Rotating Ring-disk Electrode Studies Of Copper Electrodeposition: Effect of Chloride Ions And Organic Additives

By Sunghee Yoon, Morton Schwartz, CEF, and Ken Nobe

A rotating ring-disk electrode (RRDE) was used to investigate the effects of chloride ions, organic additives and hydrodynamic conditions on copper electrodeposition and deposit appearance in deoxygenated acid copper sulfate solutions. The organic additives selected included thiourea (TU), benzotriazole (BTA) and a proprietary commercial brightener (PB). Four distinct regions, the apparent Tafel, transition, limiting current, and post-limitingcurrent regions, were observed between the rest potential and -1.2 V (vs. SCE). The characteristics of the ring current behavior observed during the cathodic potential sweep of a copper disk supports the two-step electron transfer mechanism for copper electrodeposition in acid CuSO₄ with Cu(I) as an intermediate.

mall amounts of additives in copper sulfate plating baths have significant effects on copper deposit characteristics, such as brightness, grain size, hardness, ductility and internal stress. Unsaturated organic compounds containing sulfur, nitrogen or oxygen are known to brighten copper deposits.¹ About 10 to 100 mg/L

(0.28-2.8 mM) Cl⁻ are usually required with commercial brighteners to obtain bright copper deposits.²⁴

Electrodeposition and electrodissolution kinetics of copper in copper sulfate solutions have been studied by Mattsson and Bockris, who proposed a two-step mechanism for electrodeposition and electrodissolution with Cu+ as an intermediate.⁵ Their model, which assumed that the Cu⁺²/Cu⁺ reaction step was rate determining, was in good agreement with experiment.

The role of chloride ions, in copper refining electrolytes in the absence of additives, was investigated by Yao.⁶ Grain size decreased and the hardness of copper deposits increased with addition of as much as 15 mg/L (0.42 mM) Cl⁻; however, grain size increased and hardness decreased with further addition.

Even though there have been numerous studies of brightening Cu deposits with small amounts of organic additives a n d $CI^{-,7-20}$ the synergistic effect of CI^{-} and organic additives is still not well understood. Deposit characteristics are influenced by such variables as the composition of the plating solution, temperature, impurities, cathode current density, hydrodynamics and the presence of additives.^{2,21} Solution stirring is provided by gas sparging, mechanical cathode bar movement and recirculation of solution. Even though sufficient agitation of the acid copper sulfate solutions is required for bright copper deposits, there have been few fundamental studies to ascertain the basic mechanism of its effect on production of bright copper deposits.

The present study was directed to investigation of the effect of Cl⁻, organic additives and hydrodynamics on Cu electrodeposition and deposit appearance in acid copper sulfate solutions with rotating ring-disk electrodes (RRDE). Hydrodynamic conditions in the RRDE system are well defined, so that mass transfer can be precisely controlled and intermediate and product species may be detected at the ring electrode.

Experimental Procedure

A detailed description of the RRDE has been given elsewhere.^{22,23} The Cu disk diameter was 0.597 cm and the inner and outer Au ring diameters were 0.704 and 1.229 cm, respectively. Schematic representations of the RRDE system and the electrode assembly are shown in Fig. 1.

An oxygen-free pure (99.99 percent) copper rod (0.635 cm diam) was machined on a lathe to a diameter of 0.597 cm. The edge of the end of the rod was slightly tapered and the end of the rod was cut into a small disk. The flat side of each disk was polished with waterproof alumina paper of grit #400 and #600. After polishing, the copper disks were rinsed in distilled water, then degreased with hot benzene in a Soxhlet column for 5 hr. The degreased electrodes were then annealed under vacuum (< 10^{-5} torr) at 560 °C for 4 hr and cooled under vacuum to room temperature.

The electrochemical cell was made of Pyrex[™] glass with a capacity of 1.5 L. Two reference electrodes and two auxiliary electrodes were used in this system. The auxiliary electrodes were made of platinum foil (2.54 x 2.54 cm). Each auxiliary electrode compartment had a porous sintered glass frit to separate the electrolyte in the main part of the cell. The reference electrodes were saturated calomel electrodes (SCE). All potentials reported are relative to the SCE. Each reference electrode was kept in a small Pyrex[™] reservoir and connected to the Luggin capillary through a stopcock and Teflon™ tubing. The stopcock was closed during all experiments to prevent diffusion of chloride ions from the SCE to the cell. A potentiostat^a with a logarithmic current converter^b was used to control the potential difference between the disk and reference electrodes. A function generator^c was connected to the potentiostat for the potentiodynamic experiments.

The potential difference between the ring and the ring

^c Model 175, Princeton Applied Research, Princeton, NJ

^e Model 602, Keithley Instruments, Cleveland, OH

Table 1					
Comparison of D ₂ ¹² with Literature Values					

$[H_2SO_4]$ (M)	[Cu ⁺²] (M)	D _{Cu+2} (10 ⁻⁶ cm ² /sec)	References
1	0.03-0.3	4.96 0.14	this study
2	0.03-0.3	4.11 0.07	this study
1	0.1	5.23 0.13	[28]
1.75	0.77	4.81	[29]
1.8	0.155	4.89	[30]
1.8	0.24	4	[19]

^a Model 173, Princeton Applied Research, Princeton, NJ

^b Model 376, Princeton Applied Research, Princeton, NJ

^d Model PRT 10-0.5 L, Tacussel, Villeurbanne, France

Table 2 Ring Currents at Open Circuit in Additive-free Acid CuSO ₄ ; 1 hr immersion, 1000 rpm										
[Cl ⁻] (mg/L)	0	1	5	10	30	50	100	300	500	1000
[Ι _R] (μΑ)	14	13	21	23	32	23	20	36	48	88

reference electrodes was controlled by a potentiostat^d, and the ring current was measured with an electrometer.^e A PC with an input/output card was connected to the function generator, the logarithmic current converter, and the electrometer. The potentiodynamic polarization experiments were performed with computer controls. The disk potentials and the disk and ring current outputs during potentiodynamic polarization were stored in the computer.



