Copper Sulfonate Electrolytes for Metallization of Interconnect Technology

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Abstract

The deposition of copper for interconnects from sulfonate solutions has been investigated. Copper electrodeposition from methanesulfonate, ethanesulfonate, propanesulfonate and trifluoromethanesulfonate solutions into sub-micron trenches shows advantages over electrodeposition using conventional cupric sulfate/sulfuric acid electrolytes. Computer models of the copper sulfonate molecules are being used to explain the enhanced properties of the deposits. The results of studies from these copper sulfonate solutions including electrochemical studies, x-ray diffraction, x-ray photoelectron spectroscopy and electron microscopy is presented.

Introduction

In recent years, there have been numerous investigations into the use of copper as a replacement for aluminum in chip metallization[1,2]. Copper deposition for interconnect technology was developed in the early 1990s and has been shown to have advantages over aluminum including lower resistance and higher permissible current densities[3]. Although there are several methods to deposit thin copper layers, electrodeposition appears to be the best method to fill sub-micron trenches without creating voids or seams in the deposits. Fully integrated circuits using copper interconnections appeared by the mid-1990's[4,5].

Copper electrolytes used to fill 0.18 μm to 0.25 μm trenches are typically based on cupric sulfate/sulfuric acid formulations. The deposition conditions including current density and grain refining additives may affect the deposit profile within the trench. Copper deposition from additive-free solutions results in conformal filling of trenches leading to voids or seams. Studies have thus focused on the effects of grain refining additives in copper electrolytes to preferentially deposit copper at the bottom of the trench. This "bottom-up" fill process provides defect-free copper deposits.

Although there have been extensive investigations into the use of grain refining additives on the fill process and the structure of the copper deposit, little attention has been given to understanding the effects of different anions on the performance of the copper electrolytes. This study investigated the use of sulfonate anions, $R-SO_3^-$, as the counter-ion for Cu^{+2}. The effects of methanesulfonate ($CH_3SO_3^-$), ethanesulfonate ($CH_3CH_2SO_3^-$), propanesulfonate ($CH_3CH_2CH_2SO_3^-$) and trifluoromethanesulfonate ($CF_3SO_3^-$) on the deposition of copper for interconnect applications is shown to provide advantages over sulfate-based solutions.

Experimental

The copper sulfate and copper sulfonate solutions were prepared by mixing copper carbonate, $CuCO_3:Cu(OH)_2$, 57% Cu^{+2}, into doubly distilled water. After the copper slurry was adequately mixed, concentrated sulfuric acid, 70% methanesulfonic acid, 70% ethanesulfonic acid, 80% propanesulfonic acid or 50% triflic acid was slowly added until all the carbonate was removed. Additional free acid was added so the final free-acid concentrations were 0.00 M, 0.25 M, 0.75 M and 1.75 M. After dilution to volume, each solution was filtered. The solutions were then treated with 1 ml/l hydrogen peroxide, 30%, and heated to 70^oC for 180 minutes. Carbon black powder was then added and allowed to mix for 180 minutes. The solutions were cooled to room temperature and filtered.

Brass Hull cell panels were plated at 1A for 10 minutes in each of the additive-free solutions containing 50 mg/l Cl^-. After plating, the panels were rinsed in distilled water and coated with benzotriazole (BTA). The effects of grain refining additives were also studied.

Electrochemical studies were made using an EG&G PAR 273 potentiostat and a platinum working electrode. A saturated calomel and an iridium oxide mesh served as the reference and counter electrodes, respectively. Cyclic voltammetry was done by scanning from +0.5 V to -0.7 V vs SCE using scan rates from 1 – 100 mV/sec followed by reversing the scan. The negative potential limit varied from +0.05 V to -0.25 V to investigate the initial stages of deposition. Constant potential steps from +0.3 V to -0.25 V or constant current studies from -0.2 mA/cm^2 to 24 mA/cm^2 followed changes in current density of potential with time, respectively. Impedance measurement using an EG&G 5210 lock-in-amplifier from10 MHz to 10 mHz showed the effects of the sulfonate anions on the electrochemical interface. The effects of grain-refining additives on the electrochemical behavior were also monitored.

