 20 nm/Cr 5 nm) in fresh neat HDT for 24 h at 30 °C. All samples were etched at 25 °C. The experiments were performed in a class-100 clean room.

been used extensively as resists for patterning of the underlying gold film and Si/SiO$_2$ substrate.

Etching Solution for Au. Our group has investigated[3,5,28] different solutions for etching gold using SAMs as resists. We found that a solution of ferri/ferrocyanide ($K_3Fe(CN)_6$/ $K_4Fe(CN)_6$/$K_2S_2O_3$/KOH) gave the highest contrast between gold protected by a SAM of hexadecanethiolate and unprotected gold. This etching solution was used exclusively in this paper.

Optimization of Etching Solution for Au. Table 2 shows the density of pits in a 20 nm thick gold film (with 5 nm Cr as an adhesion promoter) that was protected with a SAM of hexadecanethiolate as a function of the composition of the ferricyanide-containing etching solution. A solution containing a 10:1 ratio of ferricyanide/ferrocyanide gave the lowest density of pits (~90 pits/mm^2). The concentrations of $K_2S_2O_3$ and KOH influenced the rate of etching but not the resistance of the HDT-protected areas to the chemical etch. In these experiments, the optimal time of etching was determined by the time required to remove gold completely from an unprotected surface. Of the five compositions that gave the lowest density of pits, we chose to use the solution with the following concentrations: $K_3Fe(CN)_6$ (0.01 M)/$K_4Fe(CN)_6$ (0.001 M)/$K_2S_2O_3$ (0.1 M)/KOH (1 M). The etching solution was prepared using deionized water at 25 °C.

Influence of the Thickness of Gold on the Density of Pits. The thickness of the gold film influences the density of the pits detected by this assay system. To determine the thickness of the gold film that was most appropriate for this assay, we performed a series of control experiments. First, we wanted to verify that the pits we observed originated from defects in the SAMs and not from defects inherent in the gold films. Substrates (SAM/Au/Cr/Si) that had not been exposed to the ferricyanide solution (etchant for Au) were subjected to the etching solution for Si. For 7 nm-thick gold, we observed a density of pits of ~1 × 10^3 pits/mm^2. For gold films with a thickness between 20 nm and 120 nm (the thickest films we investigated), no pits were observed. Experiments that used Au/Cr/Si substrates without a SAM gave similar results. These experiments indicated that gold films that were at least 20 nm thick provided continuous, pinhole-free coverage of the silicon wafer against the etching solution for Si.

In a second set of control experiments, we investigated the effect of the thickness of the gold on the observed density of pits. SAMs of hexadecanethiolate were prepared on gold films of varying thicknesses (20, 35, 40, 50, 100, and 120 nm). The density of pits (ρ_0) in these

Table 3. Density of Pits at Time t_0 as a Function of the Thickness of the Gold Film[a]

thickness of gold film (nm)	etching time (t_0, min)	density of pits observed at time t_0 by chemical amplification (pits/mm^2)
20	7.0	90
35	8.5	36
40	9.0	5
50	14.5	5
100	29.0	5
120	38.0	5

[a] t_0 is the time required to remove a film of bare gold of this thickness completely. SAMs were prepared by immersing fresh gold substrates (Au on Cr or Ti 5 nm) in fresh neat HDT for 24 h at 30 °C. All samples were etched with a ferri/ferrocyanide solution at 25 °C. The experiments were performed in a class-100 clean room.
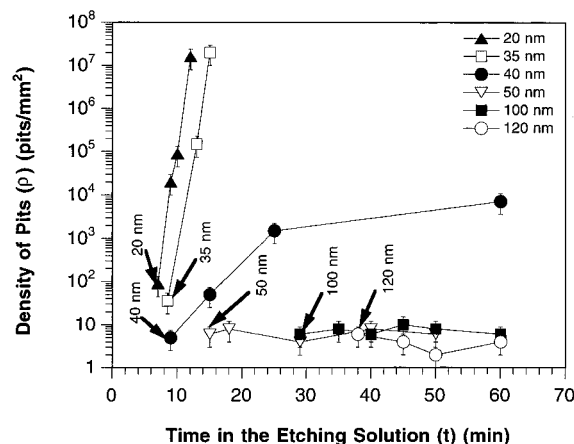

