A Quartz Crystal Microgravimetric Study Of Copper Corrosion in Alkaline Carbonate Solutions

By D.A. Dudek & P.S. Fedkiw

Quartz crystal microgravimetry is used to measure the open-circuit corrosion rate of copper in the presence of alkaline carbonate-containing electrolytes at 50 °C. The results are consistent with anodic formation of a porous Cu_2O film on the copper surface. The film is nonpassivating and, after reaching a critical, pH-dependent thickness (~0.1 μm at pH 8 and ~0.4 μm at pH 12), dissolves anodically at the film/electrolyte interface at the same rate it forms at the copper/film interface. After initial formation of the film, the electrodes lose mass at a pH-independent rate of 6.4 μg/cm2·hr in solutions that are open to the atmosphere, which corresponds to a corrosion rate of 2.5 mil/yr. Bubbling the electrolyte with N_2 decreases the corrosion rate by 22 percent. The open-circuit potential increases dramatically (120-160 mV in pH 8; 210 mV in pH 12 electrolytes) at the same time that the maximum in electrode mass is observed. Thus, simultaneous *in situ* measurement of open-circuit potential and electrode mass results in clear verification that the corrosion process has two distinct steps.

Build-up of carbonates is experienced in a variety of plating baths; copper cyanide, zinc cyanide, and alkaline non-cyanide zinc plating baths are examples.[1,2] The corrosion of copper in the presence of carbonates has been studied by methods that include X-ray diffraction,[3] voltammetry,[4] and impedance,[5] but to our knowledge the quartz crystal microbalance (QCM) has not been used for this purpose. Over a fairly wide range of mass, the relationship between the resonant frequency f of a quartz crystal and the mass M rigidly attached to the crystal surface is linear[6]

$$\Delta f = -K\Delta M \qquad (1)$$

where K is a positive constant. Thus, the resonant frequency of oscillation is strongly dependent upon the mass of species absorbed or deposited on the crystal surface. The ability of the QCM to perform sensitive *in situ* monitoring of mass attached to an electrode immersed in a liquid electrolyte is unique among experimental techniques, and makes quartz crystal microgravimetry an ideal approach to study corrosion of metal surfaces.[7]

The goal of the quartz crystal microgravimetry experiments is to determine how carbonates in plating baths affect copper metal surfaces over the

Table 1
Acid Disassociation Constants
For Carbonic Acid & Bicarbonate at 25 & 50 °C

	25 °C	**50 °C**
$K_{a,H2CO3}$ (M)	4.4×10^{-7}	5.5×10^{-7}
$K_{a,HCO3-}$ (M)	4.7×10^{-11}	7.6×10^{-11}

Table 2
Thermodynamic Quantities
For Electrolyte Components at 25 °C[10]

Component	**ΔH_f° (kJ/mol)**	**ΔG_f° (kJ/mol)**	**ΔS_f° (J/mol K)**
Solid Cu	0	0	33.16
Cu^{2+}	64.64	65.52	-99.6
$CO_{2\,aq}$	413.8	-386.0	117.6
CO_3^{2-}	-677.14	-527.90	-56.9
HCO_3^-	-691.99	-586.85	91.2
H_2CO_3	-699.65	-623.16	187.4
H^+	0	0	0
OH^-	-229.99	-157.28	-10.75
H_2O	-285.83	-237.14	69.96

Table 3
Calculated Electrolyte Concentrations
For the Four Electrolyte Compositions, 50 °C