Copper deposits plated without additives and with additives were studied using electron microscopy (EM), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and atomic force microscopy (AFM). A Leo 1560 field emission microscope with accelerating voltages varying from 1 kV to 15 kV imaged the copper deposits. A Kratos Axis 115 XPS instrument equipped with an aluminum target and a monochromator was used to study the surface composition of the copper deposits plated from the additive-free and additive-containing electrolytes. XPS spectra from 0 – 1400 eV were recorded within two hours after preparing the films. Detailed spectra of specific regions after ten sweeps and deconvolution of overlapping peaks was done using a Gauassian fit. XRD patterns from 10 -100° using a 0.01^o step scan were acquired on the as-deposited samples using a Philips APD 3720 instrument with variable slit

optics. Removal of the K_β was accomplished using a nickel filter. Analysis of diffraction patterns was performed using computer programs[16]. A convoluted algorithm combining an instrumental broadening and Lorentzian function assisted in the curve fitting analysis. AFM analysis was performed using a Digital Nanoscope III instrument. Several scanning heads were employed, the largest capable of eight microns. Imaging was done using a deflection mode

Surface tension measurements were made using a Kruss goniometer. The copper solutions were applied to the surface of a freshly prepared copper-plated panel. Drops approximately 10 µL were allowed to contact the copper surface. The angle, θ, was measured 5 seconds after contact. An average of five readings was made.

Conductivity measurements of the pure acid solutions and the copper plating solutions were made using an Orion Model 142 conductivity meter. The cell constant was determined using KCl standards. The pH was also determined on each of the pure acids and the copper solution using an Orion Model 611 pH meter. The pH was recorded 30 minutes after the pH probe was inserted into the solution.

Copper-seeded wafers were plated with copper using a standard cupric sulfate/sulfuric acid solution using commercially available additives. The free sulfuric acid concentration was 170 g/l (about 1.7 M). Copper propanesulfonate and copper triflate were also used to deposit copper using the same additive formulation as with the copper sulfate process. However, the free propanesulfonic acid was 75 g/l (0.6 M) and the free triflic acid was 90 g/l (0.6 M). The current density used to plate the trenches was 13 mA/cm^2 and the over-plate current density was 20 mA/cm^2.

Results and Discussion

Hull cell panels plated with additives showed the effects of the sulfonate anions compared to the sulfate anion as well as the effects of free acid concentration on the bright plating range. Table 1 shows the copper sulfate and copper methanesulfonate solutions deposit bright coating at high free acid concentrations. Rougher deposits were seen at current density at and below 10 mA/cm^2. The copper ethanesulfonate and copper propane sulfonate solutions produce commercially acceptable deposits at low to intermediate free acid levels. The copper triflate solutions showed the widest operating window for free acid. The copper triflate panels were very bright and smooth at all free acid concentrations. The ability to deposit copper with low free acid is important in IC technology. A copper seed layer is used to provide a catalytically active surface for copper deposition and may be susceptible to dissolution.

As feature size decrease with increased complexity, the copper seed layer thickness also decreases along the lower portions of the feature sidewalls. High free acid concentrations such as those used in sulfate electrolytes may increase the propensity for copper seed-layer corrosion. Thus, there is a need for a copper electrolyte with low to intermediate free acid that deposits a smooth copper layer through nucleation and subsequent film growth without affecting other properties of the copper layer. The copper sulfonate solutions show the ability to deposit copper

in small diameter trenches and provide enhanced leveling properties than the sulfate based electrolyte coatings.

Solution conductivity measurements showed at a given free acid concentration, the copper sulfate solutions exhibited the highest conductivity. This was followed by the copper methanesulfonate. With increasing length of the organo-sulfonate chain, the solution conductivity decreased. Figure 1 shows the solution conductivity for copper sulfate and copper propanesulfonate. The effects of lower solution conductivity may manifest themselves by changes in the primary current distribution thus affecting the leveling performance of the copper deposits.

The surface tension of additive-free copper solutions showed variability dependent upon the nature of the substrate, copper counter-anion and the concentration of free acid. Pure water on a freshly plated copper surface showed a θ value of 29.1^o. The wetting properties of copper electrolytes vary with free acid concentrations and the type of anion. Typically, the copper sulfonate solutions showed a smaller θ value compared to copper sulfate at an equivalent free acid concentration. Figure 2 shows the change in θ with acid concentration for the copper triflate and copper sulfate solutions. The copper triflate solution appears to wet the copper surface better than the copper sulfate electrolyte. The triflate solution, unlike the copper sulfate solution, also shows no changes in surface tension with changes in free acid concentration. At the high free sulfuric acid concentration currently used in today's copper interconnect electrolytes, the wetting properties of the cupric sulfate electrolytes are poor. The ability to wet the small features seen in today's IC may be beneficial for bottom-up fill.