Figure 2. Plot of density of etched pits (ρ) on SAM-protected gold films of different thickness as a function of the time (t) that the films were immersed in the ferri/ferrocyanide etching solution. SAMs were prepared by immersing fresh gold substrates (Au on Cr 5 nm) in fresh neat HDT for 24 h at 30 °C. All samples were etched at 25 °C. The experiments were performed in a class-100 clean room. Arrows indicate the densities of pits (ρ_0) measured when unprotected gold of the same thickness was removed completely by etching ($t = t_0$). These values are useful for the lithographic processing, since they represent the time at which maximum contrast between etched and unetched features would be obtained.

substrates was determined by chemical amplification (Table 3). For each thickness, the gold was etched for a time (t) equivalent to the time (t_0) required to remove completely unprotected gold of the same thickness. The lowest density of pits (5 pits/mm^2) occurred for films of gold thicker than 40 nm. Gold films that were 20 and 35 nm thick had ~10 times higher density of pits than did films that were 40–120 nm thick. We also explored longer etching times ($t > t_0$, Figure 2). The density of pits increased with increased time of etching for films that were 20, 35, and 40 nm thick; for films thicker than 40 nm, the density of pits did not change measurably with increased time of etching (up to ~45 min past t_0).

We considered four possible explanations for the dependence of the density of pits on the thickness of the gold film: (i) the activity of the etching solution decreased with time because the ferricyanide was either consumed or degraded (by exposure to light, for example); (ii) the adhesion promoters (Cr^{29-32} or $Ti^{33,34}$) diffused through

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Table 4. Effect of Etching Solutions on Materials Used in Control Experiments

solution	Au	Ti	Cr	SiO$_2$	Si
Ce(NH$_4$)$_2$(NO$_3$)$_6$, HNO$_3$, H$_2$O[a]	−[b]	−	+[c]	−	−
48% HF	−	+	−	+	−
4.8% HF	−	+	−	+	−
ferricyanide etch	+	−	+	−	−
Si etch	−	−	−	−	+

[a] See ref 36. [b] − = solution did not etch material. [c] + = solution etched material.

the gold and acted as nucleation sites for defects; if thinner gold films had a higher percentage of Cr or Ti than did thicker films (since the adhesion promoter would need to diffuse a shorter distance to reach the surface in the former), a higher density of pits in thinner films could result; (iii) diffusion of the ferricyanide etch through nanometer-scale pits was slower for thicker gold films (40−120 nm) than for thinner gold films (20−35 nm); and (iv) an undefined layer that slowed the growth of etch pits formed on the surface of the substrates as the substrates were in the etching solution for longer times.[35] We address each of these possible explanations in turn below.

To eliminate the possibility that the etching solution decreased in activity at longer times, we changed the etching solution by preparing a new solution every 7 min until the unprotected Au (35−120 nm) was completely removed. Although we observed an increase (<20%) in the rate of etching when fresh (≤7 min old) solution was used, the *density* of pits was not affected. Since ferricyanide is known to degrade upon exposure to light, we also tried etching substrates in the absence of light: this precaution also did not affect the density of pits. Finally, we observed that the volume of etching solution (300 mL) used in our experiments was capable of completely removing 120 nm thick gold films (∼1 cm^2 area) from several (3−5) unprotected samples (significantly more gold than would be removed by etching several (3−5) samples where gold was removed from only a few nanometer-scale defects) without a noticeable decrease in activity. Together, these observations indicated that a decrease in the activity of the etching solution was not responsible for the observation that samples with thicker films of gold had fewer pits (by chemical amplification) than did samples with thinner films of gold.

