# Copper Dissolution in Aqueous Ammonia-Containing Media during Chemical Mechanical Polishing

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Copper dissolution in ammonia-containing media during chemical-mechanical polishing (CMP) was investigated. Both a stationary and a rotating disk electrode (RDE) were used for electrochemical characterization. Ammonia can etch copper in the presence of oxidizers by dissolving the oxide film on the copper surface and the dissolution rate varied from about 8 to 30 nm/min, depending on the hydrodynamic conditions. The copper dissolution rate in $NH_4NO_3$ or $(NH_4)_2SO_4$ solution does not vary significantly with solution pH. Ammonium nitrate results in a higher dissolution rate, due to the extra oxidizing power of the nitrate ion. The addition of an inhibitor, benzotriazole (BTA), reduces the copper dissolution rate significantly, even though the dissolution rate can be increased by rotating the copper disk. The dissolution of copper in stagnant aqueous ammonia solutions is controlled by oxygen diffusion at high $NH_4OH$ concentrations and by mixed kinetics at low $NH_4OH$ concentrations (≤0.3 wt %).

## Introduction

Chemical-mechanical polishing (CMP) of copper has emerged as a new technology in integrated circuit fabrication.[1,2] During copper CMP, a slurry containing copper etchant(s) is used to remove copper from a wafer surface by abrading the copper surface against a polishing pad. The protruding region is removed faster than the recessed region, resulting in global planarization. CMP of copper can be performed in either acidic or neutral or alkaline media.[3−7] The CMP slurry chemistries in various media have been investigated by Carpio et al.[8] In acidic media, an inhibitor, benzotriazole (BTA), is used to control the removal rate and avoid isotropic etching.[3,4] In neutral polish slurries, $H_2O_2$ can be utilized as an oxidizer. Experimental results obtained using $H_2O_2$ as the oxidizer have been reported by Stavreva et al.[5] and Jirabayashi et al.[6] Ammonia is used in alkaline polish media because of its ability to form complexes with copper ions. The CMP of copper in ammonia-containing slurries has been investigated extensively by Steigerwald et al.[9−13] They concluded that the mechanism for copper removal is the mechanical removal of copper, followed by the dissolution of abraded copper particles.[12,13]

Ammonia does not etch copper directly in the absence of oxidizers since copper is a noble metal. However, it can react with copper oxides forming $Cu(NH_3)_4^{2+}$ and $Cu(NH_3)_2^{+}$ complexes. Since some dissolved oxygen exists in the solutions in our experiments, the dissolution of copper in $NH_4OH$ solutions can occur. Halpern[14] investigated the kinetics of copper dissolution in aqueous ammonia solutions. He found that the copper dissolution rate was proportional to the surface area of copper and, at low oxygen pressure, was determined by the transport of dissolved oxygen to the surface. When the pressure of oxygen was increased, the chemical reaction at the surface became rate-controlling. The dissolution of copper−gold alloys in aqueous ammonia and ammonium salt solutions was investigated by Fisher and Halpern.[15] They found that only copper was dissolved in the solutions and a gold-rich film was left behind on the surface of the alloy. As the gold content of the alloys was increased, the dissolution rate of copper decreased. Copper oxides formed on the alloy surface contribute to the film structure and limit the corrosion rate.

The dissolution behavior of elemental and Ag/Cu alloys in ammonia-containing solution was also studied using a rotating disk electrode.[16] The dissolution rate