The effects of the sulfate and sulfonate anions on the initial stages of copper deposition in the additive-free solutions are shown in Figures 3a - 4c. CV scans from +0.3 to +0.035 made in the copper solutions containing 1.75 M free acid show the triflate solution initiates copper deposit but the sulfate solution evolves only hydrogen, Figures 3a and 3b. The maximum peak current density for the cupric sulfate solution was -0.46 mA/cm^2 but for the copper triflate solution, the peak current density was -1.96 mA/cm^2. The shape of the CV trace for the copper triflate solution implies a nucleation and growth process. The large increase in current density and the cross-overpotential is indicative of a deposition process. Also, the anodic or stripping peak in Figure 3b centered at +0.09 V is due to the dissolution of copper from the electrode. The lack of a strong cathodic peak on the forward scan and no sign of a stripping peak on the reverse scan from the sulfate solution confirms that no copper was deposited at this limiting cathodic potential. Copper did not deposit from the sulfate solution until a potential of +0.03 V was reached on the forward scan in the 1.75 M free acid solution.

Decreasing the free acid to 0.25 M shifted the potential for copper deposition from the sulfate solution to +0.025 V compared to the +0.03 V at 1.75 M free acid, Figures 4a and 4b. At +0.025 V, the cathode efficiency was only 5.78%. For the copper methanesulfonate system at 0.25 M free acid, copper deposition commenced at +0.04 V and the cathode efficiency was already 11.3%. At +0.025 V, Figure 4c, considerably more copper was deposited from the methanesulfonate solution compared to the sulfate electrolyte. The cathode efficiency at +0.025 V for the methanesulfonate solution was 62.1%. Comparison of Figs. 4b and 4c show the limiting cathodic current density in fig. 4c is about -1.5 mA/cm^2 but only 0.16 mA/cm^2 in Fig.

4b. Therefore, the sulfonate electrolytes in the absence of additives appear to initiate copper deposition at more positive potentials compared to solutions based on cupric sulfate/sulfuric acid.   The ability to deposit copper at more anodic potentials and at lower free acid concentrations is important when trying to plate copper in low current density areas of IC's. Fast initiation of copper also minimizes copper seed-layer dissolution.

XRD studies of the additive-free copper deposits showed the strongest reflection was the (220), second order (110). This reflection was the strongest in all copper deposits indicating the anions had little effect on the orientation of the deposit. Copper plated in the presence of additives exhibited a (111) orientation, Figure 5. This close-packed orientation of copper was seen in all deposits. The (111) orientation is important in copper interconnects because it is the close-packed plane (e.g., highest atomic density plane).

To ensure the copper sulfonate solutions are stable with electrolysis, the four sulfonate solutions were electrolyzed in the absence of additives for 150 A-min/l. Copper deposits were then analyzed for occluded sulfur and fluoride in the deposits using XPS. A typical XPS scan seen in Figure 6 shows no traces of sulfur. The sulfonate anions are thus stable under these deposition conditions. Similarly, no fluoride was detected in the copper deposit plated from the triflate solution.

The enhanced solution properties of the copper sulfonate solutions manifest themselves during the deposition of copper into small features such as those seen in IC's. Seeded wafers were plated with copper from propanesulfonate and triflate solutions using additives. These deposits were compared to standard copper deposits plated from copper sulfate also using additives. The images seen in Figures 7a - 7c show all deposits filled the 0.14 μm trenches with no signs of voids. Partial-fill studies showed the sulfonate electrolytes exhibit the "bottom-up" fill process. The over-plate step from the copper sulfate solution was about 0.67 μm. However, the over-plate height from the propanesulfonate and triflate solutions were 0.47μm and 0.24 μm, respectively.

Complete fill of 0.14 μm trenches is seen in Figure 8 using the cupric trifluoro-methanesulfonate solution. Partial fill studies show bottom-up fill using this electrolyte. No voids or seams are seen in any of the trenches.

Conclusions

Copper sulfonate solutions have been investigated as alternatives for copper sulfate electrolytes in IC technology. The ability to alter the organo-chain length allows one to change the electrochemical deposition behavior as well as coating properties. Sulfonate electrolytes appear to initiate copper deposition at more noble potentials compared to cupric sulfate/sulfuric acid electrolytes at a given free acid concentration. Copper sulfonate solutions allow for deposition of copper at low free acid concentrations and provide for superior over-plate characteristics.