	Concentration (M)			
	pH 12		**pH 8**	
Species	**Deaerated**	**Open to atm**	**Deaerated**	**Open to atm**
$[Na_2CO_3]^o$	1.57	1.57	1.57	1.57
$[H_2SO_4]^o$	0	0	0.79	0.79
CO_3^{2-}	1.513	1.513	0.011	0.011
HCO_3^-	0.053	0.053	1.527	1.527
$H_2CO_{3\,aq}$	1.1×10^{-7}	1.1×10^{-7}	0.028	0.028
$CO_{2\,aq}$	$< 1.1 \times 10^{-7}$	1.1×10^{-7}	< 0.019	0.019
$O_{2\,aq}$	$<< 2.6 \times 10^{-4}$	2.6×10^{-4}	$<< 2.6 \times 10^{-4}$	2.6×10^{-4}
H^+	1.1×10^{-12}	1.1×10^{-12}	1.0×10^{-8}	1.0×10^{-8}
OH^-	0.053	0.053	5.8×10^{-6}	5.8×10^{-6}
Na^+	3.13	3.13	3.13	3.13
SO_4^{2-}	0	0	0.79	0.79

Table 4
Corrosion Rates & Cu_2O Film Thicknesses
For Copper Electrodes Immersed in 1.57 M Na_2CO_3, 50 °C

	pH 12		**pH 8**	
	Deaerated	**Open to atm**	**Deaerated**	**Open to atm**
corrosion rate (mil/yr)	2.0	2.4	1.8	2.6
film thickness (μm)	0.39	0.38	0.09	0.12

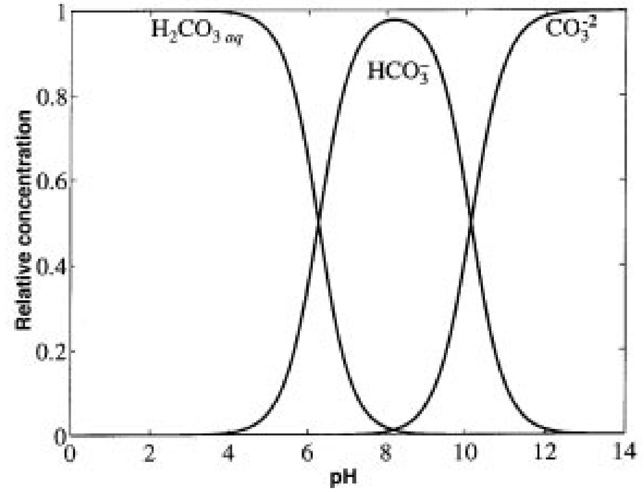

Fig. 1—Relative concentrations of carbonate species as a function of pH, 50 °C.

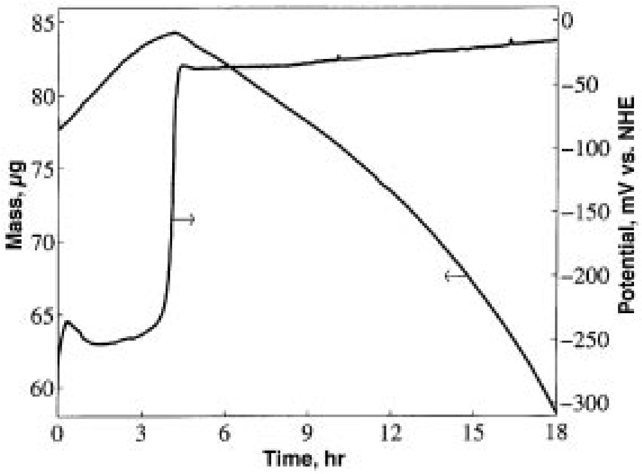

Fig. 2—Electrode mass and open-circuit potential of a fresh 25-mm² copper surface immersed in deaerated 1.57 M Na_2CO_3 pH 12 electrolyte, 50 °C.

course of several hours. The circumstances can be compared to leaving copper anodes in a dormant copper plating bath overnight. Most baths are operated significantly above room temperature and, in baths for which carbonate build-up is a problem, can have up to 3 M total carbonate.[1] Accordingly, all experiments were performed at 50 °C, and solutions with total carbonate of 1.57 M were examined. To investigate how exposure to alkaline carbonate solution affects copper surfaces, quartz crystal microgravimetry was used to measure the open-circuit corrosion rate of copper at several values of pH, in the presence and absence of oxygen.