Fig. 1—Rotating ring-disk electrode system: (a) electrochemical cell; (b) ringdisk electrode.

All electrolytes were prepared with deionized-distilled water and analytical reagent grade chemicals. The acid CuSO₄ solution in this study consisted of 0.3 M CuSO₄ and 2 M H₂SO₄, unless otherwise noted, which is similar to plating solutions used for printed wiring board manufacturing, because of their high throwing power. The electrolyte was maintained at room temperature (23 ± 1 °C) and deoxygenated for at least 12 hr prior to an experiment with pre-purified nitrogen gas that was first saturated with water vapor by sparging through 2 M H₂SO₄. The nitrogen gas was passed over the electrolyte during an experimental run.

Before each run, each copper disk was repolished by using a waterproof alumina paper of grit #600 and a polisher/grinder with a polishing microcloth containing levigated alumina (0.2 μ m). The ring-disk holder was polished lightly with a wet polishing microcloth also. The surface of the ring-disk electrode was checked to ensure that the Cu disk lay horizontally on the same plane as the Au ring surface, then the ring-disk electrode was degreased with acetone, rinsed in distilled water, and blown dry with flowing air.

Ring potentials were set at 0.6 V to register the cuprous species that oxidize to cupric; then cathodic polarization was started from the rest potential three min after the electrode was immersed in the electrolyte. Background ring currents were measured before polarization.

The sweep rate was maintained at 2 mV/sec at the disk electrode for potentiodynamic polarization while the ring electrode was set at a constant potential. The surface appearance of the disk electrode was visually checked during the cathodic potential sweep by illuminating the disk electrode surface with a side lamp.

In the potentiostatic experiments, when the surface appearance of the copper deposits was being examined under various conditions, a potential step was applied immediately after the electrode was immersed in the electrolyte to minimize disk surface changes at open circuit. The surface appearance of the copper deposits was checked either visually or with an optical microscope after potentiostat setting of the disk electrode, until a total cathodic charge of about 20 C/ cm^2 was passed.

Results and Discussion

The experimental collection efficiency of the RRDE was determined by measuring the Cu disk and ring currents in the apparent anodic Tafel region, with the potential of the ring electrode set at 0.6 V (vs. SCE), in 1 M HCl. In this region, cuprous species is the only product of Cu electrodissolution. The experimental collection efficiency (0.552 \pm 0.007) agreed well with the theoretical value (0.559).

Cu Electrodeposition in Additive-Free Acid CuSO

Typical polarization behavior of Cu electrodeposition in additive-free acid $CuSO_4$ at various rotation rates is shown in Fig. 2a. In the potential range examined (rest potential to -1.2 V), four distinct regions were observed: (1) the Tafel region, (2) the transition region, (3) the limiting-current region and, (4)



Fig. 2—Effect of rotation rate on Cu electrodeposition in acid $CuSO_{4^{-}}$ (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential.

the post-limiting-current region. The disk current represents the net rate of electrochemical reactions at the disk; the ring current corresponds to the Cu(I) flux from the disk to the ring during deposition.

Figure 2a shows that the disk currents in additive-free acid $CuSO_4$ are independent of rotation rate in the Tafel region, dependent on disk potential and rotation rate in the transition region, independent of disk potential in the limiting-current region, and dependent on disk potential and rotation rate in the post-limiting-current region.

As the rotation rate increased, the limiting-current region narrowed and the onset of the post-limiting-current region occurred at more positive potentials. Rough surfaces were observed for rotating electrodes around the inflection point in the limiting-current region, while rough surfaces were not observed for stationary electrodes until the occurrence of vigorous hydrogen evolution in the post-limiting-current region. In order to determine whether or not the early appearance of the post-limiting-current region at higher rotation rates was affected by hydrogen evolution, cathodic potential sweeps were applied to rotating electrodes in 2 M H₂SO₄ at various rotation rates. Hydrodynamic effects on the hydrogen evolution rate were not observed, indicating that the early appearance of the post-limiting-current region at higher rotation rates probably resulted from formation of rough deposits and not from hydrogen evolution.