References

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Table 1. Hull Cell Panel Characterization

| Electrolyte	Low Free Acid (0.25 M)	Intermediate Free Acid (0.75 M)	High Free Acid (1.75 M)
$CuSO_4$	Rough Deposit at 30 - 40 ASF; Bright Deposit from 30 to 1 ASF	Bright Panel from 40 - 1 ASF	Bright Panel from 40 - 1 ASF
$Cu(CH_3SO_3)_2$	Rough Deposit at 30 - 40 ASF; Bright Deposit 30 to 10 ASF	Bright Deposit to 10 ASF	Bright Panel from 40 - 1 ASF
$Cu(CH_3CH_2SO_3)_2$	Very Slightly Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF	Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF	Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF
$Cu(CH_3(CH_2)_2SO_3)_2$	Very Slightly Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF	Slightly Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF	Rough Deposit at > 40 ASF; Bright Deposit from 30 to 1 ASF
$Cu(CF_3SO_3)_2$	Bright Panel from 40 - 1 ASF	Bright Panel from 40 - 1 ASF	Bright Panel from 40 - 1 ASF
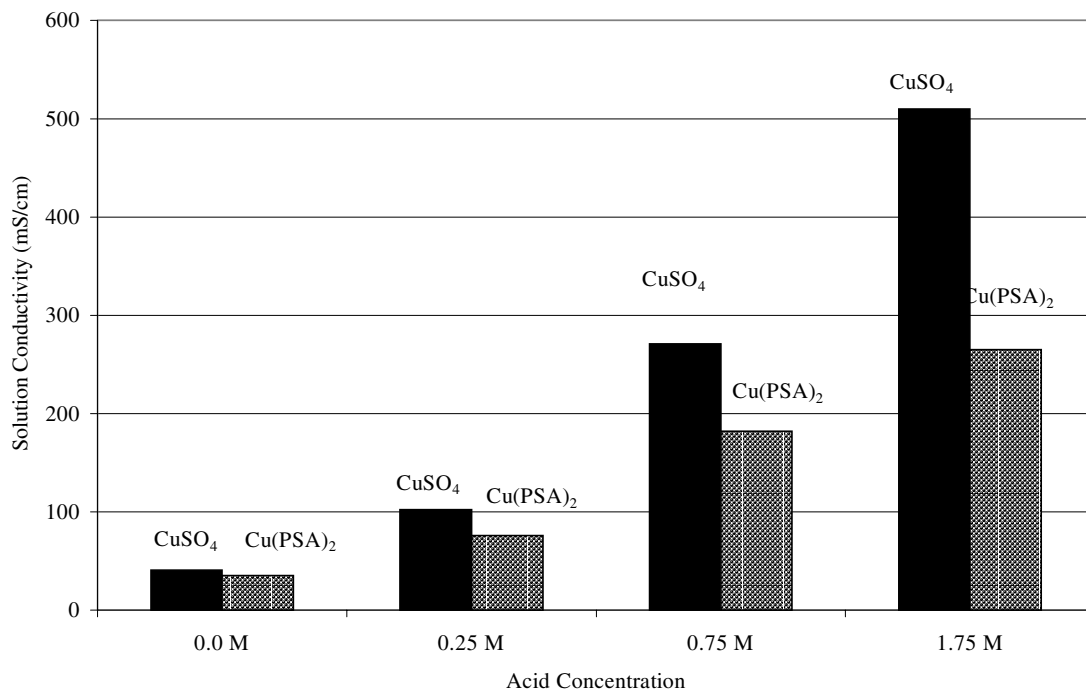
Figure 1. Conductivity Measurements of Copper Sulfate
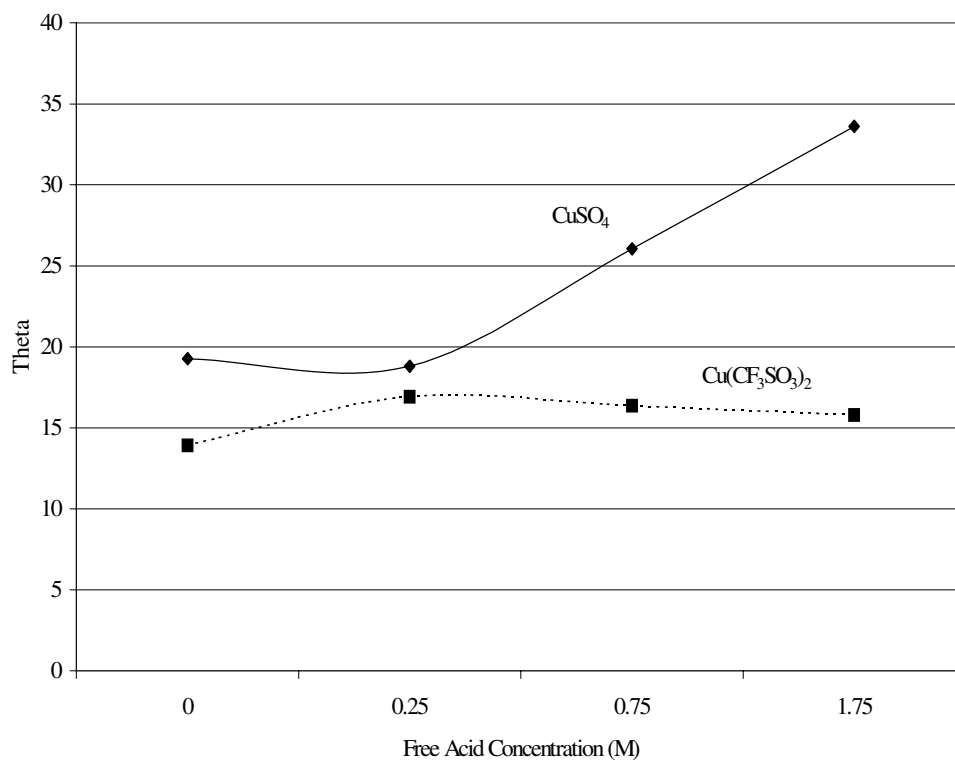and Copper Propanesulfonate Solutions

