The Decomposition of the Sulfonate Additive Sulfopropyl Sulfonate in Acid Copper Electroplating Chemistries

Aaron Frank and Allen J. Bard*,z

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA,
International Sematech, Austin, Texas 78741-6499, USA, and
*Texas Instruments, Dallas, Texas 75243, USA*

The decomposition of sulfopropyl sulfonate (SPS, 4,5-dithiaoctane-1,8-disulfonic acid) in acid copper electroplating chemistries was studied using scanning electrochemical microscopy (SECM), UV-visible spectroscopy, high pressure liquid chromatography, liquid chromatography mass spectrometry, and electron spin resonance. The primary decomposition product is proposed to be the thiolsulfonate of SPS. Although this oxidation product can be formed by reaction with hydrogen peroxide, SECM studies of oxygen reduction on copper showed that there is not a peroxide intermediate and the product of oxygen reduction on copper in dilute sulfuric acid is water. The data suggests that SPS stabilizes Cu(I) and this complex is the intermediate. For this scheme, oxygen reacts with the SPS/Cu(I) complex in solution to form the thiolsulfonate of SPS and Cu(II).
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Several copper plating bath chemistries currently used by the integrated circuit (IC) industry contain two additives. Both additives work together to fill the features from the bottom up; sometimes this is referred to as super fill.[1-6] Sulfopropyl sulfonate, or SPS, is a commonly used additive for printed wiring board and IC acid copper plating applications. Under normal plating conditions SPS has a half-life on the order of 12 h and is the most unstable of the additives that are currently in use. State-of-the-art plating tools have systems that automatically replenish the additives to maintain some nominal concentration. However, even if the bath additive concentrations are tightly controlled, the bath life is not indefinite. The plating bath needs to be periodically dumped and replaced, or replenished by a bleed and feed scheme. Bath replacement is required because the SPS decomposes and the decomposition products are detrimental to super fill. The goal of this work was to understand the decomposition mechanism of SPS so that the bath life can be extended. The most detailed work on the decomposition of SPS to date is by Healey *et al.*[7] who studied the decomposition of SPS at open circuit. Based on extensive electrochemical studies they proposed that SPS is decomposed to a Cu(I)-thiolate complex in the absence of oxygen. They determined that the decomposition requires the presence of SPS, Cu(II), and Cu^0 and speculated that the Cu(I)-thiolate complex might be formed by the following reactions (Eq. 6 and 7 in Ref. 7)

$$4Cu^+ + [S(CH2)_3SO_3H]_2 \rightarrow 2Cu^{2+} + 2Cu(I)S(CH_2)_3SO_3H \quad [1]$$
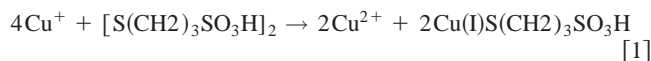
followed by the oxidation of this complex by dissolved oxygen

$$Cu(I)S(CH_2)_3SO_3H + O_2 \rightarrow Cu^{2+} + S \text{ product} \quad [2]$$
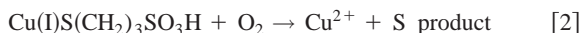
Where S product is not SPS, and is probably an oxidized form of mercaptopropanesulfonic acid (MPS).

Experimental

Apparatus.—A Dionex high pressure liquid chromatography (HPLC) instrument with a NS1 column was used to monitor the concentration of the SPS and the decomposition product of SPS. A gradient method with two eluents was used. Both eluents contained 150 mN H2SO4. Eluent A contained 10% acetonitrile (ACN) and B contained no ACN. The gradient ramped linearly from 0.25 to 10 vol % ACN in 20 min. The absorbance detector was set to 240 nM. The flow rate was 2 mL/min. A CH Instruments (Austin, TX) model 900 scanning electrochemical microscope and a CH Instruments CH108

25 μm diam platinum microelectrode were used for scanning electrochemical microscope (SECM) collection experiments. Ag/AgCl (CH Instruments) and Hg/Hg$_2$SO$_4$ (Radiometer) were used as reference electrodes. A schematic of the SECM instrument is shown in Fig. 1. For liquid chromatography (LC) mass spectrometry with electrospray ionization, a Varian LC 9050 with a Wacker Siltronic C18 column coupled to a Finnegan MAT mass spectrometer with a LCQ electrospray ionization source were used. All samples were analyzed in negative mode. The eluents were 0.1% formic acid and 1% ACN in water (A) and 0.1% formic acid and 90% ACN in water (B). Eluent B was ramped from 0–75% in a gradient fashion in 15 min. The flow rate was 50 μL/min and the injection volume was 20 μL. Electron spin resonance (ESR) was carried out with an IBM Instruments ER 300.

Chemicals.—CuSO$_4$ · 5H$_2$O was Analytical Scientific ACS reagent grade. The sulfuric acid was Ashland Megabit grade. Millipore milliQ DI water was used to make all solutions. SPS [SO$_3$H(CH$_2$)$_3$-S-S-(CH$_2$)$_3$SO$_3$H] was obtained from Raschig. The thiolsulfonate is [SO$_3$H(CH$_2$)$_3$-SO-SO-(CH$_2$)$_3$SO$_3$H]. MPS (Fluka) is the monomer of SPS and has the formula SO$_3$H(CH$_2$)$_3$SH.

Bulk electrolysis of plating chemistry.—Bath aging experiments were run on a custom-made bench top plating cell. This cell utilized a round chuck designed to hold a 1.5 in^2 tile that was cut from a 200 mm wafer. Silicon wafers with 4000 Å of thermally grown SiO$_2$ were metallized with 250 Å of sputtered Ta followed by 1000 Å of sputtered Cu using a Novellus Inova Sputtering tool. The wafers were cleaved into square tiles after sputtering. When assembled with a wafer tile, the cathode was disk shaped and completely copper coated. The anode was a phosphorus-doped (0.05%, Nimtek) copper disk with the same diameter as the cathode. Both were contained in a cylindrical cell with an inner diameter just slightly larger than the electrodes, a standard configuration yielding nearly straight field lines and uniform current density. Mass transfer was enhanced by rotation of the cathode.

