Technical Article

Corrosion of Copper in Acid-Sulfate Plating Baths with Additives

by D. Hua & D. Barkey*

Acid copper plating baths exposed to air present a corrosive environment for copper. With feature sizes in some plating applications falling well below the micrometer scale, dissolution of metal at open circuit potential may become a consideration in process design. This paper presents a reaction-zone model of the corrosion process that can be used to estimate corrosion rates based on process parameters and opencircuit potential measurements. Corrosion of copper in acid-sulfate plating baths with additives chloride, benzotriazole and bis (3-sulfopropyl) disulfide is examined experimentally with the aid of the model.



Nuts & Bolts: What This Paper Means to You

Corrosion of copper has never been thought to be a serious concern, until now. Acid copper baths exposed to air do present a corrosive environment for copper. Feature sizes in electronic circuits are getting smaller and smaller, down to the nanometer scale. At this level, copper corrosion is real and must be considered in process design. This paper considers the theory and develops a model so the design process can avoid this. The model was compared to real-world conditions in acid-sulfate plating baths.



Fig. 2—Cathodic Tafel Plot for additive-free solution with a least squares fit to the two-electron Butler-Volmer Equation.

Most copper electroplating baths are exposed to air, and they are commonly sparged with air to provide agitation. In aerated solution, copper is thermodynamically unstable to corrosion and may dissolve between plating steps. In damascene processing, features as small as a few hundred nanometers are now electrodeposited. As the size of electrodeposited components decreases, loss of material to corrosion in the plating bath may become a significant limitation on process performance.

In acid solution, copper corrodes by the overall reaction,

$$Cu^{0} + \frac{1}{2}O_{2} + 2H + \Rightarrow Cu^{+2} + H_{2}O$$
 [1]

This reaction may take place through two coupled, heterogeneous processes.

$$Cu^0 \Leftrightarrow Cu^{+2} + 2e^{-}$$
[2]

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \Rightarrow H_2O$$
 [3]

Under this mechanism, the metal assumes a mixed potential between the equilibrium potentials of the two half-cell

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Table
Effects of Additives on the Kinetic
& Equilibrium Parameters

Solution	ϕ^e, \mathbf{mV}	$i_0, A/dm^2$	k _c , cm/s	k _a , cm/s
Additive-Free	105	0.37	6.02 E - 02	4.98 E-05
Chloride	104	0.38	6.06 E-02	5.42 E - 05
BTA	117	0.41	8.42 E-02	$2.74 \mathrm{E}{-}05$
SPS	117	0.59	1.21 E-01	3.94 E-05

reactions. The corrosion potential is thus positive of the equilibrium potential of the plating reaction (Reaction 2).

In acid solution containing copper ions, Reaction 1 may also proceed by a mechanism that involves two heterogeneous processes and one homogeneous reaction.^{1,2,3}

$$Cu^0 \Rightarrow Cu^{+1} + e^{-}$$
[4]

$$Cu^{+2} + e^{-} \Rightarrow Cu^{+1}$$
^[5]

$$2Cu^{+1} + \frac{1}{2}O_2 + 2H^+ \Longrightarrow 2Cu^{+2} + H_2O$$
[6]

The homogeneous reaction of cuprous ion with oxygen, Reaction 6, occurs within a reaction zone inside the boundary layer. Between the bulk solution and the reaction zone, there is no cuprous ion, and between the metal surface and the reaction zone, there is no dissolved oxygen. In this scheme, the reaction zone is approximated as a plane if the homogeneous reaction is fast.⁴ Models of this type have been used to describe the etching of copper⁵ and differential corrosion rates on different surface orientations of copper single crystals.⁶

A model of copper corrosion in plating solutions based on Reactions 4-6 is constructed as follows. Because Reaction 4 is fast, the interfacial concentration $[Cu^{+1}]^i$ of Cu^{+1} can be assumed to remain in interfacial equilibrium and to obey the Nernst equation.

$$[Cu^{+1}]^{i} = [Cu^{+1}]^{\theta} \exp \frac{F(V - V_{4}^{\theta})}{RT}$$
[7]

F is Faraday's constant, *V* the potential of the metal, V_4^{θ} the standard potential of Reaction 4 (295 mV vs Ag/AgCl), $[Cu^{+1}]^{\theta}$ a reference concentration (1 mol/L), *R* the gas constant and *T* the absolute temperature.