Figure 2. Surface Tension Measurements of Copper Sulfate
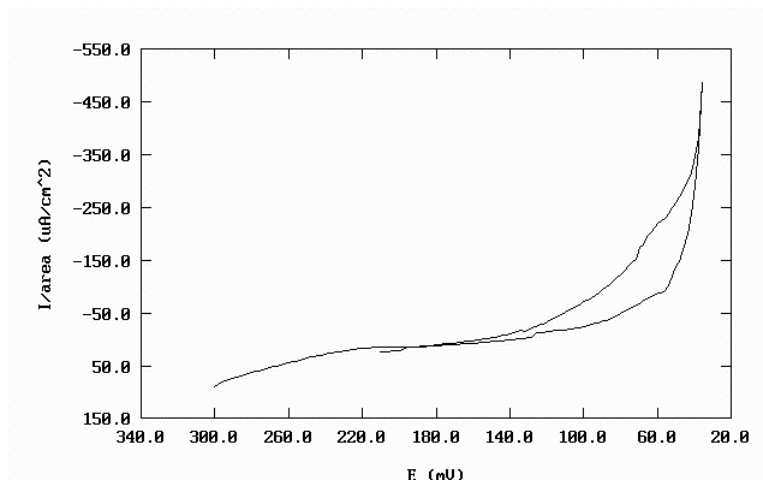and Copper Triflate Solutions

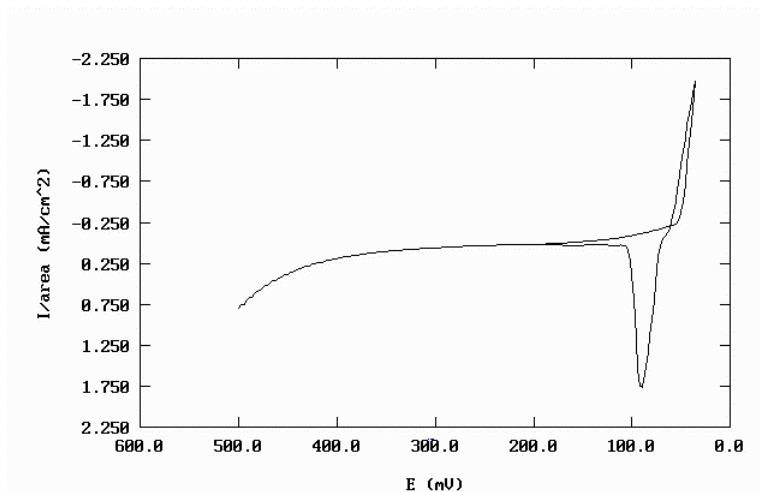Figure 3a. Polarization to +0.035 V in CuSO$_4$ Solution
Containing 1.75 M Free Acid

Figure 3b. Polarization to +0.035 V in Cu(CF$_3$SO$_3$)$_2$ Solution
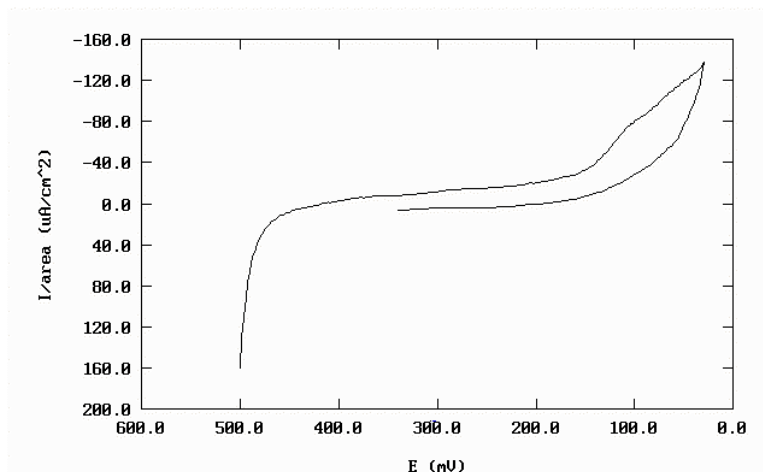Containing 1.75 M Free Acid