Results and Discussion

Analysis of decomposition product with LC.—A commercially available plating bath was used for this study. This plating bath uses SPS and although the actual concentration is proprietary, it is probably in the 3 to 50 μM range. The suppressor (polyethylene glycol, PEG, or polypropylene glycol, PPG) concentration was the supplier recommended nominal, as were Cl$^-$ (50 ppm), H$_2$SO$_4$ (180 g/L), and Cu(II) (18 g/L). The solution was electrolyzed for 15 min at 12 mA/cm^2 and 100 rpm in the bulk electrolysis cell, with and without dissolved oxygen. Dissolved oxygen was removed by sparging the
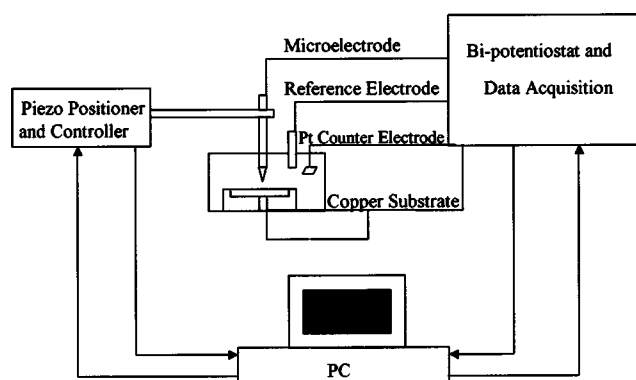
Figure 1. Schematic of scanning electrochemical microscope setup.

copper sulfate solution with nitrogen through a glass frit for 15 min. After plating, samples of the electrolyte were analyzed with HPLC. The results are shown in Fig. 2. The large peak that elutes after one minute contains copper sulfate. The small peak at 3.6 min is the decomposition product. The peak at 11.38 min is the SPS peak. Note that the decomposition product peak for the deaerated electrolyte was much smaller than it was in an experiment where the solution contained oxygen. Although not shown here, a virgin bath contained roughly the same amount of decomposition product as the deaerated electrolyzed bath. An experiment was also carried out where the solution contained 10 times the normal operating concentration of accelerator (SPS), *i.e.*, a solution in the 30–500 μM range. The concentration of all other bath constituents was the same as the previous experiment. Hydrogen peroxide was added to this solution to produce a 10 vol % solution concentration. After mixing, a sample was removed for HPLC analysis. In this experiment, the SPS was completely decomposed and the only peak present in the chromatogram (not shown) was a large breakdown product peak that eluted at the same time (3.6 min) as the breakdown product peak in Fig. 2. It is possible that dissolved oxygen is converted to hydrogen peroxide in the plating bath. Hydrogen peroxide is known to oxidize the disulfide bond.[8] These hydrogen peroxide/disulfide oxidation products can have one to four oxygen atoms bonded to the S atoms of the disulfide group, yielding thiolsulfinate (1), thiolsulfonate (2), sulfinyl sulfone (3), or α-disulfone (4).[8]

Healy[7] *et al.* showed that the oxidation of SPS by H_2O_2 is slow when the concentrations of the two species are equal, but the preceding experiment showed that the oxidation can occur at a rapid rate when large excesses of H_2O_2 are present. Allen and Brook[8] carried out a study of oxidation of disulfides to thiolsulfinates by hydrogen peroxide. In their study they used 5 g *n*-dodecyldisulfide in 500 mL acetic acid (40–45°) and 3.25 g 27.1% hydrogen peroxide (a 100% excess). When the mixture was allowed to react
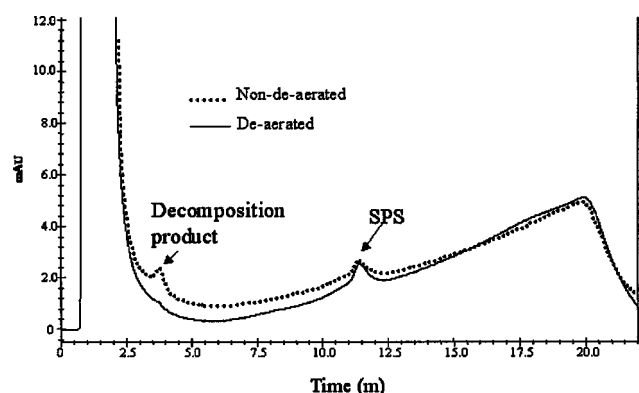

Figure 2. Chromatogram of electrolyzed plating bath.

for a day, there was an 80% conversion to the thiolsulfinate (RSOSR) and 10% conversion to thiolsulfonate (RSO_2SR).

Since the concentration of SPS used in commercial plating baths is on the order of 3 to 50 μM, situations might exist where a large excess of peroxide is present in the bath. The formation of peroxide requires dissolved oxygen, protons and an electron source. The two most likely electron sources are Cu^+ or the cathode.

Typical copper sulfate plating baths contain 2 M sulfuric acid and 0.28 M Cu(II). Since sulfate ion is not a strong complexing agent for copper, the main form is Cu(II), the aquated ion of Cu(II). In this system the concentration of Cu(I) is low. When this electrolyte is in the presence of copper metal, the following equilibrium occurs[9]

$$Cu + Cu^{2+} = 2Cu^+ \quad K_{Cu} = [Cu^+]^2/[Cu^{2+}] \qquad [3]$$
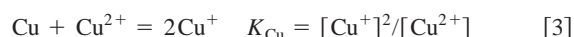
Tindall and Bruckenstein[9] studied this equilibrium using ring-disk techniques and determined that $K_{Cu} = 5.8 \times 10^{-7}$. In our solution, this produces a Cu(I) concentration of 4 mM. However, in the diffusion layer close to the anode, the concentration of Cu(I) may be higher than in the bulk solution. For example, when the wafer is made anodic, a nonequilibrium condition can exist, leading to Cu(I) concentrations near the anode that could be several orders of magnitude higher than the local SPS concentration. This Cu(I) species is thermodynamically capable of reducing oxygen to H_2O_2 $[E^0(O_2,H_2O_2) = 0.695$ V; $E^0(Cu^{2+},Cu^+) = 0.159]$, so it is possible that the concentration of peroxide near the anode is also one or two orders of magnitude higher than the SPS concentration.