We next performed several experiments designed to determine whether Cr or Ti was present at the surface of the gold films and whether their presence affected the density of pits observed by chemical amplification (Table 4). First, we exposed Au/Cr/Si substrates to an etching solution for Cr.[36] Etched pits on the Au/Cr/Si samples were visible to the naked eye after 20 s exposure to the solution for all thicknesses of Au (20−120 nm, Cr 5 nm). Substrates of Au/Ti/Si that were exposed to the same solution did not show pits. The second observation indicates that the etching solution for Cr did not etch the gold film; together with the first observation, it suggests that Cr was present at the surface of the gold in Au/Cr/Si samples of all thicknesses. Similar experiments for Au/Ti/Si samples were conducted using both concentrated

(48%) and dilute (4.8%) aqueous HF. In both cases, pits on the surface of the substrate were visible after 20 min. This observation and the observation that HF did not induce pits in Au/Cr/Si substrates indicated that Ti was present at the surface of the Au/Ti/Si substrates. It was not possible (from these experiments), however, to determine the amount of Cr or Ti at the surface of the sample. It was also not possible to determine whether there was more Cr or Ti present at the surface of the thinner (20−35 nm) gold films than on thicker (40−120 nm) films.

We also measured the density of defects in a SAM of hexadecanethiolate on a double-layer (Au 20 nm/Cr 5 nm/Au 20 nm/Cr 5 nm/Si) substrate. The densities of pits observed at different etching times (ts) were similar to those observed on Au 40 nm/Cr 5 nm/Si. This observation indicated that even if the amount of Cr present at the surface of the thinner (20 nm) and thicker (40 nm) Au films might be different, this difference did not cause any noticeable changes in density of pits.

In independent experiments, we exposed 20 nm thick films of Cr and Ti to the ferricyanide-containing etching solution. Under these conditions, films of Cr were etched at a rate of ∼10 nm/min, while films of Ti were not etched to any detectable extent. We then compared the density of pits observed by chemical amplification for HDT-protected films of gold that had either Cr or Ti as adhesion promoters: for all thicknesses of gold, we found that substrates prepared using Cr as an adhesion promoter had the same density of pits as did those samples that used Ti. This observation (and the observation that the ferricyanide-containing solution etched Cr but not Ti) indicated that, under the conditions used for chemical amplification, the presence of Cr or Ti at the surface of the films of gold did not nucleate defects during etching.[37] We infer that defects in the gold must therefore originate from defects in the SAM.

We consider next the possibility that diffusion of the etching solution into the nanometer-scale etch pits (or diffusion of etched gold out of the pits) is slower for pits in thicker (40−120 nm) films of gold than for pits in thinner (20−35 nm) films of gold. We estimate (by SEM) that the pits in the gold are ∼100 nm in diameter. Thus, for 40 nm thick gold, the pits are wider than they are deep (that is, the pits are more like shallow craters than deep holes): the thickness of the gold is therefore not a limiting factor in diffusion of the etchant.

Finally, we address the hypothesis that a protective layer that prevents corrosion of the gold film deposits on the surface of the sample upon longer exposure (>15 min) to the etching solution.[35] Occasionally (<20% of samples) we observed a white powder on the surface of etched samples: this powder was only observed when the etching time was greater than 15 min. Attempts to identify the composition of the powder by X-ray photoelectron spectroscopy (XPS) were inconclusive. The only observable change in the XPS spectrum in regions where white powder was present was a twofold increase in the intensity of the C 1s peak relative to the intensity of this peak in

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(34) Ashwell, G. B. W.; Heckingbottom, R. *J. Electrochem. Soc.* **1981**, *128*, 649−654.

(35) There are many examples where corrosion products form a protective coating over a metal and thus protect it from extensive reaction. See: Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley and Sons: New York, 1990; p 320 and references therein.