Typical ring current behavior during the cathodic polarization of Cu in additive-free acid $CuSO_4$ at various rotation rates

Table 3 Appearance of Cu Deposits in TU-containing Acid CuSO

Potential			[Cl ⁻] (m	ig/L)		
(V vs. SCE)	0	1	10	50	100	500
-0.175	D	S	S	D	D	D
-0.2	D	S	D	В	D	D
-0.225	D	S	D	В	D	D
-0.25	D	S	D	S	D	D
-0.3	D	S	D	D	D	D
(Alata D. Dull C. Cami brickt D. Drinkt)						

(Note: D=Dull, S=Semi-bright, B=Bright)

Containing 5 mg/L TU at various CI⁻ concentrations and potentials; 1000 rpm, 20 C/cm².

is shown in Fig. 2b. As the applied disk potential of rotating electrodes was decreased from the rest potential, the ring current reached a maximum near 0.03 V and decreased to a minimum around -0.1 V, then was nearly constant in the transition and limiting-current regions until the ring current abruptly increased in the post-limiting-current region. Ring currents in additive-free acid CuSO₄ increased with increasing rotation rates in all potential regions examined. The rapidly increasing ring current is attributed to a short circuit developed by Cu deposits extending from the disk to the ring. In acid CuSO₄, background ring currents of about 2 μ A were measured, using rotating ring electrodes (without the disk), that were independent of rotation rate.

Electrodeposition of Cu in acid CuSO₄ has been assumed to proceed in two electron transfer steps with Cu⁺ as an intermediate, with a rate-determining first step at high current densities:^{5,24,25}

$Cu^{+2} + e^{-} \rightarrow Cu^{+} $ (slow)	(1)
$Cu^+ + e^- \rightarrow Cu$ (fast)	(2)

Cu⁺ can also be formed by the disproportionation reaction,

$$Cu^{+2} + Cu \rightarrow 2Cu^{+} \tag{3}$$

The equilibrium constant for the disproportionation reaction at 25 °C was reported as 5.6 x 10^{-7} by Tindall and Bruckenstein.²⁶

The formation of Cu^{+} as an intermediate during Cu electrodeposition in $CuSO_4$ -Na₂SO₄ solutions was first detected by Nekrasov and Berezina, using a rotating ring-disk elec-

Table 4					
Appearance of Cu Deposits in BTA-containing Acid $CuSO_4$					

Potential			[Cŀ] (ı	ng/L)		
(V vs. SCE)	0	1	10	50	100	500
0.05	0	D	_	D		D
-0.25	5	D	D	D	D	D
-0.3	S	D	D	D	D	D
-0.35	В	D	D	D	D	D
-0.4	В	D	D	D	D	D
-0.425	В	D	D	D	D	D
-0.45	BL	D	D	D	D	D

(Note: D=Dull, S=Semi-bright, B=Bright; BL=Bright but loosely adherent) Containing 1 mM/ BTA at various CI concentrations and potentials; 1000 rpm, 20 C/cm².



Fig. 3—Limiting-diffusion-current density of Cu electrodeposition in acid $CuSO_4$ vs. $\omega^{1/2}$.



Fig. 4—Limiting-diffusion-current density of Cu electrodeposition in acid $CuSO_4$ vs. concentration of $CuSO_4$; 1000 rpm.

trode.²⁷ At open circuit, their measured ring current was greater than the background ring current. The ring current increased as the disk potential decreased, reached a maximum, then decreased to the background ring current. This ring current behavior was similar to that shown in Fig. 2b.

The appearance of the ring current peak at approximately 0.03 V can be explained as follows. The rate of formation of Cu^{+} [Eq. (1)] increases with increasing cathodic polarization. At the same time, the consumption rate of Cu^{+} [Eq. (2)] increases with increasing cathodic polarization. The maximum in the ring current is reached when the rates balance at 0.03 V. Subsequent increase in cathodic polarization decreases the ring current; that is, the net rate of production of Cu^{+} declines.

Limiting-cathodic-current density vs. $\omega^{1/2}$ plots are shown in Fig. 3; plots of limiting-cathodic-current density vs. [Cu⁺²] in 1 and 2 M H₂SO₄ at 1000 rpm are shown in Fig. 4. The limitingcathodic current values were determined at the inflection point in the limiting-current region. The straight lines passing through the origin in Fig. 3 indicate that electrodeposition of Cu in the limiting-current region is controlled by mass transport of Cu⁺² from the bulk electrolyte to the electrode. In 1 and 2 M H₂SO₄, diffusion coefficients of Cu⁺² in the range 0.03 M < [Cu⁺²] < 0.5 M, were determined from the slopes of the lines in Figs. 3 and 4; these values are $4.96 \pm 0.14 \times 10^{-6}$ and $4.11 \pm 0.07 \times 10^{-6}$ cm²/sec, respectively, and are in good agreement with literature values obtained for similar electrolyte compositions (Table 1).

Effect of CI

The effect of Cl⁻ on the cathodic polarization of Cu in acid $CuSO_4$ is shown in Fig. 5a. As the Cl⁻ concentration increased, the limiting-current region narrowed, and the onset of the post-limiting-current region occurred at more positive potentials. The limiting current was not dependent on Cl⁻. Rough surfaces were visually observed to develop around the inflection point in the limiting-current region.

The decrease in the disk current by addition of Cl⁻ at low concentrations in the transition region may be a result of strong adsorption of Cl⁻ and, at high concentrations, a result of formation of an insoluble CuCl film on the Cu disk. In the limiting-current region, both steps [Eqs. (1) and (2)] in the electrodeposition of Cu were much faster than mass transport of Cu⁺² from the bulk electrolyte to the surface. Cl⁻ appeared to increase the effective surface area of the Cu deposit in this region, resulting in the post-limiting-current region's beginning at a lower polarization in the presence, rather than the

absence, of Cl⁻.