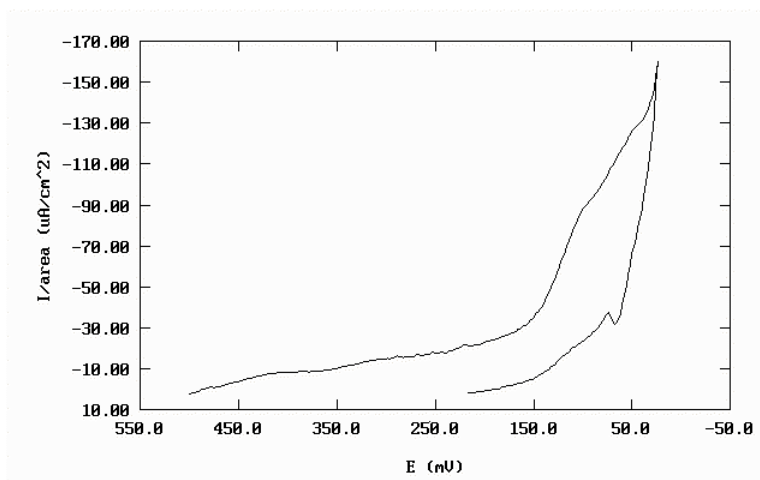Figure 4a. Polarization to +0.030 V in CuSO$_4$ Solution
Containing 0.25 M Free Acid