(36) The composition of the etch used was 49.3 g of Ce(NH$_4$)$_2$(NO$_3$)$_6$, 27 mL of concentrated HNO$_3$, and 273 mL of H$_2$O. See refs 29−32.

(37) Since the etch for Cr induced pits on the surface of Au/Cr/Si substrates but did not dissolve gold (in independent measurements), we infer that there were regions of the surface where Cr was exposed or where there was a sufficiently thin layer of gold on the Cr to allow penetration of the etching solution for Cr. The observation that the presence of Cr in the gold film did not affect the density of pits observed by chemical amplification for SAM/Au/Cr/Si substrates, even though the ferricyanide-containing etch dissolved Cr, suggests that regions where Cr or Ti were present were protected at a level equivalent to areas of SAM-protected gold. On the basis of this observation, we infer that there was a thin layer of gold (and a SAM) covering the Cr or Ti. Our results do not indicate whether the Cr or Ti was present at the surface as discrete particles or whether it was present as "tubes" that extended entirely through the gold film.

regions without the powder. No peaks indicating K, Fe, or N (elements present in the constituents of the etching solution) were observed by XPS. A possible source of the increased signal for carbon might be the presence of CO_3^{2-}, which might originate from dissolved CO_2 in the basic etching solution, but we have no evidence to confirm or refute this possibility. These powders were observed only occasionally, however, and the density of pits on samples where the powders were present was not measurably different from the density of pits in samples where no powders were present. We therefore concluded that the white powders were not responsible for the observed dependence of the density of pits on the thickness of the gold films. We cannot, however, rule out the possibility that some other undefined film (which deposits on the surface at longer etching times) prevents corrosion.

Our experiments failed to determined conclusively why the density of pits observed by chemical amplification decreased with increasing thickness of the gold films. We chose to use 20 nm-thick gold films for all continuing development. This decision was based on the following considerations: (i) The 20 nm-thick gold films are sufficiently continuous to provide complete protection against the etch for Si; the densities of pits observed by chemical amplification can therefore be attributed to the defects in the SAMs (and not defects in the gold film); (ii) gold films that are thicker than 20 nm require longer etching times; these longer etching times are inconvenient; and (iii) The 20 nm-thick gold films seem to be particularly sensitive to the conditions of our experiments (the time of etching, for example). We emphasize that although 20 nm-thick films are advantageous for continuing development of chemical amplification, films that are at least 50 nm thick (which have the lowest density of pits) are more appropriate for real applications in fabrication and lithography.

Influence of Temperature of the Etching Solution on the Density of Pits. To determine the optimal temperature for the etching solution, we measured the density of pits that resulted from etching gold with the ferricyanide-containing solution at four different temperatures (10, 25, 45, and 55 °C). The rate of etching of unprotected gold increased with increasing temperature. No noticeable etching was observed after 30 min at 10 °C. The rate of etching at 25 °C was ~ 3 nm/min, at 45 °C, ~ 10 nm/min, and at 55 °C, ~ 20 nm/min. The density of pits at 45 or 55 °C was >3 × 10^5 pits/mm^2. The density of pits (90 pits/mm^2) was lowest (for 20 nm thick films of gold protected by SAMs of hexadecanethiolate) at 25 °C.

Etching of Si. We adjusted the time required to etch Si for samples with different densities of pits such that there were at least 3 visible pits per image (there were as many as several hundred pits in some cases). For samples with high densities of pits (1000 pits/mm^2, for example), we reduced the time of etching to avoid merging many adjacent pits into one large pit. For samples with low densities of pits (5 pits/mm^2, for example), we increased the time of etching so that the pits were big enough to be visualized by SEM at low magnification (which was required to view an area large enough to count a statistically significant number of pits). Even at low densities (<100 pits/mm^2), it was possible to resolve two or more pits separated by a distance that was less than the size of the etched pit in the Si (<1 μm). In these cases, the shape of the border of the pit in the silicon was not a square; instead, it resembled two or more squares that were partially overlapped.