Figure 5b shows that the ring currents in acid CuSO₄ were unchanged from open circuit to approximately -0.6 V by addition of as much as 10 mg/L Cl⁻. Addition of 100 mg/L Cl⁻, however, substantially increased ring currents, which reached a peak near -0.10 V. For 10 and 100 mg/L Cl⁻, ring currents rapidly increased in the post-limiting-current region, where deposits formed between the disk and ring, causing short circuits. Background ring currents were essentially the same in the presence or absence of Cl⁻.

To assess the effect of Cl⁻ on the ring currents at open circuit, measurements were conducted with increasing Cl⁻ concentration after a steady state rest potential was attained (about 1 hr); the results are given in Table 2, which shows that the ring currents at open circuit in acid CuSO₄ increased by addition of as much as 30 mg/L Cl⁻, decreased with further additions, up to 100 mg/L Cl⁻, then increased again above this concentration.

Similar ring current behavior at open circuit with addition of Cl⁻ to CuSO₄ solutions was reported by Yokoi *et al.*³¹ They attributed the increase in ring current by addition up to a "critical Cl⁻ concentration" to the formation of Cu⁺ and "an intermediate complex" of Cu⁺-Cl⁻, which are transported to the ring and electrooxidized; ring current decreased by addition of Cl⁻ above the "critical concentration" because of formation of insoluble CuCl and increased again at higher Cl⁻ concentrations by dissolution of CuCl to CuCl₂⁻.

In the presence of Cl⁻, and depending on Cl⁻ concentration, the following reactions take place during cathodic polariza-

Appearance of Cu Deposits in PB-containing Acid CuSO ₄							
Potential			[Cl ⁻] (m	ig/L)			
(V vs. SCE)	0	1	10	50	100	500	
-0.15	D	D	S	S	D	D	
-0.2	D	D	В	В	S	D	
-0.25	D	D	В	В	S	D	
-0.3	D	D	В	В	S	D	
-0.35	D	D	В	В	S	D	
-0.4	D	D	D	S	S	D	

(Note: D=Dull, S=Semi-bright, B=Bright)

Containing 1 vol% PB at various CI concentrations and potentials; 1000 rpm, 20 C/cm².



Fig. 5—Effect of Cl on Cu electrodeposition in acid $CuSO_{4}$: (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential; 1000 rpm.

tion of Cu in acid CuSO₄:

$$\begin{array}{ll} \mathsf{Cu}^{+} + \mathsf{Cl}^{-} \to \mathsf{Cu}\mathsf{Cl} & (4) \\ \mathsf{Cu}\mathsf{Cl} + \mathsf{Cl}^{-} \to \mathsf{Cu}\mathsf{Cl}_{2}^{-} & (5) \end{array}$$

Above a "critical Cl⁻ concentration," CuCl precipitates by reaction (4) and dissolves to CuCl₂⁻ by reaction (5). High Cl⁻ concentrations (above 1 M Cl⁻) lead to higher complexes such as CuCl₃⁻² and CuCl₄⁻³.³² Because [Cl⁻] was << 1 M in this study, CuCl₂⁻ was the only Cu(I) species considered as a dissolution product of CuCl.

The "critical CI⁻ concentration" for formation of the CuCl surface film in acid CuSO₄ was calculated to be about 40 mg/ L Cl⁻ using the equilibrium constant of the disproportionation reaction (5.6 x 10⁻⁷) and the solubility product for CuCl (4.5 x 10⁻⁷).^{26,32} This "critical Cl⁻ concentration" is in satisfactory accord with the experimental value of about 30 mg/L (Table 2). Therefore, the decrease in the ring current at open circuit above a concentration of 30 mg/L Cl⁻ is ascribed to the formation of an insoluble CuCl film. The increase in ring current above a concentration of 100 mg/L Cl⁻ was a result of the dissolution of CuCl to soluble CuCl₂⁻ [Eq. (5)].

Effect of Organic Additives

The organic additives selected for this study were thiourea (TU), benzotriazole (BTA) and a proprietary commercial brightener (PB, a composite three-component additive containing a polyethylene glycol, a dye derivative and a surfac-



Fig. 6—Effect of organic additives on Cu electrodeposition in acid $CuSO_{4}$: (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential; 1000 rpm.

tant) for through-hole plating of Cu. Cathodic polarization of Cu in chloride-ion-free acid $CuSO_4$ containing the organic additives is shown in Fig. 6a. For each additive, electrodeposition of Cu was inhibited between the rest potential and potentials just before the limiting-current region. It was noted that the magnitude of the limiting current was not affected by the presence of the organic additives. The corresponding ring currents during Cu electrodeposition are shown in Fig. 6b. The PB closely followed the additive-free ring current behavior from the rest potential to -0.6 V. BTA greatly suppressed the maximum at 0 V vs. SCE. On the other hand, ring currents in the presence of TU were substantially larger.