Figure 4b. Polarization to +0.025 V in CuSO$_4$ Solution
Containing 0.25 M Free Acid
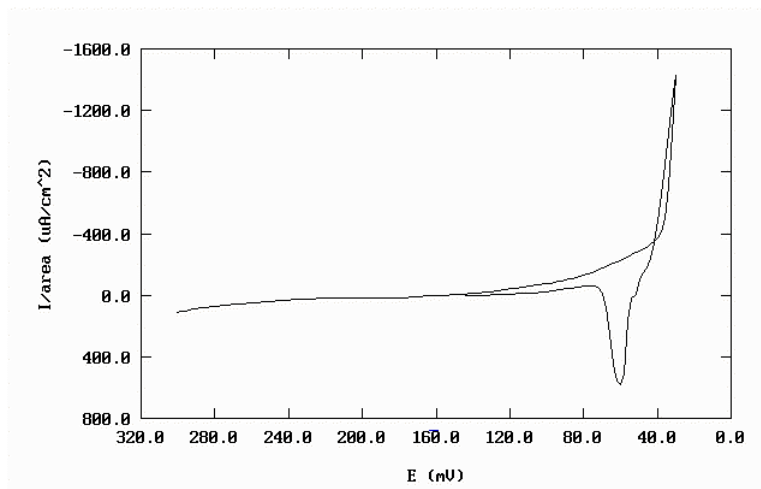
Figure 4c. Polarization to +0.025 V in Cu(CH₃SO₃)₂ Solution
Containing 0.25 M Free Acid
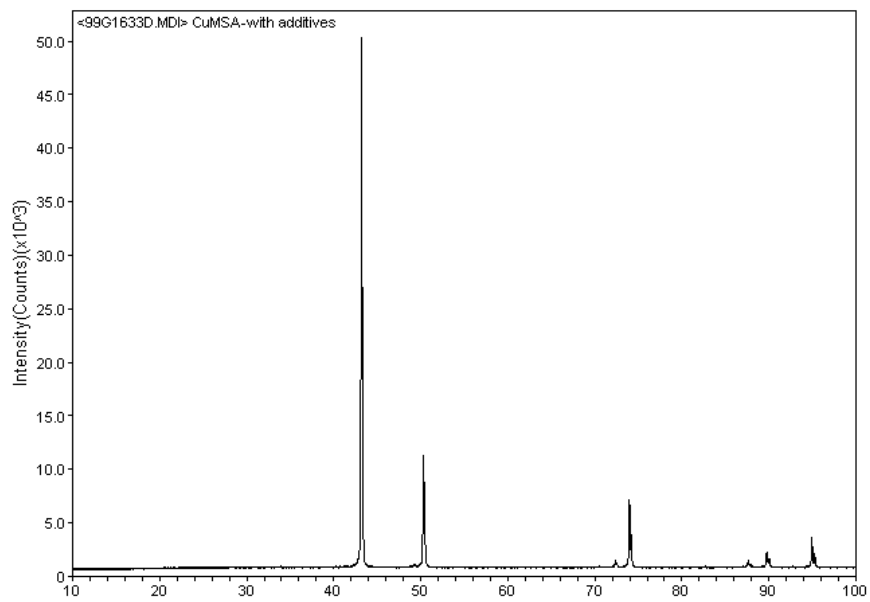
Figure 5. XRD Scan of Copper Methanesulfonate Deposit Plated with Additive
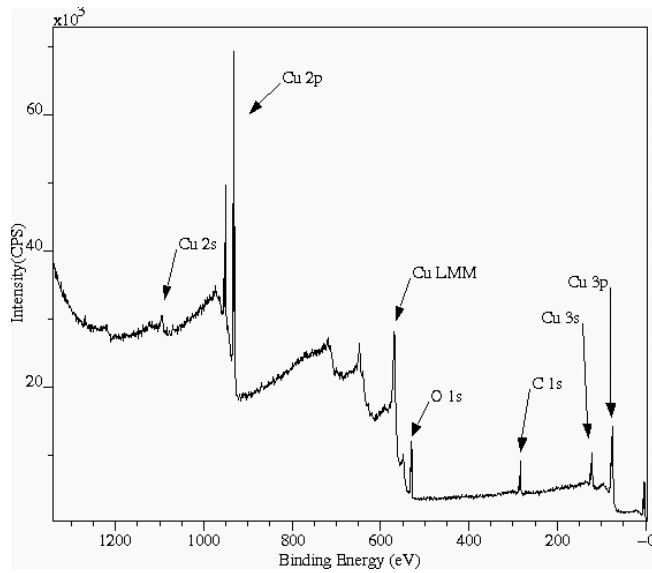
Figure 6. XPS Trace of Copper Ethanesulfonate Deposit Plated without Additives
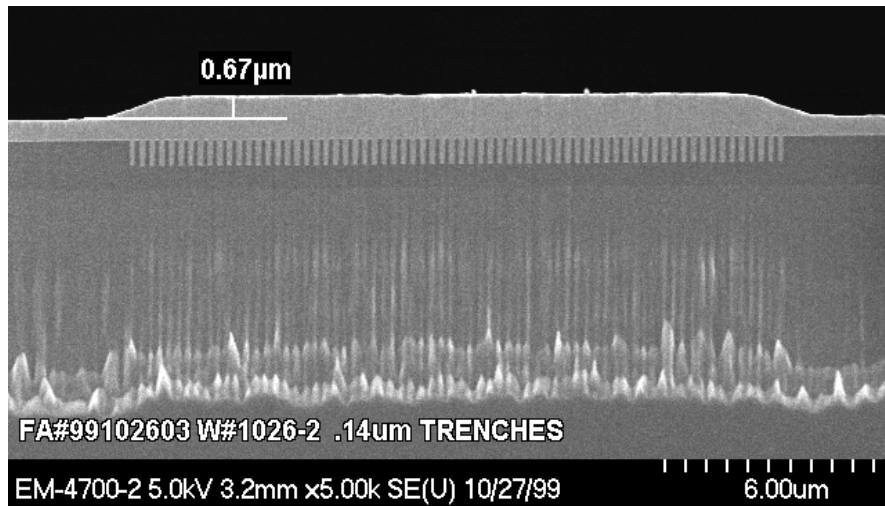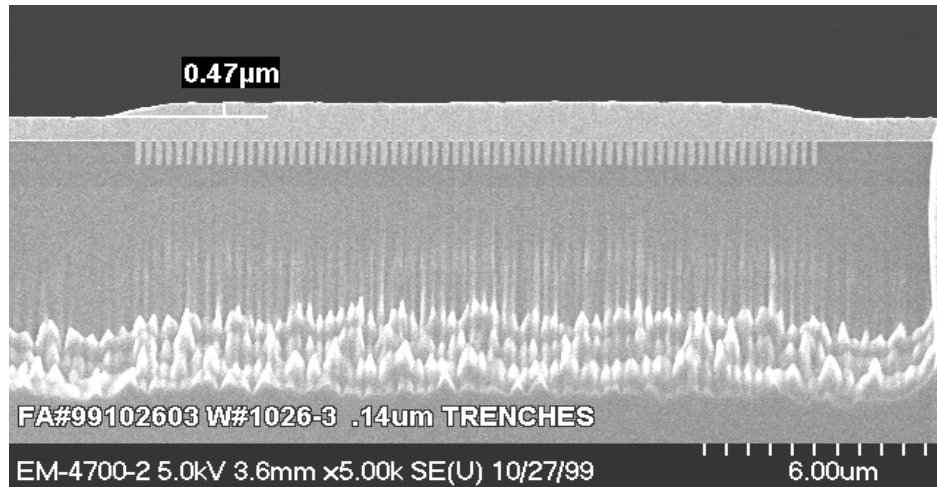