Analysis of by-products and intermediates by LC mass spectrometry.—Healey[7] *et al.* studied the open circuit decomposition of SPS. The controlled variables in their experiments were the presence or absence of Cu^0, Cu(II), O_2, and platinum. Platinum was included because platinum-coated titanium baskets are used to hold the copper nuggets which serve as the anode in the PCB industry. The response variable was the half-life of SPS. In the absence of O_2, they found that if Cu^0, Cu(II), and SPS were present, the SPS decomposed rapidly and the solution turned green. If O_2 was also present, the SPS still decomposed rapidly, but the solution remained blue. Linear sweep voltammetry (LSV) of the green solution yielded a reduction wave at -0.16 V *vs.* a saturated Hg/Hg sulfate electrode (SMSE), but this wave was not present in the blue solution. They also mixed a solution of MPS and Cu(II) and found that it turned green immediately after mixing. They found that the green solution made in this manner also showed a wave at -0.16 V *vs.* SMSE. This wave occurred at potentials that are consistent with the Cu(I)/Cu(II) couple. They proposed that SPS decomposition occurred in a two-step reaction, where the intermediate species, copper thiolate, is formed as follows

$$4Cu^+ + (S(CH_2)_3SO_3H)_2 \rightarrow 2Cu^{2+} + 2CuS(CH_2)_3SO_3H$$
$$[4]$$
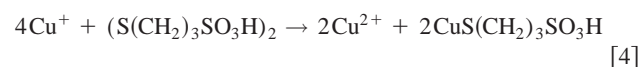
The copper thiolate then reacts with O_2 to give Cu(II) and "S-product". They speculated that S-product was an oxidized form of MPS such as propane-1,3 disulfonic acid. In this scheme, the disulfide bond is reduced by Cu(I) and thus, broken. They believed that the intermediate formed by exposing the SPS to the Cu(II)/Cu^0 couple in the absence of oxygen is the same species as that formed by mixing MPS and Cu(II) in the absence of oxygen. To gain additional insight into these reactions, we repeated these experiments, but LC mass spectrometry with electrospray ionization was used to analyze the intermediate and final products. The electrolyte consisted of 0.28 M $CuSO_4$ and 0.2 M H_2SO_4. The SPS concentration was 0.14 M. The solution was sparged with N_2 for 20 min through a glass frit prior to adding the SPS. A sample was drawn prior to electrolysis. Next, the solution (volume, 150 mL) was electrolyzed for 30 min at a current density of 26 mA/cm^2 in the absence of oxygen using the cell described earlier. A total of 2700 C were

Table I. Mass matches.

Detected m/z	Possible molecule	m/z	Delta m/z
97.1	HSO_4^-	96.93	0.17
155.1	$MPS - H^+$	154.9	0.20
277.1	$SPS - S - H^+$	276.76	0.34
309.1	$SPS - H^+$	308.82	0.28
311.0	$SPS - H^+$ with one S^{64}	310.82	0.18
331.1	$SPS + Na^+ - 2H^+$	330.80	0.3
341.0	$SPS + 2O^{16} - H^+$	340.81	0.19
341.0	$SPS + S^{62} - H^+$	340.88	0.12
371.0	$SPS + Cu^{+(63)} - 2H^+$	370.74	0.26
406.8	$SPS + HSO_4^-$	406.75	0.05
618.7	$2SPS - H^+$	618.64	0.06
679.7	$2SPS + Cu^{2+(63)} - 3H^+$	680.17	0.47

passed. During electrolysis the solution was sparged with N_2. As a result of the electrolysis, the solution became green. A sample of this solution was removed and maintained under N_2. Finally, the electrolyzed solution was sparged with oxygen until it turned from green back to blue.

The chromatograms and mass spectra for the three solutions are not shown. Table I lists the most likely matches for the masses that are present in these three spectra. Masses 113.1, 226.8, and 262.9 are background residuals left over from the previous experiments run on the instrument and are only present in significant concentrations in the first run. The most significant difference between the starting and electrolyzed solutions are masses 155.1 and 277.1, which are present in the starting solution but not the electrolyzed "green" solution. These are probably MPS and SPS minus one sulfur or two oxygen atoms, respectively. The predominant masses in each peak are listed in Table II. Part B contains data for the electrolyzed oxygen-free SPS solution. In this table, at an elution time of 10.6, the relative intensity of the signals for 309.1 and 371.0 m/z are

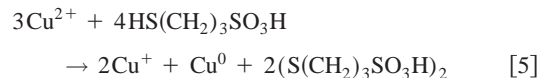**Table II. Mass spectrometry results of SPS and MPS solutions.**

Elution time, min	Predominant mass	Secondary mass
A. SPS solution prior to electrolysis		
5.01	226.8	113.1
5.69	277.1	226.9
5.92–5.97	309.1	618.7
6.18–7.00	309.1	618.7
7–7.7	309.1	618.1
7.82–8.9	309.1	618.7
8.89–10.49	309.1	113.1
B. SPS solution after electrolysis		
5.44–5.54	401.9/403.9	594.7/596.7
6.40	309.1/311.1	406.7
7.93	309.1/311.1	618.7/620.7
10.6	309.1/311.1	371.0/373.0
11.19–17.72	309.1/311.1	618.7/620.7
C. Electrolyzed SPS solution after oxygen sparging		
2.48	401.9/403.9	594.7/596.7
3.28	309.1/311.1	618.7/620.7
4.15–4.44	341.0/343.0	309.1/311.1
5.38–8.38	309.1/311.1	618.7/620.7
D. MPS/Cu solution (green solution)		
3.8–5.9	309.1	331.1/401.9
6.0–7.5	309.1	371.0/373.0
7.5–8.4	371.0/373.0	309.1
8.4–10.2	309.1	371.0/373.0
10.6–15.2	309.1	371.0/373.0
E. MPS/Cu solution after O_2 sparging		
5.4–5.9	309.1	371.0/373.0
6.4–9.1	309.1	618.7/620.7
11.4–14.6	341.0	309.1