Experimental Procedure

Materials

Solutions were prepared from reagent grade Na_2CO_3, $CuSO_4$, and H_2SO_4, using deionized water. Deoxygenated solutions were bubbled with humidified high-purity N_2 gas (99.998%) prior to and during experiments. A 14-mm diameter, platinum-coated, 10-MHz AT-cut quartz crystal with an exposed electrode area of 25 mm² was used for all experiments. A saturated calomel electrode was used as a reference electrode. The counter-electrode during copper deposition was a high-purity copper foil (99.999%), spot-welded to a platinum wire as a current collector. All experiments were performed in a 35-mL water-jacketed glass cell heated with water from a constant-temperature bath.

Instruments

A quartz crystal microbalance was used to measure the difference between the resonant frequencies of the working and reference crystals. The microbalance has a mass sensitivity of 0.5 ng/cm², or about 0.9 percent of a monolayer of copper. A personal computer with a data acquisition card running appropriate software was used to record mass and open-circuit potential during corrosion experiments, and to control the potentiostat and record mass, applied potential and current during electrode preparation. A potentiostat was used to deposit and strip copper on the Pt-covered portion of the crystal before and after experiments. Open-circuit potentials were measured with an electrometer.

Procedures

Copper was deposited on the Pt-coated portion of the quartz crystals by holding the working electrode at -0.1 V vs. SCE for 20 sec in 0.37 M $CuSO_4$ + 1.4 M H_2SO_4 solution.[8] This procedure results in a reproducible copper deposit of 78 µg (about 0.4 µm thick) that appears bright and uniform. The cell and crystal were thoroughly rinsed, the counter electrode was removed, and the carbonate-containing electrolyte of interest was added to the cell. The electrode mass and open-circuit potential were recorded for 18 hr, which appeared to be sufficient to capture all interesting phenomena. Deaerated and open-to-the-atmosphere solutions of various carbonate concentrations and pH were used. The pH of the carbonate-containing electrolyte was measured immediately before and after an experiment. All experiments were performed at 50 °C. After a corrosion experiment was completed, the deposit was stripped in 0.37 M $CuSO_4$ + 1.4 M H_2SO_4 solution by holding the electrode at +0.5 V vs. SCE for 2 min. The electrode returned to the original matte-gray appearance, and the microbalance indicated that the electrode had returned to within 0.2 µg of its original mass.

The microbalance used automatically converts measured changes in frequency to mass via the Sauerbrey Equation (Eq. 1), using a non-adjustable value for K (≈0.15 Hz/ng). An odd phenomenon was observed during copper deposition and stripping from the cupric sulfate plating solution (0.37 M $CuSO_4$ + 1.4 M H_2SO_4): The current efficiency for both processes was 77 percent, as calculated by comparing the mass indicated by the microbalance to the charge calculated by integrating the current. This observation is odd because it is unlikely that anodic and cathodic side reactions would consume the same fraction of the current, and the expected current efficiency[9] for an acidic cupric sulfate plating bath is 95–100 percent. Upon further inspection, this same current efficiency was observed for a variety of deposition and stripping potentials. To calibrate the mass measurements, all mass values output from the microbalance were divided by 0.77. Calibration procedures of this kind have been advocated by Ward.[6]