We also observed a distribution in the sizes of pits in the Si within a single sample. We hypothesize that larger pits in the Si originated from larger pits in the Au (and

possibly from larger pinholes in the SAM). We were not able, however, to establish a correlation between the size of the pits in the silicon and the size of the pits in the SAMs, since it was possible neither to image directly the pits in the SAMs nor to follow individually the evolution of pits over each step in the process.

Statistics/Counting. Values for densities of pits were obtained as an average from images of 10 different areas evenly distributed over each sample. A minimum of 10 samples were tested for each reported value. The density of pits calculated from different pictures of the same sample was within ±20% of the average value.

II. Application of Chemical Amplification: Minimization of the Densities of Pits for SAMs Used as Resists for Lithographic Processing. We used chemical amplification to determine the conditions (composition of the monolayer, protocols for the preparation and processing of substrates and SAMs, influence of the environment) that minimized the density of pits in structures of gold formed by using SAMs as resists for lithographic processing. In these experiments, we used exclusively 20 nm thick films of gold (with 5 nm Cr as an adhesion promoter) deposited on Si ⟨100⟩ wafers as our substrates.

Composition of the Monolayer. We prepared SAMs from alkanethiols, fluorinated alkanethiols, dialkyl disulfides, lithium alkanethiolates, and alkylphosphine on freshly evaporated gold and subjected them to the chemical amplification process (Table 5). In general, SAMs formed from alkanethiols provided better protection against the etchant than did SAMs formed from all other ligands. SAMs formed from HDT (neat or 10 mM ethanolic solution) gave the lowest density of pits (~90 pits/mm^2). SAMs formed from HDT in the vapor phase (120 pits/mm^2) were less resistant to the penetration of the etchants than SAMs formed in the liquid phase. This observation is in agreement with results published by Crooks *et al.*[38] SAMs formed from hexanethiol ($CH_3(CH_2)_5SH$, no protection), decanethiol ($CH_3(CH_2)_9SH$, 290 pits/mm^2), and neat (melted) longer chain alkanethiols ($CH_3(CH_2)_nSH$, $n = 25$, 1.2 × 10^5 pits/mm^2 and $n = 33$, 1.3 × 10^5 pits/mm^2) yielded a higher density of pits than did SAMs formed from HDT. We observed a change in color (from colorless to yellowish) of the melted $CH_3(CH_2)_{25}SH$ and $CH_3(CH_2)_{33}SH$ at 85 °C, which indicated that the thiols were slightly oxidized. We think the degradation of the thiols at the temperature at which the SAMs were formed caused the poor quality of the SAMs. SAMs formed from dilute ethanolic solutions of longer-chain alkanethiols ($CH_3(CH_2)_nSH$, $n = 25$ and 33) gave protection against the etch comparable to that provided by SAMs formed from HDT.

On the basis of these experiments, we chose a long-chain alkanethiol ($CH_3(CH_2)_{15}SH$, HDT) as the optimal ligand to form SAMs for use as resists for lithographic processing. Two other factors led us to choose HDT over other alkanethiols ($CH_3(CH_2)_{25}SH$ and $CH_3(CH_2)_{33}SH$) that provided comparable protection against the ferri-cyanide-containing etch. First, longer chain alkanethiols such as $CH_3(CH_2)_{25}SH$ and $CH_3(CH_2)_{33}SH$ had very low solubilities in solvents commonly used to form SAMs (such as ethanol, octanol, heptane, and hexadecane) and were thus more difficult to work with than HDT. Second, they were solids at room temperature. The technique most widely used to prepare patterned SAMs for lithographic processes—microcontact printing (μCP)—requires that the molecules from which SAMs form remain in the liquid phase during μCP. Since μCP is typically performed at