Figure 7a. Cross Section of CuSO$_4$ Deposit
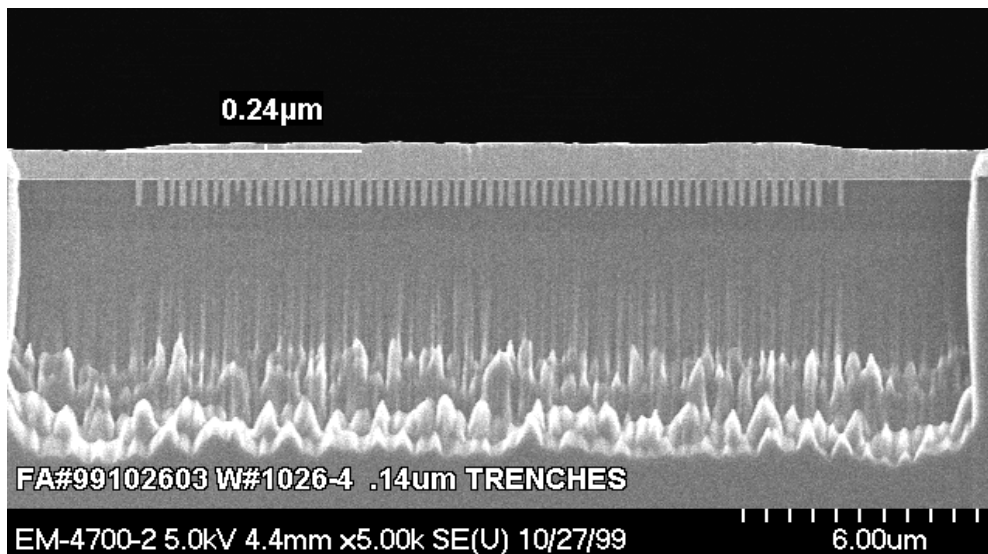
Figure 7b. Cross Section of Cu(CH$_3$(CH$_2$)$_2$SO$_3$)$_2$ Deposit

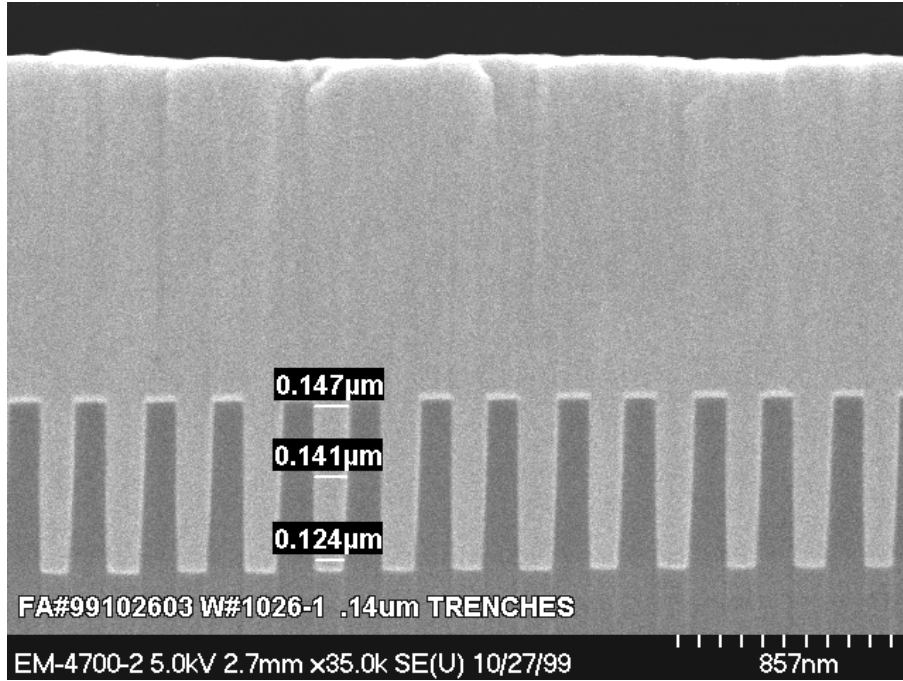
Figure 7c. Cross Section of Cu(CF$_3$SO$_3$)$_2$ Deposit

Figure 8. Complete Fill of 0.14 μm Trenches using Cupric Triflate Solution