100 and 80, respectively, so the concentration of the 371.0 species in this peak is significant. Part A contains data for the starting solution. Note that at an elution time of 8.9–10.5 min, neither the predominant or second most predominant species are at mass 371. This indicates that the concentration of the 371 species is lower in the starting solution than in the intermediate solution. Comparison of the mass spectra for the electrolyzed "green" solution and the same solution after oxygen sparging show the peak at m/z=371.0 is eliminated by the oxygen, while one at m/z 341.0 is formed. The m/z 371 peak has a related peak at 373 amu. The ratios of these two peaks are consistent with the naturally occurring isotopic ratios of copper and sulfur if the species is a complex of SPS and Cu(I). SPS + $Cu(I)^{63} - 2H^+$ corresponds to an m/z of 370.74. The measured m/z was 371.0 and the difference between these two numbers is 0.26 amu. $SPS - H^+$ has a m/z of 308.82 while the detected mass was 309.1. The difference is 0.28 amu. This serves as an internal calibration in this mass range and is further evidence that the 371.0 mass is an SPS Cu(I) complex. Although the 371/341 signal is rather weak, differences in the three chromatograms are apparent.
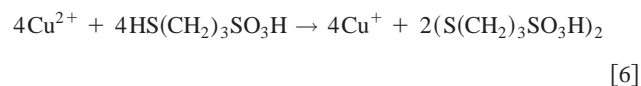
Similar experiments were carried out with MPS. The same electrolyte as in the previous experiments was used and was sparged with N_2 for 20 min, and then 0.28 M MPS was added. When the MPS was added, the solution became black and cloudy. After a short time it turned green. A sample of this solution was taken and bottled in a N_2 atmosphere. When the parent solution was sparged with oxygen, it turned from green back to blue. The predominant species for the entire mass spectra (not shown) is 309.1, SPS minus one proton. The species with the second highest abundance is 371.0/373.0 m/z, most likely the Cu(I)/SPS complex. The 371.0 m/z peak is not present in the chromatogram (not shown) for this solution after sparging with oxygen. The starting and oxidized MPS solutions both have peaks at 341.0 m/z. While the size of these peaks did not look significantly different, note that the quantities of each species are referenced to the predominant species. Thus, it can be misleading to compare the size of the 341.0 m/z signal in each spectrum, since the green solution has a significant signal from both the 309.1 and 371.0 m/z. The 371.0 species is almost totally absent from the oxidized MPS solution. The oxygen probably not only oxidizes the Cu(I) but it also liberates SPS and therefore, makes the concentration of the 309.1 m/z species larger. Since every other species is referenced to the 309.1 species, the magnitude of their signal becomes smaller. Parts D and E of Table II provide details about the spectra within each chromatographic peak.

The MPS and SPS spectra both show a 371.0 m/z species in the green unoxidized solution. The relative abundance of this species is greatly reduced in the oxidized solution compared to part D, the green unoxidized solution. Both the MPS and SPS spectra also show a 341.0 mass present in greater concentrations in the oxidized solutions compared to the green unoxidized solutions. The mass spectra suggest that SPS stabilizes the Cu(I) species. This Cu(I)/SPS complex probably reacts with oxygen to form Cu(II), SPS, and thiolsulfonate.
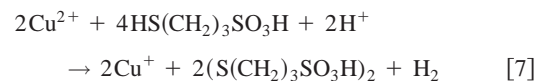
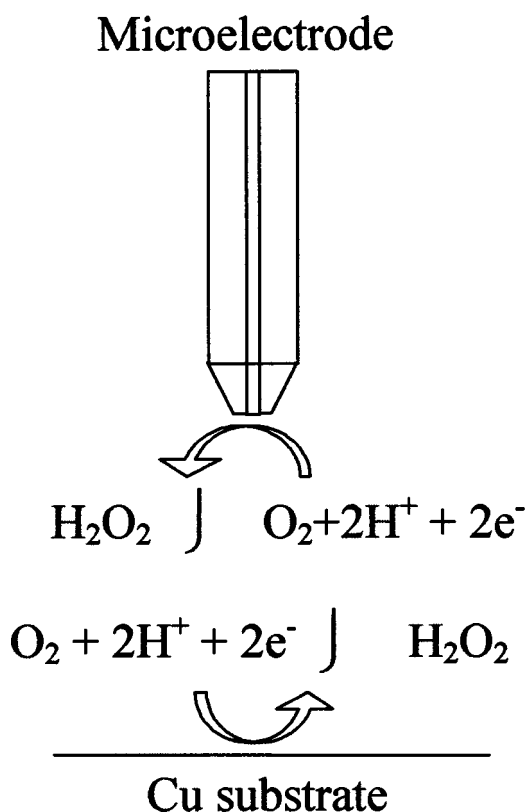In MPS solutions the reduction of Cu(II) to Cu(I) could be attributed to the HS group as follows

$$3Cu^{2+} + 4HS(CH_2)_3SO_3H$$
$$\rightarrow 2Cu^+ + Cu^0 + 2(S(CH_2)_3SO_3H)_2 \qquad [5]$$

or

$$4Cu^{2+} + 4HS(CH_2)_3SO_3H \rightarrow 4Cu^+ + 2(S(CH_2)_3SO_3H)_2$$
$$[6]$$

or

$$2Cu^{2+} + 4HS(CH_2)_3SO_3H + 2H^+$$
$$\rightarrow 2Cu^+ + 2(S(CH_2)_3SO_3H)_2 + H_2 \qquad [7]$$

Microelectrode

Figure 3. SG/TC experiment.

Cathodic reduction of oxygen on copper.—Although reduction of oxygen on different metals is one of the most widely studied electrochemical reactions, only one reference[10] for oxygen reduction on copper was found. In this paper, the authors used a ring disk electrode (RDE) and reported that oxygen reduction on copper produces water without a peroxide intermediate. We repeated the study of oxygen reduction on copper using the SECM[11-12] in the substrate (Cu) generation/tip collection (SG/TC) mode. The aim of these experiments was to see if hydrogen peroxide generated by reduction of oxygen at the copper substrate would be collected at a Pt tip by oxidizing the peroxide back to O_2. The tip was positioned about 20 μm from the substrate in the SECM apparatus. Figure 3 shows a schematic of the collection experiment.