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Table 5. Densities of Pits in Gold Protected by Different SAMs[a]

compound	formula	concentration	temperature at which SAMs were prepared (°C)	density of pits (pits/mm²)
alkanethiol	$CH_3(CH_2)_5SH$	pure[b]	20	no protection[c]
	$CH_3(CH_2)_9SH$	pure[b]	20	290
	$CH_3(CH_2)_{15}SH$	pure[d]	30	90
		10 mM in ethanol	20	90
	$CH_3(CH_2)_{25}SH$	pure[e]	85	1.2×10^5
		saturated solution[f]	20	88
	$CH_3(CH_2)_{33}SH$	pure[g]	85	1.3×10^5
		saturated solution[f]	20	92
	$CH_3(CH_2)_{15}SH$	vapor	20	120
disulfide	$[CH_3(CH_2)_7S]_2$	pure[b]	20	no protection[c]
	$[CH_3(CH_2)_{15}S]_2$	pure[h]	70	170
		1 mM in heptane	20	no protection[c]
fluoroalkanethiol	$CF_3CF_2CH_2-O-(CH_2)_{11}SH$	pure[b]	20	no protection[i]
lithium thiolate	$CH_3(CH_2)_{15}SLi$	saturated solution in ethanol	20	no protection[c]
phosphine	$[CH_3(CH_2)_7]_3P$	pure[b]	20	no protection

[a] SAMs were prepared by exposing fresh gold substrates (Au 20 nm/Cr 5 nm) to active compounds for 24 h. All samples were etched with a fresh ferri/ferrocyanide solution at 25 °C for 7 min. The experiments were performed in a class-100 clean room. [b] Liquid at room temperature. [c] SAMs slightly slowed down the etching rate of gold, but there were countless etched pits, most of which merged with each other, so densities of pits were not available. [d] Melting point = 19−20 °C. [e] Melting point = 55.5−56.5 °C. [f] We have used ethanol, octanol, heptane, and hexadecane. We did not observe solvent effects on the density of pits. [g] Melting point = 75−77.5 °C. [h] Melting point = 54−54.5 °C. [i] The SAM provided better protection on gold against the ferri/ferrocyanide etch than did $CH_3(CH_2)_5SH$, but still, the density of pits was so high that many etched pits merged with each other. The density of pits was not available.
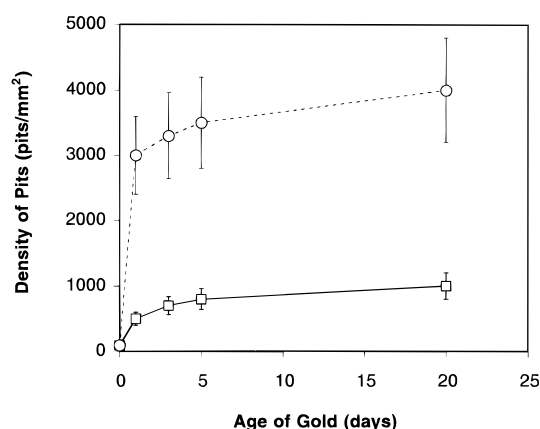

Figure 3. Plot of density of etched pits obtained by chemical amplification for 20 nm thick gold protected by a SAM of hexadecanethiolate vs the age of the gold on which the SAMs were formed. SAMs were prepared by immersing gold substrates in fresh neat (at 30 °C) or 10 mM ethanolic solutions (at 20 °C) of HDT for 24 h. All samples were etched with a fresh ferri/ferrocyanide solution at 25 °C for 7 min. The experiments were performed in a class-100 clean room. The density of pits increased with increasing age of the gold. For gold of the same age, SAMs formed from 10 mM solutions of HDT in ethanol (○) had higher densities of pits than did SAMs formed from neat HDT (□).

room temperature, the results obtained with neat HDT (which is a liquid at room temperature) may be applicable to μCP.

