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Accelerator Aging Effects During Copper Electrodeposition

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Slow sweep rate voltammetric analysis of the Cu/Cu(II) deposition reaction is shown to be an effective tool for examining aging effects associated with thiol and disulfide additives that are widely employed as brighteners. Sulfonate-terminated short chain thiols are spontaneously oxidized by Cu(II) to form disulfide molecules with the conversion being complete within a few hours of electrolyte preparation. An additional aging effect occurs during electrolysis in conventional unseparated electrochemical cells. At the anode, the disulfide is reduced by Cu(I) forming thiolate complexes which subsequently affect the copper deposition reaction occurring at the cathode. The latter effect may be avoided by using a cation selective membrane to isolate the anode compartment.
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The application of electrodeposition in state of the art manufacturing of microelectronic devices together with advances in analytical methods has revitalized scientific investigations into the role of organic additives in electroplating. Of particular interest is the combined use of rate accelerating and inhibiting species for copper ''superfilling,'' or ''bottom-up'' filling, of submicrometer features in dual damascene processing.[1] Sulfonate-terminated alkanethiols or disulfides are representative of a class of accelerators which are usually present at micromolar concentrations in bright plating baths.[2,3] These species adsorb on the copper surface as either thiolates or disulfides and, when combined with a sulfonate end group, disrupt the inhibiting function of the polyether-halide-Cu(I) layer.[3,4] The superconformal growth mode that arises from this competition is well described by the curvature enhanced accelerator coverage mechanism (CEAC) whereby surface area decrease of an advancing surface of concave curvature results in enrichment of the more strongly bound surface species.[5-10] In the thiol/disulfide-polyether-halide system, it is the accelerating thiol or disulfide species that are more strongly chemisorbed; they thus become concentrated during deposition on concave surfaces of trenches and vias leading to bottom-up filling. The overriding importance of this geometrical effect in superfilling was recently demonstrated by first derivitizing a patterned electrode with submonolayer quantities of thiolate or disulfide followed by electrodeposition of copper from an electrolyte containing only the polyether-halide inhibitor precursors as additives.[11] Feature filling proceeded in a manner analogous to that observed when the thiol or disulfide were present in the copper plating solution. This indicates that homogeneous thiol/disulfide chemistry has little to do with the superconformal feature filling process per se. Nevertheless, evidence of accelerator aging effects associated with homogeneous chemistry, beyond simple consumption, have been widely noted with an emphasis on the interactions occurring between copper, Cu(I), Cu(II), thiol/disulfide, oxygen, and related products.[12-15] From a practical perspective these reactions appear to significantly hamper process control.[12-15]

A previous study of the instability of thiols and disulfides in copper plating indicates that Cu(II) slowly oxidizes thiols while Cu(I) stimulates the decomposition of disulfides.[12] The report was based on examination of the oxidation behavior of these compounds at glassy carbon electrodes in combination with colorimetric studies which were generally performed in electrolytes containing high accelerator concentrations (up to 1 mmol/L).[12] The high concentrations were used to provide a strong analytical signal although plating operations usually employ accelerator concentrations in the 5 μmol/L range. It was anticipated that the effect of concentration might be simply reflected in the kinetics of the stated decomposition reactions.

From a technological perspective, aging effects are usually dealt with by using a ''bleed and feed'' scheme whereby new additives are continually added to the electrolyte while used electrolyte is drained to maintain the cell volume. In this paper, the sensitivity of the kinetics of the copper deposition reaction to accelerator chemistry will be exploited in order to examine accelerator aging under conditions directly relevant to the superfilling process. It is shown that these effects can be understood in terms of conversion between disulfides and thiols and vice-versa. Furthermore, it is demonstrated that significant improvements in process stability can be obtained by using a cation selective membrane to separate the anode and cathode compartments.