Thiourea (TU) has been reported to brighten Cu deposits for concentrations of 3 to 8 mg/L in CI⁻free acid CuSO₄.³³ Figure 6a shows that in the presence of 5 mg/L TU, a very distinct current plateau is observed at potentials between 0 and -0.2 V, followed at the latter potential by a potential plateau, where disk current increased rapidly. Between 500 and 2,000 rpm, the current and potential plateaus were independent of rotation rate (Fig. 7). The distinct current and potential plateaus observed have also been reported by others.^{10,11,13,34}

In the bulk electrolyte, TU and ${\rm Cu}^{\rm +2}$ react to form ${\rm Cu}^{\rm +}$ and formamidine disulfide (FD), $^{\rm 13}$

$$2Cu^{+2} + 2(NH_2)_2CS \to 2Cu^{+} + (NH_2)_2(NH)_2C_2S_2 + 2H^{+}$$
(6)

TU and FD form the redox couple,¹³

$$2(NH_2)_2CS \to (NH_2)_2(NH)_2C_2S_2 + 2H^+ + 2e^-$$
(7)

Within the Cu disk diffusion layer, FD would be completely electroreduced (Eq. 7) at about 0 V vs. SCE.

In solution, thiourea resonates between two tautomeric forms,³⁵ It is proposed that isothiourea (isoTU) can be stabilized by adsorption on the Cu disk,

$$\begin{array}{ll} (\mathsf{NH}_2)_2\mathsf{CS} \to (\mathsf{NH}_2)(\mathsf{NH})\mathsf{CSH} & (8) \\ (\mathsf{NH}_2)_2\mathsf{CS} \to \left[(\mathsf{NH}_2)(\mathsf{NH})\mathsf{CSH} \right]_{\mathsf{ads}} & (9) \end{array}$$

and react with Cu^{+} , produced during Cu electrodeposition, to form a Cu(I)-isothiourea complex,

$$[(NH_2)(NH)CSH]_{ads} + Cu^{+} \rightarrow [(NH_2)(NH)CSCu(I)]_{ads} + H^{+} (10)$$

It is surmised that the adsorbed Cu(I)-isoTU complex inhibits the surface diffusion of adsorbed Cu atoms in the mechanism of Cu electrodeposition,²⁵

$$Cu^{+2} + e^{-} \rightarrow Cu^{+}$$
 (1)

$$\begin{array}{ll}
\text{Cu} + e \rightarrow \text{Cu}_{\text{ads}} & (2a) \\
\text{Cu} &= \text{Cu} & (2b)
\end{array}$$

so that step (2b) is the rate-determining step. This leads to the limiting current (0 to -0.2 V), which is independent of rotation rate between 500 and 2000 rpm. Then, at about -0.2 V, the Cu(I)-isoTU complex undergoes electroreduction,

$$\begin{split} & [(\text{NH}_2)(\text{NH})\text{CSCu}(\text{I})]_{\text{ads}} + \text{H}^* + \text{e}^- \rightarrow [(\text{NH}_2)(\text{NH})\text{CSH}]_{\text{ads}} + \text{Cu} \\ & (11) \\ & [(\text{NH}_2)(\text{NH})\text{CSH}]_{\text{ads}} \rightarrow (\text{NH}_2)_2\text{CS} \end{split} \tag{12}$$

The potential remains constant during the electroreduction process until the adsorbed complex is completely removed from the disk surface.

Because TU is expected to electrooxidize to FD at the Au ring set at 0.6 V (Eq. 7), background ring currents in 2 M H_2SO_4 and acid CuSO₄, both containing 5 mg/L TU, were



Fig. 8—Effect of rotation rate on the background ring current (no Cu disk) in 2 M H_2SO_4 and acid CuSO₄, both containing 5 mg/L TU.



Fig. 7—Effect of rotation rate on Cu electrodeposition in acid CuSO₄ and TU (5 mg/L): (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential.



Fig. 9—Effect of TU concentration on the background ring current (no Cu disk) in 2 M H_2SO_4 and acid CuSO₄; 300 rpm.

measured with rotating ring electrodes (no Cu disk). The results are shown in Fig. 8. Large background ring currents were observed in the presence of TU, compared to TU-free H_2SO_4 and acid $CuSO_4$ solutions. Further, background ring currents increased with increasing rotation rate. The reaction order of one with respect to TU (Eq. 7) was obtained (Fig. 9). Therefore, the large ring current minimum for Cu electrodeposition in acid $CuSO_4$ containing 5 mg/L TU is attributed to electrooxidation of TU at the ring.

In the potential range between the rest potential and approximately 0 V vs. SCE, FD is electroreduced to TU, leading to increased flux of TU from the disk to the ring and increasing the ring current resulting from increased TU electrooxidation; at this point, TU and the Cu(I) produced during Cu electrodeposition forms $[(NH_2)(NH)CSCu(I)]_{ads}$, causing the decrease in ring current at potentials below 0 V.

It has been reported that BTA can brighten copper deposits³⁶ and inhibit the corrosion of copper and copper alloys.³⁷ It is considered to be chemically adsorbed on the Cu surface, where it forms a stable protective film, Cu(I)BTA polymer.³⁷⁻³⁹ The thickness of the protective film depends on solution pH.^{40,41} In near neutral solutions, thin films (< 60 Å) grow on top of Cu₂O, while in acidic solutions, thick films (up to several thousand Å) are formed on Cu.

Suppression of the disk current before the limiting-current region in the presence of BTA (Fig. 6a), is ascribed to the formation of a stable Cu(I)BTA film on the Cu surface. The lower disk current in the post-limiting-current region in the

presence of BTA was likely the result of decreased build-up of the powdery deposits observed to form within the limitingcurrent region. These Cu deposits were readily removed by wiping with a tissue. In contrast to TU-containing solutions, background ring currents were unaffected by the presence of BTA.