Preparation of Gold Substrates. SAMs of hexadecanethiolate were formed on films of gold that had been allowed to age (protected by Teflon wafer holders) for different periods of time after evaporation. The density of pits for these samples was evaluated by chemical amplification (Figure 3). The lowest densities of pits were obtained by using gold films that were immersed in neat HDT immediately after they were removed from the high-vacuum chamber of the evaporator. The density of pits increased with increasing time between removal from the evaporator and immersion in HDT. We think the contaminants (dust and/or organic particles) adsorbed on the surface decreased the quality of the SAMs. SAMs formed from dilute solutions of HDT were more sensitive to the age of the gold than were SAMs formed from neat HDT.

Table 6. Dependence of Density of Pits on Methods Used to Clean the Gold Film Prior to Formation of the SAM[a]

methods of cleaning	fresh gold (pits/mm²)	20-day-old gold[b] (pits/mm²)
no cleaning	90	1000
sonication in ethanol[c]	90	900
electrochemical cleaning[d]	90	336
UV/ozone cleaning[e]	90	200

[a] SAMs were prepared by immersing gold substrates (Au 20 nm/Cr 5 nm) in fresh neat HDT for 24 h at 30 °C. All samples were etched with a fresh ferri/ferrocyanide solution at 25 °C for 7 min. The experiments were performed in a class-100 clean room. [b] The gold samples were stored in a class-100 clean room in sealed Teflon wafer-holders. [c] The gold samples were sonicated in ethanol for 15 min. [d] The gold substrates were electrochemically cleaned by cycling the electrical potential of the gold films between −0.4 V (SCE) and 0.9 V (SCE) in an aqueous solution of 0.1 M H_2SO_4 until the voltammograms were invariant between cycles. [e] The gold substrates were cleaned in a UV/ozone cleaner (UV_Clean, models 135500 & 135500-2, Boekel Industries, Inc.) for 5 min.

No methods of cleaning older/contaminated gold were able to duplicate the performance of freshly evaporated gold (Table 6).

Preparation of SAMs. Figure 4 shows the density of pits observed by chemical amplification as a function of the length of time used to form the SAMs. Soaking gold surfaces in neat HDT, at 30 °C, for times between 20 min and 48 h, produced samples with the highest resistance to the ferricyanide etch (the density of pits was 90−100 pits/mm²). SAMs formed by immersing the gold film in HDT for less than 20 min (but more than 1 min) had pit densities between 120 and 300 pits/mm². Gold surfaces that remained in neat HDT longer than 48 h also showed a modest increase in the density of pits (140 pits/mm² at 96 h, 190 pits/mm² at 17 days). We did not determine the origin of this increase. Atomic scale corrosion of the gold surface by short term (several hours) exposure to ethanolic solutions of alkanethiols has been observed by scanning tunneling microscopy (STM).[23] We do not know whether the increased density of pits observed here is a macroscopic manifestation of this atomic-scale corrosion or if it occurs by some other mechanism.

Other Factors. We surveyed other conditions to see if we could reduce the density of pits observed by chemical amplification. First, we examined the influence of a ligand that might block etching. Neither etching in the presence
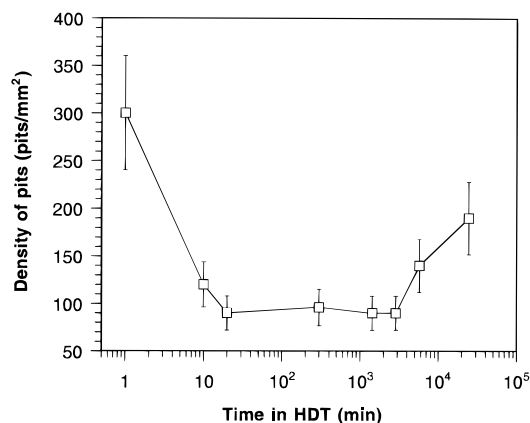
Figure 4. Plots of density of pits as a function of the time allowed for formation of SAMs. SAMs were prepared by immersing fresh gold substrates (Au 20 nm/Cr 5 nm) in fresh neat HDT at 30 °C. All samples were etched with a fresh ferri/ferrocyanide solution at 25 °C for 7 min. The experiments were performed in a class-100 clean room.