Experimental

Slow sweep cyclic voltammetry was used to examine the aging effects associated with thiol and disulfide-based accelerators. For all the experiments described herein, the base electrolyte was 0.24 mol/L $CuSO_4$, 1.8 mol/L H_2SO_4, 1 mmol/L NaCl, and 88 μM poly(ethylene glycol) (PEG, 3,400 Mw). The catalytic additives, $NaSO_3(CH_2)_3SH$, (MPS) and $Na_2[SO_3(CH_2)_3S]_2$ (SPS), were added to the cell either by direct salt addition or by pipette injection from a concentrated solution of either SPS or MPS dissolved in the matrix. In the latter case, the stock solutions were 500 umol/L SPS, 0.24 mol/L $CuSO_4$, 1.8 mol/L H_2SO_4, 1 mmol/L NaCl, and 88 μmol/L PEG (3,400 Mw), or 1 mmol/L MPS, 0.24 mol/L $CuSO_4$, 1.8 mol/L H_2SO_4, 1 mmol/L NaCl, and 88 μmol/L PEG (3,400 Mw). For all the experiments, the organic additives were added only after the acidified cupric sulfate solution had cooled to room temperature. The MPS was obtained from Aldrich, Inc.[a] and the SPS from Raschig GmbH.[a]

Two different electrochemical cells were used for the aging studies. Early studies utilized a conventional cell based on a round-bottom flask with four ports which fixed the relative positions of the copper working electrode, saturated calomel reference electrode (SCE), and copper counter electrode. The cell typically contained 350 to 400 mL of electrolyte. The working electrode was a freshly abraded, oxygen-free high conductivity (OFHC) copper plate which was masked with 3M plater's tape[a] to expose a circular area of $\sim$2.62 cm^2. The counter electrode was prepared in a similar fashion leaving an exposed area of $\sim$13.3 cm^2. In order to examine the effect of anode reactions on the aging process, a separated cell was constructed. The working electrode compartment was a cylindrical vessel containing $\sim$900 mL of electrolyte. A Nafion 417[a] membrane sealed counter electrode compartment containing 40 mL of accelerator-free electrolyte was placed on one side of the main cylindrical vessel. The reference and working electrodes (2.62 cm^2) were fixed in position on the opposite side of the vessel. A watch glass combined with a paraffin sheet was used to cover the cell in

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[a] Certain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

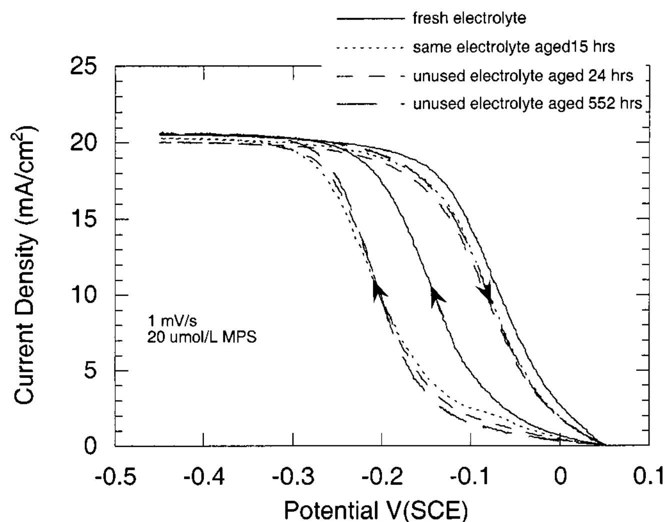


Figure 1. Hysteretic i-V curves revealing the aging effect associated with MPS additions to an acidified cupric sulfate plating solution. (Experiments performed in a conventional cell).