Results & Discussion

Carbonate acid-base chemistry

Because carbonates participate in acid-base chemistry,

$$H_nCO_3^{-(2-n)} \longrightarrow H^+ + H_{n-1}CO_3^{-(3-n)} \qquad (2)$$

where n = 1 or 2, knowledge of the electrolyte pH is neces-

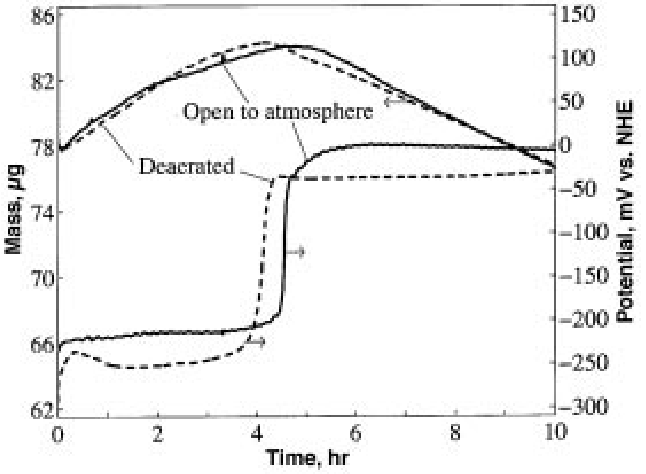

Fig. 3—Electrode mass and open-circuit potential of fresh 25-mm² copper surfaces immersed in open-to-the-atmosphere and deaerated 1.57 M Na_2CO_3 pH 12 electrolytes, 50 °C.

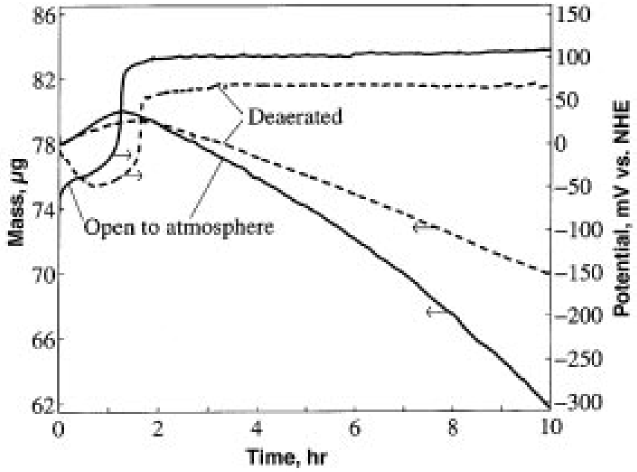

Fig. 4—Electrode mass and open-circuit potential of fresh 25-mm² copper surfaces immersed in open-to-the-atmosphere and deaerated 1.57 M Na_2CO_3 pH 8 electrolytes, 50 °C.

sary to determine the species present in solution. Figure 1 shows the calculated relative equilibrium concentrations for carbonates as a function of pH at 50 °C. These concentrations were calculated from the equilibrium constants

$$K_{a,HnCO_3} = \frac{[H^+][H_{n-1}CO_3^{-(3-n)}]}{[H_nCO_3^{-(2-n)}]} \qquad (3)$$

listed in Table 1, which are based on the thermodynamic quantities in Table 2. In this study, carbonate solutions with a pH of 8 and 12 are examined. As seen in Fig. 1, the most prevalent carbonate-containing species shifts from H_2CO_3 to HCO_3^- to CO_3^{-2} as pH increases. At pH below 4, the most prevalent carbonate species is H_2CO_3. This species is only slightly soluble, and readily decomposes into carbon dioxide and water

$$H_2CO_{3\ aq} \longrightarrow CO_2\uparrow + H_2O \qquad (4)$$

The concentrations of carbonic acid and dissolved carbon dioxide at the solubility limit (0.436 STP mL CO_2 per mL H_2O)[10] are both about 0.019 M. As a result of the low solubility, carbonate accumulation is not a problem in acidic plating baths.