The tip potential for H_2O_2 oxidation was determined by cyclic voltammetry (CV). Figure 4 shows overlays of two CV plots using a 25 μm platinum microelectrode (CH Instruments). The flat trace is a solution containing 2 M H_2SO_4 (Ashland Megabit Grade) in deionized (DI) water (Millipore milliQ). The curve with larger current excursions is a CV plot with the addition of 2 mM H_2O_2. The peak current at 0.6 V is the result of oxidation of H_2O_2 ($H_2O_2 = O_2 + 2H^+ + 2e^-$). Therefore, we can determine the presence of H_2O_2 by holding the tip at 0.6 V *vs.* Ag/AgCl or by doing tip CV and looking for the peroxide oxidation wave. LSV was used to determine the potential range for oxygen reduction on the copper substrate. This occurs at potentials where Cu(II) is also reduced to copper metal. In a typical plating bath solution, the Cu(II) concentration is much larger than that of the dissolved oxygen, so the current from Cu(II) reduction will be much larger than that from O_2. To avoid this problem, a solution containing only 2 M H_2SO_4 with ambient oxygen concentrations was used for LSV. For experiments detailed in the rest of this paper, the Hg/Hg$_2$SO$_4$ (SMSE) reference electrode was used to prevent excursions in the Cl$^-$ concentration. For the voltammogram shown, the electrode was taken from an 8 in. silicon wafer. The film stack consisted of 4000 Å of thermal SiO_2, 250 Å
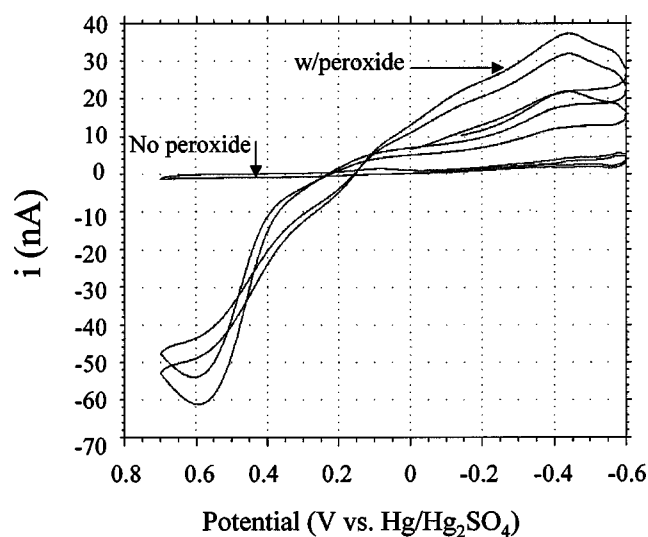

Figure 4. CV plots on 25 μm Pt microelectrode, 2 M H_2SO_4 with and without 2 mM H_2O_2.

Ta, and 1000 Å Cu, with both metals deposited using a Novellus Inova HCM plasma vapor deposition tool. Figure 5 shows an oxygen reduction wave with $E_p = -0.925$ V. This wave was highly irreproducible. A rolled copper sheet never exhibited this wave, electroplated copper sometimes exhibited this wave, and sputtered copper usually exhibited this wave.

One problem that was encountered in doing these measurements was due to a background current from Cu(II) ions in solution. Although Cu(II) was not intentionally added, it was present as the product of copper corrosion. The background current was often much larger than current due to the reduction of oxygen and masked the oxygen reduction wave. The Cu(II), and therefore the background current, can be removed by holding the substrate at -500 mV *vs.* Hg/Hg$_2$SO$_4$ before taking an LSV scan. Figure 6 is a graph with several LSV traces for 2 M H_2SO_4 solutions. Trace 1 is for a solution that was sparged with oxygen through a glass frit and has one wave that has a half wave potential of roughly -0.66 V. This is the copper reduction wave. Trace 2 represents a scan in 2 M H_2SO_4 with "ambient" concentrations of dissolved oxygen. The copper reduction wave is still present. It also has a second wave at roughly 0.9 V with respect to the Hg/Hg$_2$SO$_4$ reference. This wave is not
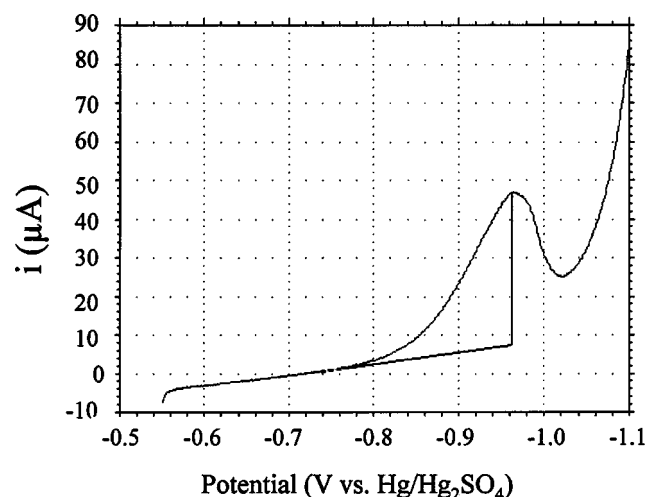

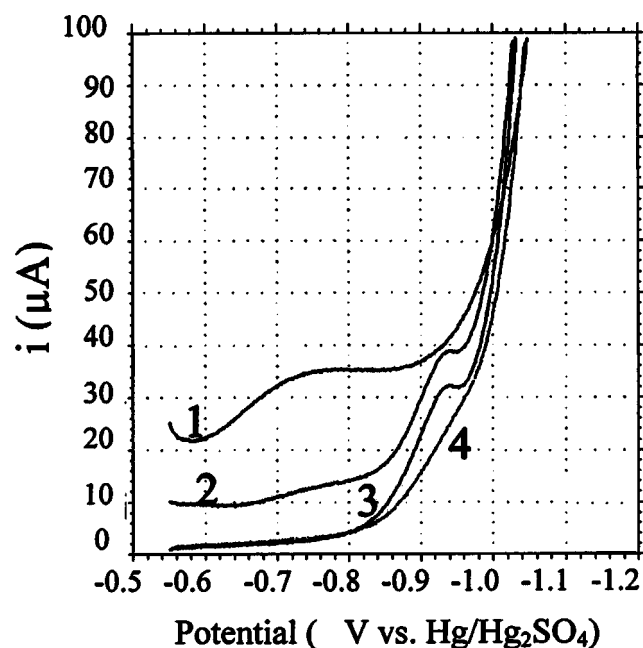**Figure 5.** LSV plots on Cu electrode, 2 M H_2SO_4 *vs.* Hg/Hg$_2$SO$_4$ reference.