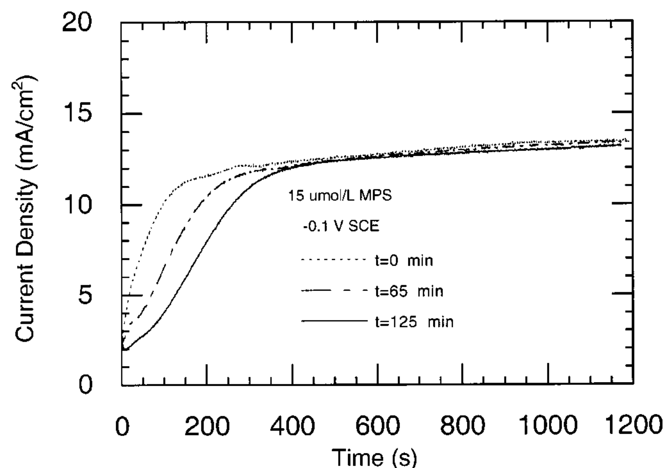


Figure 2. Chronoamperometric transients revealing the effect of MPS aging. The transients were initiated sequentially following the addition of MPS salt and an elapsed aging period denoted by t.

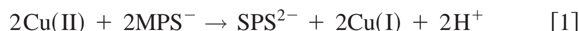
order to minimize particulate deposition from the laboratory ambient.

Results and Discussion

The hysteretic current density-voltage (i-V) behavior for copper deposition in electrolytes containing MPS-PEG-Cl and/or SPS-PEG-Cl has been described previously.[3-6] The hysteresis arises from displacement of an inhibiting PEG-Cl-Cu(I) layer by the adsorption of sulfonate-terminated short chain thiol or disulfide molecules. A detailed description of the dependence of the metal deposition kinetics on the accelerator coverage will be published elsewhere.[16] The present report focuses on the sensitivity and insight provided by simple voltammetric analysis of accelerator stability and aging.

Instability of MPS.—The i-V curve recorded immediately following the addition of MPS salt is observed to be distinctly different from that measured after various aging treatments, a typical example is shown in Fig 1. Evidently, a significant decrease in reactivity accompanies electrolyte aging. The counter and reference electrode were removed from the cell during all aging series. After a few hours the electrode response is independent of time. This condition was sustained for more than three weeks of aging at which point the experiment was terminated. The aging effect was also monitored by chronoamperometric experiments. In this system rising current density-time (i-t) transients are observed that correspond to a vertical trajectory across the breadth of the cyclic i-V curve at a given potential. A series of transients are shown in Fig. 2 as a function of the electrolyte age, defined relative to the moment of MPS addition (as salt). The characteristic rise time is seen to increase with electrolyte aging time. Eventually the system stabilizes, and characteristics are obtained that are, roughly speaking, independent of acquisition time. The above combination of experiments indicates that the instability of MPS has a time constant of several hours and that this particular aging process has little to do with electrolysis.

In sharp contrast to the MPS aging dynamics, similar studies with freshly prepared SPS solutions revealed no such time dependent behavior. A close comparison between the i-V curves for an aged MPS solution with that for SPS plating solutions yields some insight into what is happening during the MPS aging process. As shown in Fig. 3, the system response is indistinguishable if the SPS results are compared with aged (>24 h) MPS solutions that were prepared with twice the accelerator concentration, *i.e.*, [SPS] = 1/2[MPS]. This convergence provide strong evidence for oxidative dimerization of MPS to SPS



$$2Cu(II) + 2MPS^{-} \rightarrow SPS^{2-} + 2Cu(I) + 2H^{+} \quad [1]$$

This is most likely followed by the rapid consumption of Cu(I) by dissolved oxygen

$$4Cu(I) + O_2 + 4H^{+} \rightarrow 4Cu(II) + 2H_2O \quad [2]$$

The reaction sequence more than likely also involves the formation and consumption of Cu(I)MPS-intermediate.[12,15]

Oxidative thiol-disulfide reactions are, in fact, well known in the world of protein chemistry and similar observations relevant to copper plating chemistry in the presence of thiourea have been noted.[17] In contrast to prior analytical work[12,13,15] that was based on the direct measurement of the solution borne precursor, we use the pronounced impact of the accelerators on the copper deposition reaction as a probe of the accelerator chemistry. This is essentially the same strategy that underlies the cyclic voltammetric stripping analysis (CVS) which has been widely used for process monitoring.[13,14]