The calculated compositions of the four solutions examined in this study are reported in Table 3. The pH of 1.57 M Na_2CO_3 is about 12; lower pH solutions were obtained by addition of H_2SO_4. In the pH 8 electrolyte, the calculated “equilibrium” concentration of carbon dioxide is 0.028 M, which is greater than the solubility limit (0.019 M). As a result, the pH 8 solutions are in a non-equilibrium state as prepared and, in non-deaerated solutions, evolve CO_2 until equilibrium is attained. This decrease in total carbonate concentration results in an increase in pH during the course of the experiment. Because bubbling with humidified nitrogen strips carbon dioxide in addition to oxygen, solution compositions of deaerated solutions are likely to have less than equilibrium carbon dioxide, causing a further pH rise during an experiment. The calculated concentration of CO_2 is considerably larger in the pH 8 electrolyte than in the pH 12 electrolyte (0.028 vs. 1.1×10^{-7} M). As a result, stripping of CO_2 during experiments has a negligible effect on the solution composition in the more basic electrolyte, but causes an experimentally observed increase of over 1 pH unit in pH 8 electrolytes. While this may appear to be a large change, the distribution of carbonate-containing species remains over 90% HCO_3^- over this pH range (Fig. 1). Solutions that are open to the atmosphere are assumed to be saturated with oxygen, and the oxygen concentration in deaerated solutions is considerably smaller.

Porous-film Model

Copper corrosion in carbonate electrolytes is a well-studied system.[3-5,11] These investigations have led to a model of copper corrosion in alkaline electrolytes, including carbonate-containing solutions, that involves the anodic formation and growth of a porous Cu_2O film.

$$2\ Cu° + 2\ OH^- \longrightarrow Cu_2O_{(s)} + H_2O + 2\ e^- \qquad (5)$$

As the porous film grows, consumption of hydroxide at the interface of the copper substrate and the cuprous oxide film causes the local pH to decrease. As this occurs, Reaction (5) becomes more difficult. After the film reaches a critical thickness, it begins to dissolve anodically

$$Cu_2O_{(s)} + H_2O \longrightarrow 2\ Cu^{+2} + 2\ OH^- + 2\ e^- \qquad (6)$$

such that a critical film thickness is maintained. The thickness of the film is such that the rates at which hydroxide formed by Reaction (6), transported through the porous film, and consumed by Reaction (5) are all equivalent. The rate of growth and critical film thickness are influenced by a variety of factors, including electrolyte oxygen content, solution pH, electrolyte convection, copper crystallographic orientation and exposure to light. Summing Reactions (5) and (6) yields the overall anodic process:

$$2\ Cu° \longrightarrow 2Cu^{+2} + 4e^- \qquad (7)$$

The reduction half-cell reaction that complements Reaction (7) is oxygen reduction,

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (8)$$

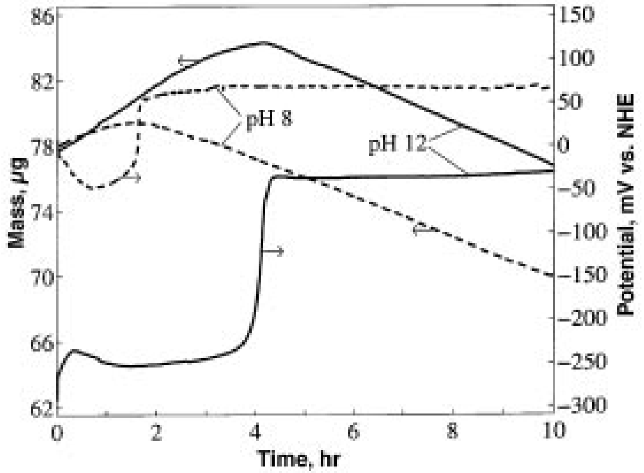

Fig. 5—Electrode mass and open-circuit potential of fresh 25-mm² copper surfaces immersed in deaerated 1.57 M Na_2CO_3 pH 8 and pH 12 electrolytes, 50 °C.