The addition of 1 vol. percent PB to acid $CuSO_4$ showed that Cu electrodeposition was considerably suppressed between 0.03 and -0.05 V. The decrease in Cu electrodeposition in this potential region suggests formation of a stable Cu(I)PB film on the disk surface.

Effect of C Γ on Electrodeposition of Cu in Acid CuSO₄ Containing Organic Additives

The presence of 10 to 100 mg/L Cl⁻ is usually required for commercial bright acid copper plating solutions. The effect of Cl⁻ in acid CuSO₄ containing TU, BTA or PB has been investigated.

The effect of Cl⁻ on Cu electrodeposition from acid CuSO₄ containing 5 mg/L TU is shown in Fig. 10a. As the Cl⁻ concentration increased, the current plateau becomes less distinct and can no longer be distinguished. This may be the result of the formation of an isothiourea-Cu(I)...Cl bridge complex⁴² that may be less strongly adsorbed, resulting in increased surface diffusion of the adsorbed Cu atoms being deposited. Increased Cl concentration (> 100 mg/L) results in



Fig. 10—Effect of Cl on Cu electrodeposition in acid $CuSO_4$ containing 5 mg/ L TU; 1000 rpm: (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential.



Fig. 11—Effect of Ct on Cu electrodeposition in acid CuSO₄ containing 1 mM BTA; 1000 rpm: (a) cathodic polarization of Cu disk; (b) ring current vs. disk potential.

formation of the CuCl₂ complex and thiourea. Electrooxidation of the released CuCl₂ and thiourea results in increased ring currents at -0.2 V (Fig. 10b). The knee in the cathodic polarization curve just before the limiting-current region was more pronounced; the potential range of the limiting-current region was narrower, and the onset of the post-limitingcurrent region appeared at more positive potentials. The magnitude of the limiting current was not dependent on either CI⁻ or TU. Figure 10b shows that in the presence of CI⁻, the ring current peak near 0 V is no longer clearly seen because of the much greater rate of formation of Cu(I) at the disk. It is evident that CI⁻ had a significant effect on Cu electrodeposition in Tu-containing acid CuSO,.

The effect of Cl⁻ on the cathodic polarization of Cu in acid $CuSO_4$ containing 1 mM BTA is shown in Fig. 11a. It appears that the disk current increases at more positive potentials with increasing Cl⁻ concentrations, indicating a lessened inhibiting effect of BTA or the BTA-Cu(I) film with the formation of a BTA-Cu(I)...Cl bridge complex, similar to the TU complex. This would permit Cu deposition at more positive potentials, as well as the onset of the limiting-current and post-limiting-current regions. In the transition region, the disk current increased with increase in Cl⁻ concentration. Also, the onset of the post-limiting-current region appeared at more positive potentials with increase in Cl⁻ concentration. The limiting current was not affected by the presence of Cl⁻. Ring currents during Cu electrodeposition from the BTA solution were

slightly suppressed by the presence of CI^- (Fig. 11b). The slightly increased ring current between 0 and -0.1 V may be a result of electrooxidation of Cu(I) in the transition region.

The effect of Cl⁻ on the cathodic polarization of Cu in acid CuSO, containing one volume percent PB is shown in Fig. 12a. At potentials above the limiting-current region, inhibition of Cu electrodeposition increased with increase in Cl⁻ concentration up to 100 mg/L. As Fig. 12b shows, ring currents were not affected by the presence of Cl⁻ between -0.2 and -0.6 V. At potentials above -0.2 V, however, addition of 100 mg/L Cl⁻substantially increased the ring currents as the result of production of soluble CuCl₂. Moreover, at -0.7 V, precipitation of the CuCl film led to a short circuit path between the disk and the ring. The synergistic inhibition of Cu electrodeposition by the presence of both PB and Cl⁻ seems related to brightening of copper deposits. Addition of Cl⁻ eliminated or greatly decreased the transition region, in effect, extending the apparent Tafel region. This, combined with an inhibiting effect, may account for an increased current density range of bright deposits (*i.e.*, an increase in the optimum I/I, ratio).

The decrease in disk current is probably the result of the formation of either PB-Cl or PBCu(I)-Cl complexes. Further decrease in disk current at 100 mg/L Cl⁻ may result from precipitation of CuCl in addition to these complexes. At 500



Fig. 12—Effect of Cl on Cu electrodeposition in acid $CuSO_4$ containing 1 vol percent PB; 1000 rpm: (a) cathodic polarization of the Cu disk; (b) ring current vs. disk potential.

Table 6 Effect of Rotation Rates on Appearance Of Cu Deposits in Acid CuSO₄

Rotation rate (rpm)	Reynolds number	TU solution	PB solution	BTA solution
0	0	D	D	D
100	69	S	S	S
200	138	В	В	В
300	206	В	В	В
500	344	В	В	В
1000	688	В	В	В
2000	1375	В	В	В
4000	2751	В	В	В

(Note: D=Dull, S=Semi-bright, B=Bright)

Containing organic additives with and without Cl⁻, at various rotation rates, 20 C/cm² (TU solution: 5 mg/L thiourea, 50 mg/L Cl⁻, -0.2 V; PB solution: 1 vol% proprietary brightener, 50 mg/L Cl⁻, -0.2 V; BTA solution: 1 mM benzotriazole, no Cl⁻, -0.35 V).