The rate of Reaction 4 is controlled by diffusion of cuprous ions from the metal surface. The diffusion flux N depends on the diffusivity D, the interfacial concentration $[Cu^{+1}]^i$ and a characteristic penetration length ε determined by the position and extent of the reaction zone (see Fig. 1).

$$N = D \ \frac{[Cu^{+1}]^i}{\varepsilon}$$
[8]

Reaction 5 is kinetically limited, and its rate, expressed as a partial current density i_{s} , is given by the Butler-Volmer equation,

$$i_{5} = k_{a} \left[Cu^{+1} \right]^{i} F \exp \left(\frac{(1-\beta) FV}{RT} - K_{c} \left[Cu^{+2} \right] F \frac{(-\beta) FV}{RT} \right]$$
[9]

where k_a and k_c are intrinsic rate constants and β is the symmetry factor (0.5). The concentration $[Cu^{+2}]$ of cupric ion at open circuit is assumed to equal the bulk value. The standard potential of Reaction 5 is -75 mV versus Ag/AgCl.

At the open-circuit, or corrosion, potential, the partial currents i_4 and i_5 sum to zero, and the flux of Cu^{+1} from the interface is equal to the rate at which it is produced by the two reactions.



Fig. 3—Open-circuit potential of copper RDE versus square root of rotation speed in additive-free solution under nitrogen (\bullet) , under oxygen (\bullet) .



Fig. 4—Open-circuit potential of copper RDE versus square root of rotation speed in chloride solution under nitrogen (\bullet) , under oxygen (\blacklozenge) .

$$i_4 = i_5 = (i_4 - i_5)/2 = FD \ \frac{[Cu^{+1}]^i}{2\epsilon}$$
 [10]

The partial current i_4 is the corrosion current, and it gives the rate v of metal dissolution,

$$v = \upsilon \, \frac{i_4}{F} \tag{11}$$

where υ is the molar volume of copper.

In application, the open-circuit potential V is measured and used to calculate $[Cu^{+1}]^i$ with Equation 7. Equations 9 and 10 are then used to calculate the corrosion current and penetration length.

The kinetic parameters k_a and k_c are obtained by measurement of the equilibrium potential V_2^{θ} and the exchange current i_o of Reaction 2 in the high-current Tafel regime [Newman].⁷

$$V_2^e = \frac{RT}{2F} \left(\ln \left[\frac{k_c}{k_a k_4} \left[C u^{+2} \right] \right] \right)$$
[12]



Fig. 6—Open-circuit potential of copper RDE versus square root of rotation speed in BTA solution under nitrogen (\bullet) , under oxygen (\bullet) .

$$i_{o} = 2Fk_{c} \left[\frac{k_{a}}{k_{c}} k_{4} \right]^{\beta/2} [Cu^{+2}]^{(2-\beta)/2}$$
[13]

where

$$k_4 = [Cu^{+1}]^{\theta} \exp\left[-\frac{V_4^{\theta}}{RT}\right]$$
[14]

In this study, the model was applied to corrosion of copper in acid sulfate solution with the additives chloride, benzotriazole (BTA), 3-mercapto-1-propanesulfonic acid (MPSA) and bis (3-sulfopropyl) disulfide (SPS). BTA is used as a corrosion inhibitor for copper and as an additive for copper plating baths.⁸ MPSA⁹ and SPS¹⁰ are used as accelerants in multi-additive formulations for damascene processing. MPSA is formed from SPS by rupture

of the disulfide bond, and the two probably coexist in plating baths formulated with either of the components.

Experimental procedure

All measurements were performed in a glass reaction vessel equipped with a rotating disk electrode (RDE), a carbon counter electrode, a gas sparger and a Ag/AgCl reference electrode separated from the plating solution by a bridge tube filled with 1.0 M H_2SO_4 . An automated grinding and polishing system was used to prepare the copper disk electrodes.