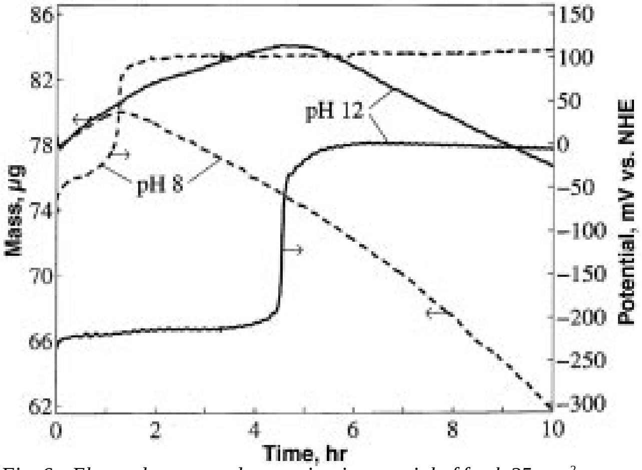

Fig. 6—Electrode mass and open-circuit potential of fresh 25-mm² copper surfaces immersed in open-to-the-atmosphere 1.57 M Na_2CO_3 pH 8 and pH 12 electrolytes, 50 °C.

even in solutions that contain only minute quantities of dissolved oxygen. The discussion of the following results is in the context of this model.

Copper corrosion in deaerated 1.5 M Na_2CO_3, pH 12

Figure 2 shows the mass and open-circuit potential of a 25-mm² fresh copper surface immersed in deaerated 1.57 M Na_2CO_3, pH 12, electrolyte. The mass of the electrode increases by 6.6 µg during the first four hr, and falls below the original electrode mass during the remainder of the 18-hr experiment. The open-circuit potential changes dramatically from approximately -250 to -40 mV vs. NHE at the same time that the maximum in electrode mass is observed. This is consistent with development of a Cu_2O film followed by simultaneous steady-state conversion of copper metal to Cu_2O at the metal/film interface and dissolution of Cu_2O to cupric at the film/solution interface. If the film is Cu_2O and has a density similar to pure Cu_2O (6.0 g/cm³),[10] it would be 0.39 µm thick. The slope of the linear portion of the mass curve (from 4 to 10 hr) is 1.3 µg/hr and corresponds to a corrosion rate of 2.0 mil/yr.

Effect of Deaeration

Figure 3 shows the mass and open-circuit potential of a 25-mm² fresh copper surface immersed in open-to-the-atmosphere and deaerated 1.57 M Na_2CO_3, pH 12 electrolytes. In both cases, the mass of the electrode increases for the first few hours, reaches a maximum of about 84 µg, and then decreases for the remainder of the experiment. The rate of mass increase during the first hour and the rate of mass decrease during the last five hours is 18 percent larger for the oxygen-containing electrolyte than for the deaerated electrolyte (6.16 compared to 5.20 µg/cm²·hr). The open-circuit potential for the deaerated electrolyte is about 30 mV lower than that of the oxygen-containing electrolyte, both before and after the maximum in electrode mass occurs. This observation suggests that similar electrode reactions are occurring in aerated and deaerated solutions, and is consistent with Reaction (8) as the reduction half-cell reaction: A decrease in open-circuit potential results when either the reduction half-cell reaction becomes more difficult, or the oxidation half-cell reaction becomes easier. If oxygen reduction (Reaction 8) is a half-cell reaction, then a decrease in open-circuit potential upon solution deaeration is expected. Thus, the overpotential for the oxidation reaction is larger when the solution is open to the atmosphere than it is when the solution is bubbled with N_2. This scenario is consistent with both the porous-film model and the observation that the initial mass increase and long-term mass decrease occur at a faster rate in the solution that is open to the atmosphere.

Figure 4 is a similar plot comparing the mass and open-circuit potential in open-to-the-atmosphere and deaerated 1.57 M Na_2CO_3, pH 8 electrolytes. The results from the experiments performed at pH 8 are consistent with the pH 12 results: In both cases, the open-circuit potential is about 30 mV lower in the deaerated solution both before and after the maximum in electrode mass occurs, and the rate of mass increase and decrease is 40 percent greater in the oxygen-rich than in the oxygen-poor electrolyte (6.60 compared to 4.72 µg/cm²·hr).