of hexadecane (which might intercalate into defects in the SAM) nor etching in the presence of HDT (which might repair defects in the SAM *in situ*) reduced the density of pits. Second, we hypothesized that a short-chain ($<C_{10}$) alkanethiol might penetrate through defects in the SAM to the surface of the gold more easily than HDT and "fill in" defects in a SAM formed from HDT. Exposing a SAM formed from HDT to heptanethiol ($CH_3(CH_2)_6SH$) before etching did not reduce the density of pits. Third, we tested the possibility that the density of pits could be reduced by heating the SAMs during preparation: these experiments were motivated by STM experiments[22,24,39,40] that demonstrated that the ordering of a SAM can be increased by "annealing" at higher temperatures. Preparing the SAMs by exposure to a neat solution of HDT for 24 h, at 60 °C, or baking the SAM/Au/Si sample for 2 h at 80 °C, however, did not reduce the density of pits. Finally, attempts to eliminate defects induced by environmental contamination (filtering neat HDT through 0.2 μm PTFE filter paper, preparing SAMs, and etching the substrates without light and under Ar) also did not reduce the density of pits.

We used 20 nm thick films gold to determine the minimum density of pits that could be obtained by using chemical amplification, since they seemed very sensitive to the conditions of our experiments. For real applications, where a minimum density of defects is required, thicker films of gold ($\geq$50 nm) would be better. Using the optimized conditions found here for 20 nm thick gold, we found that 50 nm thick films of gold had a density of pits of 5 pits/mm^2.

Final Recommendations. On the basis of the experiments that used chemical amplification, the minimum density of pits in structures of gold fabricated using patterned SAMs as resists can be obtained by using the following conditions:

(i) Gold films: freshly evaporated gold films ($\geq$50 nm thick), 5 nm Cr or Ti as adhesion promoter.

(ii) SAMs: prepared by immersing films of gold in neat HDT for at least 20 mins but no longer than 48 h at 30 °C.

(iii) Etchant for gold: freshly prepared $K_3Fe(CN)_6$ (0.01 M)/$K_4Fe(CN)_6$ (0.001 M)/$K_2S_2O_3$ (0.1 M)/KOH (1 M) in deionized water, at 25 °C, under yellow light and air, >60 mL etching solution per cm^2 surface area of sample.

(iv) Environment: in a class-100 clean room.

Conclusions

Chemical amplification provides a strategy to evaluate the density of defects in SAMs and in the structures prepared by using SAMs as resists under conditions that may be encountered in lithographic processing. Under the conditions used for chemical amplification, the lowest density of pits that we measured was 5 pits/mm^2. This density of pits was obtained by using SAMs formed from neat HDT on freshly prepared, 50 nm-thick gold films; all preparation and processing of the SAMs was conducted under clean-room (class-10000 and class-100) conditions.

The results obtained by using chemical amplification may not be directly relevant to applications other than etching with ferricyanide-containing solutions. The type and density of defects found in SAMs depend on the technique used to identify them (Table 1); it also depends on the conditions used to prepare and process the SAMs. Further, the conditions of chemical amplification are stringent; the etch may itself generate defects in the monolayer.

Despite questions regarding the generality of chemical amplification,[41] it is plausible to consider our results in the context of using SAMs as resists in commercial fabrication processes. Fabrication of microelectronics—which has perhaps the highest demands for perfection of the final product—currently requires that defects be reduced to levels fewer than 1 defect per 8 in. diameter wafer (<0.003 defects/cm^2). The minimum density of defects obtained by using SAMs of alkanethiolates as resists for etching of gold films, as measured by chemical amplification, was 5 pits/mm^2 (500 pits/cm^2). If SAMs of alkanethiolates on gold are to be used as resists for the fabrication of microelectronics, strategies that reduce the density of defects in these SAMs and in the structures produced by using them, are needed.

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