Five solutions were used: an additive-free plating solution made up of 0.2 M CuSO₄ and 1.0 M H₂SO₄ and four solutions with additives. The latter were prepared by addition of 1.0 mM chloride as hydrochloric acid, 0.1 mM BTA, 10 μ M MPSA or 5.0 μ M SPS to the additive-free solution.

In the corrosion experiments, a maximum dissolved-oxygen concentration was established by sparging with oxygen (99.99%). An intermediate dissolved-oxygen concentration was established by sparging with air. To exclude oxygen from the solution and obtain the equilibrium potential, nitrogen (99.99%) was sparged through the solution with the copper electrode in place. The opencircuit potential of the copper disk electrode under nitrogen purge was monitored at various rotation speeds until an equilibrium value was attained. This step took a minimum of one hour. After the equilibrium potential was established, air or oxygen was sparged through the solution to initiate corrosion. The rotation rate was then varied among values of 200, 400, 800, 1600 and 3200 RPM until a steady-state potential was achieved at each speed. A period of roughly 30 min was required to achieve steady state. Once the steady state condition was attained, a reproducible value of potential could be obtained at a given rotation speed within a few seconds of changing the speed.

The exchange-current density i_o was obtained from cathodic Tafel plots of potential versus log of current density obtained under kinetic control. To ensure kinetic control, a constant current was applied for 50 ms. This current pulse was long enough that double layer charging could be neglected, while short enough to prevent depletion of active ion at the interface. Current pulses of 0.1 mA to 4 μ A were applied eight times each. The optimum values of i_o and V_4^e were found by a least squares fit to a two-electron Butler-Volmer Equation (Fig. 2).

$$i = i_{o} \left[\exp \frac{1.5F(V - V_{2}^{e})}{RT} - \frac{0.5F(V - V_{2}^{e})}{RT} \right]$$
[15]

Results & Discussion

Open-circuit potentials of the RDE in solutions sparged with oxygen are plotted against the square root of electrode rotation speed in Figs. 3-6. The equilibrium potentials were constant and reproducible within a range of about 1 mV. The variation of corrosion potential with rotation speed was in agreement with the reaction-zone model. The corrosion potential was negative of the equilibrium potential, and became increasingly negative as the rotation speed was increased. At the highest rotation speed, the corrosion potential in additive free and chloride solutions was about 10 mV negative of equilibrium, whereas in solutions containing the organic additives, the difference was about 7 mV. The negative corrosion potential rules out a mechanism based on heterogeneous reduction of oxygen. The variation of corrosion potential with rotation speed is an indication that the process was in part limited by transport.

Open circuit potentials of the RDE in the four solutions sparged with air are shown in Fig. 7. The difference between the corrosion potential and the equilibrium potential was smaller with an air purge than with an oxygen purge, confirming that transport of oxygen was rate limiting. For stationary electrodes, the corrosion potentials with air sparging were, within experimental error, equal to the equilibrium potential. Under this condition, the transportlimited rate of corrosion was negligible in comparison with the rate obtained with agitation.

In additive-free and chloride solutions, the corrosion potential became increasingly negative as the rotation speed was increased. In solutions containing organic additives, at high rotation speeds, the potential also became increasingly negative as the speed was increased. At low rotation speed, however, the potential remained close to equilibrium in the presence of additives, and, in the case of BTA, was a few mV positive of equilibrium.