Figure 6. LSV plots for copper substrate in 2 M H_2SO_4 *vs.* Hg/Hg_2SO_4 reference, (1) O_2 sparged, (2) "ambient" O_2, (3) 15 m Ar sparged, (4) solution 3 after 30 m under Ar blanket and held at 0.9 V.

Figure 7. SECM collection experiment with the substrate poised at the open circuit potential, -370, -320, -270, and -220 mV *vs.* Hg/Hg_2SO_4.

apparent in the top voltammogram. For trace 3, the same solution was sparged with argon using a glass frit for 15 min prior to bringing it in contact with the copper. The copper reduction wave is absent because the solution did not corrode the copper to a significant extent. The oxygen reduction wave is still present indicating that there was still residual oxygen in solution. Trace 4 was taken from the same solution 30 min later. During the time that elapsed between the first and second scan in this solution, the cell was maintained under argon, and the copper substrate was held at a potential of -0.55 V *vs.* Hg/Hg_2SO_4. The peak at $E_p = -0.95$ V is now absent.

To determine if the oxygen reduction product was H_2O_2, an SG/TC SECM experiment was carried out. The tip was positioned at ~ 25 μm from the substrate and the electrolyte was 2 M H_2SO_4. Prior to the collection experiment it was necessary to verify that the substrate was reducing oxygen. LSV confirmed that this substrate was capable of reducing oxygen. For the collection experiment, the substrate was held at -0.95 V and CV was done on the microelectrode tip. If peroxide was present, the tip CV should have shown a wave corresponding to H_2O_2 oxidation. A control with the substrate at open circuit and therefore not generating any H_2O_2 was used for comparison. No wave for H_2O_2 was seen in these experiments. The two CV scans essentially superimposed on one another. In an earlier experiment we showed that it was necessary to remove excess copper ions from solution to see the oxygen reduction wave at -0.95 V. It is possible that a small amount of Cu(II) was introduced into solution by oxidation of copper. However, since the substrate was held at -0.95 V during the experiment, any Cu(II) would have been removed by deposition on the substrate.

Reduction of oxygen by cuprous ion.—Since cathodic reduction of oxygen to peroxide does not occur, the source of the peroxide, if peroxide is actually involved in the SPS decomposition reaction, is either in solution or on the anode. On copper anodes the dissolution of copper produces some Cu(I). The potentials of the three important half-cell reactions for copper are
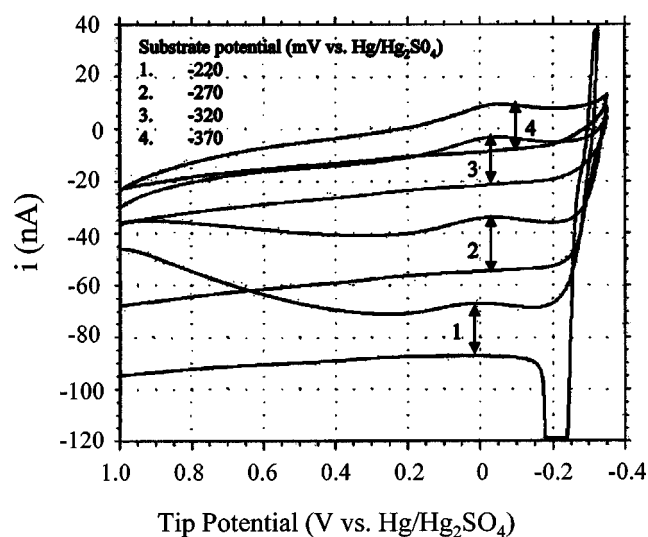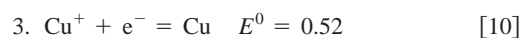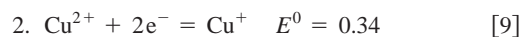
1. $Cu^{2+} + e^- = Cu^+ \quad E^0 = 0.16$ [8]

2. $Cu^{2+} + 2e^- = Cu^+ \quad E^0 = 0.34$ [9]

3. $Cu^+ + e^- = Cu \quad E^0 = 0.52$ [10]

At a copper anode, a one-electron oxidation produces Cu(I) which then disproportionates in solution near the anode surface to produce copper metal and Cu(II). Black films are known to form on copper anodes.[13] For the chemistry studied here, the film contains particles of single atoms of copper metal and also whole grains of copper which have been preferentially etched along the grain boundaries. It probably also contains some Cu(I) species and possibly chloride ion. In general, while cuprous ion can thermodynamically reduce dissolved oxygen to hydrogen peroxide in weakly complexing solutions, the rate of this reaction is probably slow. This is because the one-electron intermediate couple, superoxide/oxygen occurs at potentials negative of the Cu/Cu(I) couple. However, since it is known in the industry that the copper anode plays a role in the SPS decomposition, we investigated the possibility that the anode film was capable of making peroxide through the reaction

$$2Cu^+ + O_2 + 2H^+ = 2Cu^{2+} + H_2O_2 \quad\quad [11]$$

We used the SECM in the SG/TC mode to investigate the formation of Cu(I) and H_2O_2 from a Cu anode. The substrate was 99.999% pure copper sheet from Aldrich. The microelectrode was 25 μm Pt positioned 25 μm from the Cu substrate. In these experiments, the solution was the standard plating electrolyte consisting of 2 M H_2SO_4, 0.28 M Cu^{2+}, and 50 ppm Cl−. The counter electrode was a 99.999% copper rod (Aldrich). CV was performed with a platinum tip with a potential scan range that included peroxide oxidation to oxygen. Figure 7 was taken from a collection experiment with the substrate poised at the open circuit potential, -370, -320, -270, and -220 mV *vs.* Hg/Hg_2SO_4. The solution was 2 M H_2SO_4, 0.28 M Cu^{2+}, and 50 ppm Cl^-. Note that as the substrate potential became more positive, the tip current (anodic) increased. This current is probably due to the oxidation of Cu(I) to Cu(II), so the results suggest an increase in the concentration of Cu(I) in the vicinity of the electrode. Similar results have been found using a RDE.[14]