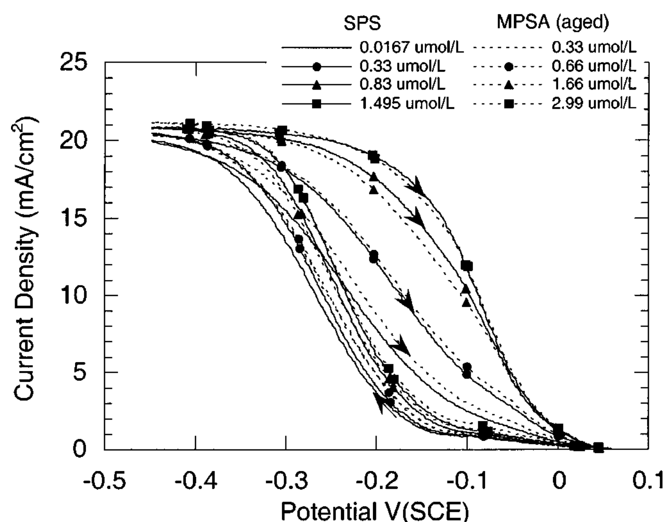


Figure 3. A series of hysteretic i-V curves demonstrating that aging of an electrolyte containing MPS may be attributed to dimerization of the MPS to SPS. The four pairs of curves obtained using electrolytes with SPS and aged MPS, [SPS] = 1/2[MPS], are practically indistinguishable. The experiments were performed in a separated cell.

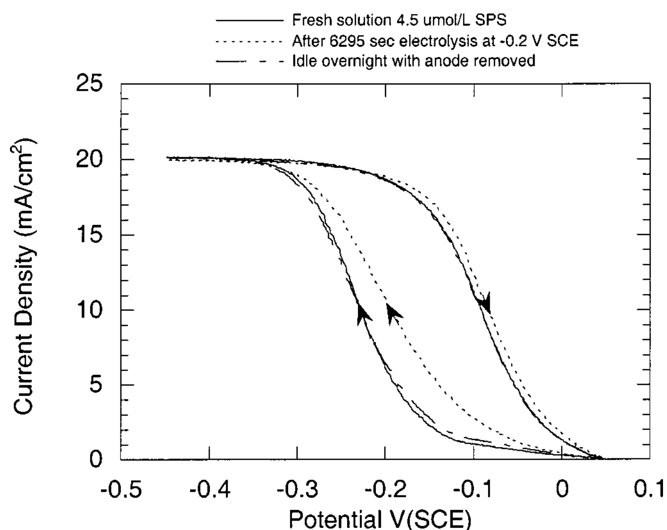


Figure 4. A series of hysteretic i-V curves showing the effect of electrolysis on a solution containing 4.5 μM SPS. The enhanced reactivity following 6295 sec of electrolysis is ascribed to MPS formation via cuprous reduction of SPS at the anode. Aging of the electrolyte overnight results in dimerization of the MPS back to SPS.

Anode reaction.—In conventional practice a copper anode is used to maintain the copper electrolyte concentration during plating. A longstanding difficulty with the use of OFHC Cu is the formation of copper powder due to disproportionation of freshly dissolved Cu(I). This results in the formation of loosely adherent particulate copper on the surface of the anode. These particles can subsequently become detached and transferred to other surfaces within the plating cell, including the cathode.

In the course of this study an additional problem became evident during extended plating with thiol or disulfide additives in a conventional unseparated cell. The hysteretic i-V curve for a freshly prepared SPS-PEG-Cl solution is shown in Fig. 4. Following ~2 h of potentiostatic plating, the i-V response of a freshly prepared electrode was observed to be shifted toward more positive potentials, indicating the formation of a new species that was more catalytic toward copper deposition than SPS. The shape of the i-V curve bears close resemblance to the behavior observed for a briefly aged MPS solution. A recent CVS and high performance liquid chromatography study of electrolyte aging also indicates that an SPS reaction product leads to increased acceleration of the copper deposition reaction.[13] Furthermore, when the electrolyte was aged overnight with the counter and reference electrodes removed, the i-V response was found to revert to that of a freshly prepared SPS-PEG-Cl electrolyte as shown in Fig. 4. Taken as a whole, these results indicate that MPS is formed during electrolysis and that it is subsequently oxidatively dimerized to SPS during the overnight aging process.