Fig. 13—Effect of rotation rate on Cu electrodeposition in acid CuSO₄ and in acid CuSO, containing 5 mg/L TU and 50 mg/L Cl.

mg/L Cl⁻ concentration, a smaller decrease in disk current and an accompanying increase in ring current are attributed to dissolution of CuCl to CuCl₂⁻.

Effect of Deposition Potential, Organic Additives, Cl and

Hydrodynamics on the Surface Appearance of Cu Deposits To assess the effect of deposition potential/current, organic additives, Cl⁻, and hydrodynamic conditions on producing bright Cu deposits, the appearance of Cu deposits was examined, either visually or with an optical microscope, after passing a total charge of about 20 C/cm².

First, the effects of deposition potential and Cl⁻ were investigated by changing the applied deposition potential and the Cl⁻ concentration at a rotation rate of 1000 rpm. These results are given in Tables 3-5. The TU and PB solutions did not produce any bright Cu deposits without addition of Cl-, while the BTA solutions produced bright Cu deposits from -0.3 to -0.4 V in the absence of Cl⁻. TU solutions produced bright Cu deposits only at 50 mg/L Cl⁻, and the PB solutions produced bright Cu deposits from 10 to 50 mg/L Cl⁻, while the BTA solution did not produce any bright Cu deposits by addition of Cl⁻ from 1 to 500 mg/L. The deposition potential (current) has a broader Cl⁻ concentration window to produce bright Cu deposits from PB solutions than TU. All three solutions produced bright Cu deposits at potentials more positive than the limiting-current region (or currents less than the limiting-current density). By comparison of the results in Figs. 10–12 and Tables 3–5, it is seen that bright Cu deposits were obtained when Cu electrodeposition was inhibited by addition of Cl⁻ in the presence of organic brighteners.

The effect of hydrodynamics on production of bright Cu deposits from TU, BTA and PB solutions is shown in Figs. 13–15. Disk current was significantly suppressed in the potential range where bright deposits were obtained by addition of organic additives and Cl⁻ (except BTA) at 1000 rpm; with stationary electrodes, disk currents were suppressed less. Therefore, the electrodeposition of bright Cu is strongly influenced by mass transport of the brightening components and Cu⁺² from the bulk solution to the cathode surface.

To assess more quantitatively the effect of hydrodynamics on production of bright Cu deposits from TU, PB and BTA solutions, the rotation rate of the Cu disk electrode in each solution was varied at a set deposition potential. These results are given in Table 6. Minimum hydrodynamic flow conditions for bright Cu deposits from all three solutions are estimated at a Reynolds number of about 140 (~200 rpm).

Summary and Conclusions

The effect of Cl⁻, with and without organic additives, on electrodeposition of Cu from acid CuSO₄ solutions was investigated, using RRDE. In the presence of Cl⁻ and additives, such as TU or PB, it is suggested that in addition to CuCl surface films, adsorbed CU(I) or Cu(I)complex...Cl bridge films inhibit surface diffusion of adsorbed Cu atoms, and that this becomes the rate-determining step in the deposition mechanism. For example, the synergistic brightening effect of PB plus Cl⁻ appears to be one of surface inhibition, with the addition of Cl⁻ extending the apparent Tafel region, resulting in an increased range of current density for bright deposits. Addition of Cl⁻, however, to solutions containing the well-known inhibitor, BTA additive, resulted in lessening of inhibition by BTA or Cu(I)BTA surface films, possibly because of formation of a Cl⁻ bridged complex.

In 1 M and 2 M H₂SO₄, diffusion coefficients of Cu⁺² in the concentration range, 0.03 M < [Cu²⁺] < 0.3 M, were computed from the RRDE results as 4.96×10^{-6} and 4.12×10^{-6} cm²/sec, respectively. The "critical CI⁻ concentration" to form a CuCl surface film on Cu was experimentally determined to be about 30 mg/L (0.85 mM) from measurements of the ring current at the rest potential of the Cu disk in solutions of various CI⁻ concentrations.

Bright copper deposits were obtained with sufficient laminar flow in acid CuSO₄ containing 5 mg/L (0.07 mM) TU with 50 mg/L (1.4 mM) Cl⁻, 1 vol. percent proprietary commercial brightener (PB), with 10 to 50 mg/L (0.28 to 1.4 mM) Cl⁻, and 119 mg/L (1 mM) benzotriazole (BTA) without Cl⁻. The minimum hydrodynamic flow conditions for bright copper deposits was a Reynolds number of about 140 (~200 rpm) for TU-, BTA-, and PB-containing acid CuSO₄.

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References

- 1. W. O. Freitag, C. Ogden, D. Tench and J. White, *Plat. Surf. Fin.*, **70**, 55 (Oct., 1983).
- W.H. Safranek, in *Modern Electroplating*, F.A. Lowenheim, Ed., John Wiley & Sons, New York, NY, 1980.
- 3. R. Walker and S. D. Cook, Surf. Tech., 11, 189 (1980).
- 4. E.W. Thompson, Trans. Inst. Met. Fin., 59, 30 (1981).
- 5. E. Mattsson and J. O'M. Bockris, Trans. Faraday Soc., 55, 1586



Fig. 14—Effect of rotation rate on Cu electrodeposition in acid CuSO₄ and in acid CuSO, containing 1 mM BTA.