When this experiment was repeated in the absence of oxygen (removed by sparging with Ar for 20 min and maintaining an Ar atmosphere for a substrate potential of -320 mV *vs.* Hg/Hg_2SO_4), the results were essentially the same as in the presence of oxygen (Fig. 8). This suggests that the anodic tip current does not have a
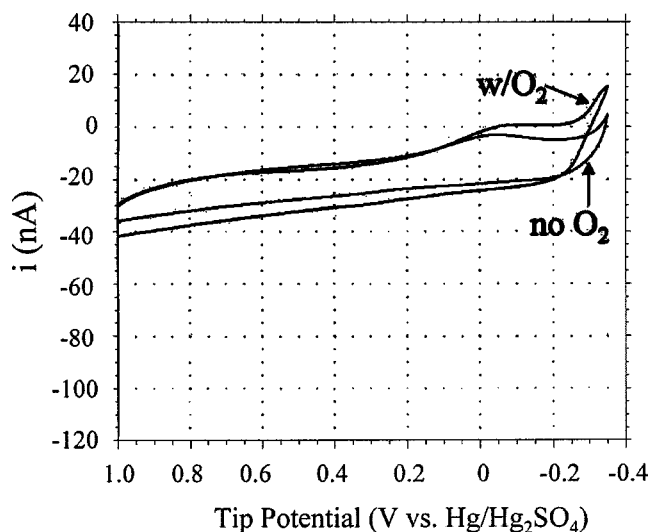
Figure 8. SECM SG/TC experiment with and without dissolved oxygen, substrate held at -320 mV *vs.* Hg/Hg$_2$SO$_4$ reference.

Figure 9. UV visible absorbance of MPS, .28 M CuSO$_4$/2 M H$_2$SO$_4$ solution.

component attributable to peroxide oxidation and that the black anodic film did not reduce dissolved oxygen to peroxide. The standard anode material in industrial acid copper sulfate plating baths is phosphorized copper (0.05% P). The addition of phosphorus gives rise to formation of a black film on the copper surface during anodic dissolution. Rashkov and Vuchkov[13] have used X-ray diffraction to show that this film contains Cl$^-$ and cuprous phosphate. In Ref. 15, the authors investigated the effect of the addition of phosphorus to the copper anode with a ring/disk electrode collection experiment. They showed that the phosphorus significantly reduces the Cu(I) concentration in solution near the anode. Similar SG/TC experiments were performed with a phosphorized copper anode (P concentration 0.05%, Nimtek). The substrate potentials were open circuit, -150, and -300 mV *vs.* the Hg/Hg$_2$SO$_4$ reference. In all cases, the tip current was in the nanoamp range and flat with no waves until 0.9 V indicating that peroxide is not formed on phosphorus doped copper anodes.

The CV curves were nearly identical for all substrate potentials. Reference 13 shows that the phosphorus dopant keeps the Cu(I) contained in the anode film. This decreases the concentration of Cu(I) present in solution near the anode. In contrast, on phosphorus free copper the tip current increased as the substrate potential was made more positive because the Cu(I) concentration increased with increasingly anodic substrate potentials.

The anode film studied in these experiments did not reduce dissolved oxygen to peroxide. The available complexing agents were water, sulfate ion, chloride, and phosphorus (anode film). In actual plating baths, organic additives are also present. The organic additives may alter the stability of the cuprous ion and therefore yield different results.

UV VIS analysis of the MPS/Cu^{2+} *mixture.*—Solutions containing 0.28 M CuSO$_4$ and 2 M H$_2$SO$_4$ were prepared as described earlier. Various MPS concentrations were added. Immediately after the MPS was added the solution turned from blue to black and then from black to various shades of green or yellow depending on the MPS concentration. For ratios of 1:1 MPS:CuSO$_4$, the solution was green while 2:1 MPS:CuSO$_4$ solutions were yellow. The color change is due to the ratio of absorption at 400–450 nm and 600–900 nm. In Fig. 9, note that the 0 M MPS curve has no absorption in the 350 to 475 nm range. When MPS is added, there is strong absorption in the 350 to 475 range and the absorption in the 600–900 nm range (the absorption peak of CuSO$_4$ $\cdot$ 5H$_2$O) decreases. When the MPS concentration is increased, the absorption peak in
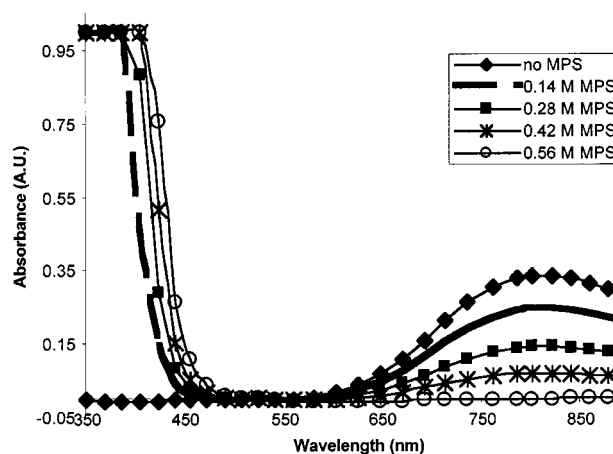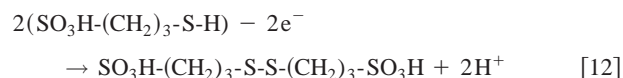
the 400–450 range shifts toward the visible region. The color differences can be attributed to a change in the ligands or to an oxidation state change of Cu(II) to Cu(I). The aquo complex of Cu(I) is not very stable; this implies that the formation of Cu(I) is also accompanied by a change in the coordination sphere. For example, the Cu(II)-MPS complex could be Cu(RS)$_2$. Analysis of the data shows that the MPS:CuSO$_4$ ratio in the new complex is 2:1. This is consistent with a Cu(RS)$_2$ complex. However, the prominent feature of the "green" MPS:CuSO$_4$ chromatogram was the large peak with an m/z of 371.0. The closest match to this mass is for SPS + Cu(I)$^{(63)}$ $-$ 2H$^+$ corresponding to an m/z of 370.74. The Cu(RS)$_2$ complex would have a m/z of 371.74, off by -0.75 amu from the reported mass and off by over 1 amu taking the internal calibration into account. This is further confirmation that the 371.0 species, and the new complex, contains Cu(I). Formation of Cu(I) requires some electron donor, *e.g.*, MPS, that can be oxidized to form SPS.

$$2(SO_3H\text{-}(CH_2)_3\text{-}S\text{-}H) - 2e^-$$
$$\rightarrow SO_3H\text{-}(CH_2)_3\text{-}S\text{-}S\text{-}(CH_2)_3\text{-}SO_3H + 2H^+ \qquad [12]$$

In this experiment, the MPS:Cu mole ratio found to eliminate the aquo complex was in fact 2:1. If the MPS is oxidized to SPS in the process, the SPS:Cu ratio is 1:1. This is consistent with the LC mass spec experiment where the complex was found to be Cu(I)/SPS. However, MPS and Cu(II) can not be the only participants in this reaction since the electrons do not balance, there must be another electron acceptor besides Cu.