In order to further investigate the source of the electrolysis aging effect, a series of similar experiments were performed in a cell using a cation selective membrane to isolate the anode and its products from the cathode compartment. As shown in Fig. 5, the separated cell enabled stable voltammetry to be obtained after ~3 h of electrolysis at −0.2 V. This demonstrates that the aging effects associated with the SPS-PEG-Cl additive combination may be ascribed to a reaction occurring at the anode. Namely, the reactive cuprous ions generated at the anode are surmised to reduce disulfide to form cuprous thiolate complexes in agreement with the proposal of Healy *et al.*[12]

$$4Cu(I) + SPS^{2-} \rightarrow 2Cu(I)(MPS^{2-}) + 2Cu(II) \quad [3]$$

The complex may be subsequently oxidized to form free MPS according to

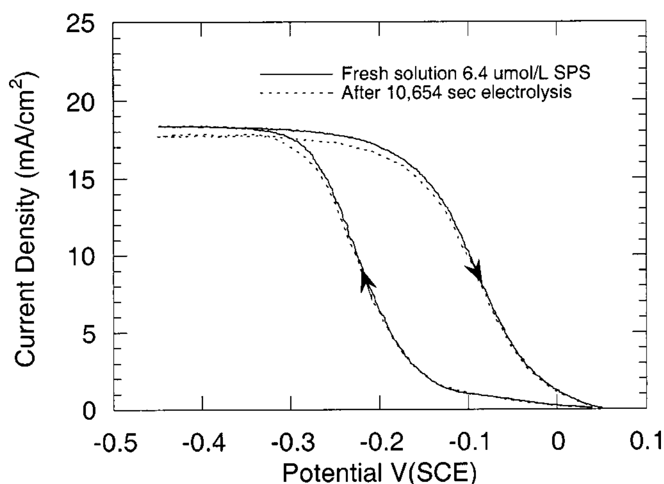
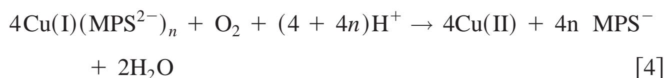


Figure 5. Stable kinetic measurements for SPS-PEG-Cl solutions are obtained by using an electrochemical cell where the anode and cathode compartments are separated by a Nafion membrane.



$$4Cu(I)(MPS^{2-})_n + O_2 + (4 + 4n)H^+ \rightarrow 4Cu(II) + 4n\ MPS^- + 2H_2O \quad [4]$$

The so-formed MPS is then subject to conversion back to SPS (*i.e.*, Eq. 1) as indicated in Fig. 4.

The proposed reactions scheme is consistent with the diminished aging effects observed when filmed copper anodes containing ~1 atom % of phosphorus are used in place of OFHC copper. The phosphorus addition leads to a surface film that minimizes the release of Cu(I) into the electrolyte as revealed by rotating ring disc experiments.[18] A Nafion[a] membrane allows the anode driven accelerator aging effect to be surmounted at the expense of having to separately provide for replenishment of the copper content in the bath, a straightforward task.

Conclusions

Spontaneous oxidative dimerization of MPS to SPS occurs in the cupric sulfate electrolyte via Cu(II) reduction. An aged MPS electrolyte is thus equivalent to an SPS solution of one-half the original MPS concentration. Furthermore, SPS is converted to MPS by Cu(I) generated at the anode during electrolysis. A stable processing environment may thus be established by using SPS as the accelerator in a membrane-separated cell.

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