Fig. 15—Effect of rotation rate on Cu electrodeposition in acid $CuSO_4$ and in acid $CuSO_4$ containing 1 vol percent PB and 50 mg/L Cl².

(1959).

- 6. Y.L. Yao, Trans. Electrochem. Soc., 86, 371 (1944).
- 7. W.H. Gauvin and C.A. Winkler, J. Electrochem. Soc., 99, 71 (1952).
- B. Ke, J.J. Hoestra, B.C. Sison and D. Trivich, *ibid.*, **106**, 382 (1959).
- L. Mandelcom, W.B. McConnell, W. Gauvin and C.A. Winkler, *ibid.*, **99**, 84 (1952).
- 10. D.R. Turner and G.R. Johnson, ibid., 109, 798 (1962).
- 11. G.R. Johnson and D.R. Turner, *ibid.*, 918 (1962).
- D.R. Gabe and D.J. Robinson, *Trans. Inst. Met. Fin.*, 49, 17 (1972).
- A. Szymaszek, J. Biernat and L. Pajdowski, *Electrochim. Acta*, 22, 359 (1977).
- M.R.H. Hill and G.T. Rogers, J. Electroanalyt. Chem., 86, 179 (1978).
- C.O. Kang and J.S. Lee, *Kumsok Pyomyon Choli*, **16**(4), 190 (1983).
- M. Yokoi, S. Konishi and T. Hayashi, *Denki Kagaku*, **51**, 456 (1983).
- 17. M. Yokoi, S. Konishi and T. Hayashi, ibid., 310 (1983).
- M. Yokoi, S. Konishi and T. Hayashi, *Kinzoku Hyomen Gijutsu*, 34, 434 (1983).
- J.D. Reid and A.P. David, J. Electrochem. Soc., 134, 1389 (1987).
- 20. J.D. White, J. Appl. Electrochem., 17, 977 (1987).
- 21. J. Jackson and D.A. Swalheim, *Plat. Surf. Fin.*, **65**, 38 (May, 1978).
- H.P. Lee, Ph.D. Dissertation, University of California, Los Angeles, CA (1983).
- 23. H.P. Lee and Ken Nobe, J. Electrochem. Soc., 131, 1236 (1984).
- J.O'M. Bockris and M. Enyo, *Trans. Faraday Soc.*, 58, 1187 (1962).
- 25. J.O'M. Bockris and H. Kita, J. Electrochem. Soc., 109, 928,

(1962).

- 26. G.W. Tindall and S. Bruckenstein, *Analyt. Chem.*, **40**, 1402 (1968).
- 27. L.N. Nekrasov and M. Berezina, *Dokl. Akad. Nauk SSSR*, **142**, 855 (1962).
- C.J. Milora, J.F. Henrickson and W.C. Hahn, *J. Electrochem.* Soc., **120**, 488 (1973).
- A.J. Arvia, J.C. Bazan and J.S.W. Carrozza, *Electrochim. Acta*, 11, 881 (1966).
- 30. A.F.W. Cole and A.R. Gordon, J. Phys. Chem., 40, 733 (1936).
- M. Yokoi, S. Konishi, and T. Hayashi, *Denki Kagaku*, 51, 460 (1983).
- 32. M. Braun and K. Nobe, J. Electrochem. Soc., 126, 1666 (1979).
- 33. L.L. Shreir and J.W. Smith, Trans. Faraday Soc., 50, 393 (1954).
- 34. C.T. Wang and T.J. O'Keefe, *Proc. Int. Symp. Electrochem. Miner. Met. Process.*, 655 (1984).
- P. Karrer, Organic Chemistry, Elsevier Publ., New York, NY, 1938; p. 209.
- 36. J.K. Prall and L.L. Shreir, Trans. Inst. Met. Fin., 41, 29 (1964).
- 37. J.B. Cotton, Proc. 2nd Int. Congr. Met. Corrosion, 590 (1963).
- 38. J.B. Cotton and I.R. Scholes, Brit. Corr. J., 2, 1 (1967).
- 39. G.W. Poling, Corr. Sci., 10, 359 (1970).
- 40. F. Mansfeld and T. Smith, *Corrosion*, **29**, 105 (1973).
- 41. I.C.G. Ogle and G.W. Poling, Can. Metal. Quart., 14, 37 (1975).
- B. Rathke, Ber. dt. Chem. Ges., 14, 1780 (1881); ibid, 17, 297 (1884).



Yoon





Schwartz

Nobe

About the Authors

Sunghee Yoon is a doctoral candidate in the Dept. of Chemical Engineering at UCLA, 405 Hilgard Ave., Los Angeles, CA 90024. He is also a project engineer at Hughes Aerospace & Electronics Co., Fullerton, CA. He holds a BS in chemical technology from Seoul National University, Korea, and an MS in chemical engineering from the University of California-Davis. He was an AESF scholarship recipient in 1986.

Morton Schwartz, CEF, is a visiting research engineer in the Dept. of Chemical Engineering at UCLA, and an instructor for AESF training courses. He holds an MA degree from Indiana University.

Prof. Ken Nobe is a faculty member in the Dept. of Chemical Engineering at UCLA. He has been employed in this capacity since receiving his PhD in 1956. Prof. Nobe undertakes research in electrochemistry and catalysis.