ESR analysis of the new complex.—The oxidation state of the copper in the new complex can be verified using ESR. Cu(I) is diamagnetic while Cu(II) is paramagnetic. We thus sought to investigate the ESR behavior of Cu(II)-MPS solutions. To allow tuning of the ESR instrument, it was necessary to decrease the conductivity of the solution. The H$_2$SO$_4$ concentration was therefore reduced to 0.2 M, with a CuSO$_4$ concentration of 0.28 M. MPS was added as required to make solutions containing no MPS, and 0.28 and 0.56 M MPS. To further reduce the conductivity, the samples were diluted by a factor of 10 with Millipore milliQ DI water. Finally, the solution was injected into glass capillaries using a glass pipette. Figure 10 shows the ESR spectra for these solutions. The curve with the largest amplitude corresponds to no MPS, the curve with the intermediate amplitude to 0.28 M MPS and the flat curve to 0.56 M MPS. This is consistent with an oxidation state of $+1$ for copper in the new complex. ESR studies by Rataczak and Pajdowski[16] with Cu^{2+} and thiourea in nitric acid solutions produced similar results.
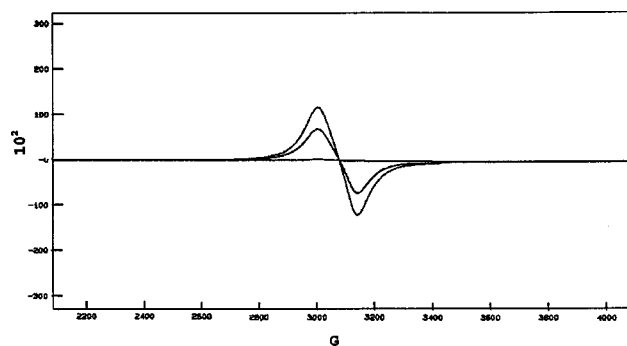
Figure 10. ESR Spectra of 0, .28, and .56 M MPS in a .28 M $CuSO_4$ solution.

Discussion

The primary decomposition product appears to be the thiolsulfonate form of SPS. HPLC with UV detection suggests that the same compound is formed by adding excess H_2O_2 to SPS. The electrochemical studies done here show that H_2O_2 is not formed at the cathode or anode even at potentials outside the normal range of operation for typical electroplating processes. The decomposition happens in solution as Healy[7] showed. Cu(I) drives the decomposition and is present when copper metal is introduced into these acid copper formulations. The LC MS work suggests that Cu(I) does not reduce the disulfide but instead forms and SPS/Cu(I) complex. LC MS showed that the same complex is formed when MPS is mixed with the acid copper sulfate electrolyte. Care must be taken when drawing conclusions for thiols and disulfides, since the MPS could be oxidized to SPS in the electrospray portion of the LC MS instrument. The electrospray source is, in effect, an electrochemical cell. UV Vis spectroscopy shows that the $CuSO_4 \cdot 5H_2O$ is removed by MPS and the ESR work demonstrates that Cu^{2+} is reduced to Cu(I) at the same time. Since this reduction is brought about by the addition of MPS to solution, the MPS must oxidize, so the MPS was probably oxidized to SPS prior to injecting it into the electrospray source. Note that the oxidation of MPS by Cu^{2+} not consistent with the copper thiolate intermediate proposed by Healey.[7] In the copper thiolate molecule the copper is reduced (Cu^+) relative to Cu^{2+}, but the MPS portion is not oxidized. The UV visible absorption results show that the ratio of MPS to Cu is 2:1 in the new complex and the ESR work shows that the oxidation state of the copper in the new complex is +1. The 2:1 MPS:Cu stoichiometry coupled with a copper oxidation state of +1 suggests that there may be another electron acceptor involved. Dissolved oxygen is most likely. Another clue is the fact that immediately after mixing the MPS with the acid copper sulfate electrolyte, the color turned cloudy black. A short while later the color changed to a green or yellow color depending on the MPS:Cu(II) ratio. The cloudy black species may have been metallic copper particles suspended in solution. Dissolved oxygen

could then oxidize the copper metal to Cu(I). The mass spectrometry work shows that Cu(I) is stabilized by SPS. The scheme with oxygen as the electron acceptor could be

$$2Cu^{2+} + 4HS(CH_2)_3SO_3H + 2H^+ + O_2$$
$$\rightarrow 2(Cu(I)((S(CH_2)_3SO_3H)_2) + H_2O_2 \qquad [13]$$
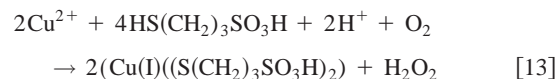
In another step, dissolved oxygen oxidizes the Cu(I) to Cu(II), with the oxygen reduced to superoxide or H_2O_2. The addition of dissolved oxygen is concurrent with the formation of thiolsulfonate. Although it is not possible to make quantitative measurements based on the MS results reported here, it appears that the conversion of the Cu(I):SPS complex to thiolsulfonate is probably incomplete. Much of the SPS may just be liberated from the cuprous complex without being oxidized. Future studies using alternative techniques are required to learn more about the Cu(I) complex. The studies should be aimed at determining which portion of the SPS molecule is involved in the complex.

The open and closed circuit decomposition reactions are probably the same. Making the copper metal anodic simply increases the rate at which Cu(I) is introduced into solution and therefore increases the decomposition rate. Although this suggests that changing to a phosphorized copper anode should slow the decomposition rate, unpublished work showed that the phosphorus-doped copper does not change the decomposition rate significantly. Future work might allow one to devise schemes to increase the bath life, *e.g.*, by addition of antioxidants that could decompose any peroxide or superoxide species present. Another would be to add an additional oxidizing agent, other than dissolved oxygen, to oxidize the Cu(I) back to Cu(II) and liberate SPS without creating thiolsulfonate.

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