Effect of Varying pH

Figure 5 illustrates the mass and open-circuit potential of a 25-mm² fresh copper surface immersed in deaerated 1.57 M Na_2CO_3 at both pH 8 and 12. In both cases, the mass of the electrode initially increases, reaches a maximum, then decreases for the remainder of the experiment. The maximum in mass attached to the electrode surface appears sooner and with a smaller gain in pH 8 electrolyte than in pH 12 electrolyte. This suggests that the critical film thickness is thinner in lower pH solutions. If a Cu_2O film density of 6.0 g/cm³ is again assumed, the film thickness in the pH 8 electrolyte is only 0.09 µm, compared to 0.39 µm for the pH 12 case. This observation is consistent with the porous anodic film model. If the thickness of the oxide film is limited by a local pH decrease near the film/metal interface, thereby lowering the rate of Reaction (5), we would expect the limit to be reached sooner in pH 8 electrolyte than in pH 12 electrolyte. Moreover, because hydroxide is a product of the film-dissolution reaction (6), it is more thermodynamically favorable for this reaction to occur in pH 8 electrolyte than in pH 12 electrolyte.

The open-circuit potential is always higher in pH 8 electrolyte than in pH 12 electrolyte. This observation is consistent with Reaction (8) as the reduction reaction. The equilibrium potential of Reaction (8) is 254 mV larger at pH 8 than at pH 12. At both values of pH, the open-circuit potential increases dramatically when the maximum in electrode mass is observed, but the increase is only half as large with pH 8 as in pH 12 electrolyte.

Figure 6 is a similar plot comparing the mass and open-circuit potential in open-to-the-atmosphere 1.57 M Na_2CO_3 for both pH 8 and 12. The results from the open-to-the-atmosphere experiments are consistent with the nitrogen-bubbled experiment results: In both cases the maximum in mass attached to the crystal occurs sooner and at a lower mass, the open-circuit potential of the pH 8 electrolyte is considerably more positive, and the difference between the open-circuit potentials at the two values of pH is smaller after than before the maximum in mass occurs. If the film density is 6.0 g/cm^3, the film thickness in the pH 8 electrolyte is 0.12 µm, compared to 0.38 µm for the pH 12 case.

Summary

Corrosion rates and Cu_2O film thicknesses for 1.57 M Na_2CO_3 deaerated and open-to-the-atmosphere electrolytes at pH 8 and 12 are summarized in Table 4. After initial formation of the film, the electrode loses mass at a pH-independent rate of about 6.4 µg/cm^2·hr in solutions that are open to the atmosphere, which corresponds to a corrosion rate of 2.5 mil/yr. Bubbling the electrolyte with N_2 decreases the corrosion rate by about 22 percent; this decrease in corrosion rate with oxygen concentration is consistent with oxygen reduction as the reduction half-cell reaction. The pH-dependence of the film thickness (the film is about four times thicker in pH 12 electrolyte than in pH 8 electrolyte) is consistent with hydroxide as a reactant in the copper/film interface oxidation and a product in the film/electrolyte interface oxidation. The dramatic shift in open-circuit potential that occurs simultaneously with the maximum in electrode mass is clear verification that the formation and steady-state dissolution of Cu_2O films is a two-step process.

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Pulse Plating

Continued from p. 67

Migration of ions in solution occurs when there is an applied potential, as in plating. Though the influence is small, there is a positive contribution to increased ionic mobility and concomitant LCD for cations, like cuprate. The opposite is true for anions, like aurocyanate. Higher potentials and increased platable ion concentrations raise the flux to the cathode, increasing with proximity

You cannot plate faster by pulsing. However, you can plate at much higher CDs. Higher CDs at short intervals tend to cause more growth nuclei uniformly about the work as well as a smaller-grained deposit. Smaller grains give the deposit higher strength/hardness, fewer voids, and a more lustrous appearance (within limits). By combining pulsed electrodeposition with turbulent solution convection, acid copper plating (1.5 M Cu and 0.5 M H_2SO_4) at 1-3 kHz can yield columnar deposits at a rate of 1 µm per second (2+ mils/min).

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