If cuprous ion played a role in the formation of adsorbed layers or films of organic additives on the metal surface, this result can be understood in terms of the reaction-zone model. Strong convection or a high concentration of dissolved oxygen removed cuprous ion from the vicinity of the metal, preventing film formation. Under weak convection or low concentration of oxygen, a protective film was formed, and corrosion was inhibited. Thus, dissolved oxygen may play a role in the function of additives in plating operations. In the absence of oxygen, cuprous ion would be present throughout the solution, and film formation would occur on all available surfaces. The reaction-zone mechanism assures that interactions between cuprous ion and additives occur only near the metal. BTA is known to form a complex with cuprous ion, and this step may be required for film formation.¹¹

The penetration length was calculated from the experimental corrosion potentials and the measured kinetic and equilibrium parameters shown in Table 1. The boundary layer thickness for the RDE was calculated with the Levich equation,¹²

$$\delta = 1.61 D_0^{1/3} \mathbf{v}^{1/6} \,\omega^{-1/2} \tag{16}$$

where ω is the rotation speed in rad/s, v the kinematic viscosity of the solution (0.011 cm²/s¹³) and D_o the diffusivity of oxygen (1.5 × 10⁻⁵ cm²/s). Figure 8 shows the ratio of boundary-layer thickness to penetration length versus the square root of rotation speed.

In the additive-free and chloride solutions, the penetration length is about one half to one fifth of the boundary layer thickness. With the organic additives, the fraction is much smaller. Evidently, the additives reduced the flux of cuprous ion from the surface. The corresponding corrosion rates are shown in Fig. 9. Shown for comparison (the solid line) is the theoretical corrosion velocity v as determined by Reactions 2 and 3 under diffusion control with a bulk oxygen concentration C_b of 0.24 mM.¹⁴ Under strong agitation, the corrosion velocity exceeds 0.5 nm/s, at which rate a structure 200 nm in size would be removed within a few minutes.

$$v = \upsilon \, \frac{i_{corr}}{2F} = \upsilon D \frac{C_b}{\delta} \tag{17}$$

In the additive-free and chloride solutions, the observed corrosion rate is higher than the theoretical rate under the mechanism of Reactions 1 and 2. The reaction zone model predicts a higher corrosion rate because the oxygen diffuses a distance of roughly $(\delta - \epsilon)$ rather than δ . As the rotation speed is increased, the boundary layer contracts, and the reaction zone moves closer to the metal, increasing the corrosion rate. In the presence of additives, the corrosion rate is very low at low rotation speeds, and the metal corrodes only in the presence of strong convection.

Because oxygen is reduced in the reaction zone at a distance from the metal, the oxidizing agent that reacts at the surface is cupric ion. As long as the concentration of cuprous ion in the bulk solution is below the equilibrium value given by Equation 7, the



Fig. 7—*Open-circuit potential of copper RDE versus square root of rotation speed under air in additive-free* (●), *chloride* (+), *SPS* (▲) *and BTA* (■) *solution.*



Fig. 8—Ratio of boundary layer thickness to penetration length under air in additive-free (\bullet), chloride (\bullet), SPS (\blacktriangle) and BTA (\blacksquare) solution.

metal will corrode, even if all of the dissolved oxygen is removed. Once cuprous ion has been removed by contact with air, the deaerated solution remains corrosive until sufficient metal has dissolved by Reactions 4 and 5 to restore the equilibrium concentration of cuprous ion.

Copper metal in equilibrium with a plating solution maintains a constant potential independent of convection. The reaction-zone corrosion mechanism is sensitive to transport and hence convection, and variation of the open-circuit potential with the strength of agitation may be taken as an indication that the metal is corroding.

Conclusion

Dissolved oxygen induces corrosion of copper metal in plating solutions by consuming cuprous ion in a reaction zone near the



Fig. 9—Corrosion velocity calculated with the reaction-zone model versus square root of rotation speed under air in additive-free (\bullet) , chloride (\bullet) , SPS (\blacktriangle) and BTA (\blacksquare) solution. The solid line is the corrosion velocity calculated on the basis of diffusion-limited reduction of oxygen on the metal surface.

metal surface. The reaction-zone mechanism produces a corrosion potential negative of the equilibrium potential, and the corrosion potential becomes increasingly negative as convection becomes stronger. The corrosion potentials measured in this study can be correlated with a characteristic penetration length which approximates the distance that cuprous ion diffuses into the plating solution before being oxidized by dissolved oxygen. In the presence of the organic additves BTA or SPS, corrosion is inhibited provided that the concentration of dissolved oxygen is not too high or convective transport of oxygen to the surface is not too strong.

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