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(1) Hu, C. K.; Luther, B.; Kaufman, F. B.; Humnel, J.; Uzoh, C.; Pearson, D. J. *Thin Solid Films* **1995**, *262*, 84.
(2) Lakshminarayanan, S.; Steigerwald, J. M.; Price, D. T.; Bourgeois, M.; Chow, T. P.; Gutmann, R. J.; Murarka, S. P. *IEEE Electron. Dev. Lett.* **1994**, *15*, 307.
(3) Luo, Q.; Campbell, D. R.; Babu, S. V. Proceedings of the 1st International VMIC Specialty Conference on CMP Planarization; Santa Clara, CA, Feb, 1996; p 145.
(4) Luo, Q.; Campbell, D. R.; Babu, S. V. *Langmuir* **1996**, *12*, 3563.
(5) Stavreva, Z.; Zeidler, D.; Plotner, M.; Drescher, K. *Appl. Surf. Sci.* **1995**, *91*, 192.
(6) Hirabayashi, H.; Higuchi, M.; Kinoshita, M.; Kaneko, H.; Hagasaka, N.; Mase, K.; Oshima, J. Proceedings of the 1st International VMIC Specialty Conference on CMP Planarization; Santa Clara, CA, Feb, 1996; p 119.
(7) Gutmann, R. J.; Steigerwald, J. M.; You, L.; Price, D. T.; Neirynck, J.; Duquette, D. J.; Murarka, S. P. *Thin Solid Film* **1995**, *270*, 596.
(8) Carpio, R.; Farkas, J.; Jairath, R. *Thin Solid Films* **1995**, *266*, 238.
(9) Steigerwald, J. M.; Zirpoli, R.; Murarka, S. P.; Price, D.; Gutmann, R. J. *J. Electrochem. Soc.* **1994**, *141*, 2842.
(10) Steigerwald, J. M.; Murarka, S. P.; Gutmann, R. J.; Duquette, D. J. *J. Electrochem. Soc.* **1994**, *141*, 3512.
(11) Steigerwald, J. M.; Duquette, D. J.; Murarka, S. P.; Gutmann, R. J. *J. Electrochem. Soc.* **1995**, *142*, 2379.
(12) Steigerwald, J. M.; Murarka, S. P.; Ho, J.; Gutmann, R. J.; Duquette, D. J. *J. Vac. Sci. Technol.* **1995**, *13B*, 2215.
(13) Steigerwald, J. M.; Murarka, S. P.; Gutmann, R. J.; Duquette, D. J. *Mater. Chem. Phys.* **1995**, *41*, 217.
(14) Halpern, J. *J. Electrochem. Soc.* **1953**, *100*, 421.
(15) Fisher, J. I.; Halpern, J. *J. Electrochem. Soc.* **1956**, *103*, 282.
(16) Guan, Y. C.; Han, K. N. *J. Electrochem. Soc.* **1995**, *142*, 1919.

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of copper from the alloys is higher than that from pure copper due to galvanic coupling and increases with an increase of the silver content in the alloy. The dissolution of copper from its pure state and alloys is mainly controlled by oxygen diffusion. As in the case of pure silver, the dissolution of silver from its alloys is determined by surface reaction.[16]

In a CMP process, the copper dissolution behavior in the recessed regions and protruding regions of a circuit pattern may be different. The dissolution in the recessed region may be similar to that in aqueous media. However, in the protruding regions, the mechanical abrasion plays an important role. Therefore, it is useful to investigate the kinetic aspects of copper dissolution during a CMP process in more detail.

The objective of this paper is to understand further the mechanism of copper removal in the recessed regions in a CMP process with slurries containing ammonia. The copper dissolution rate was determined with solutions containing typical concentrations of chemicals present in polishing slurries, but without the abrasive particles. The dissolution rate was obtained by measuring the weight loss and, when the weight loss method is not sufficiently accurate, by electrochemical means. A rotating disk electrode was used to investigate the copper dissolution behavior under hydrodynamic conditions.

## Experimental Section

A 1000 mL graduated glass flask, immersed in a constant-temperature water bath, was used as the container for the etchant solution. The temperature was maintained within an accuracy of ±0.1 °C. A mechanical stirrer, mounted through the flask neck, was used to mix the solution. The rotational speed of the stirrer was varied from 0 to 2200 rpm. The etchants investigated were ammonium hydroxide, ammonium nitrate and ammonium sulfate. The solution pH was varied by adding the appropriate amounts of sodium hydroxide. All the chemicals used in the experiments were purchased from Aldrich Chemicals and were used without further purification.

A rectangular copper coupon (10 mm × 20 mm, 0.5 mm thick, 99.99% purity) (also from Aldrich) was first degreased in acetone for 30 min, dried in an air stream, and weighed. It was then immersed in the etchant solution, which was stirred at different speeds for a predetermined time while the temperature was maintained at the desired value. During stirring, the copper coupon was not stationary and moved with the fluid, especially at higher rotational speeds. The coupon was removed and washed with deionized water and immersed in acetone, followed by drying quickly and completely in an air stream. It was reweighed and the weight loss was determined. Figure 1 shows the observed linear relationship between the weight loss of the copper coupon and the immersion time in 6% $NH_4OH$ solution (by weight). The dissolution rate of the copper coupon, in nm/min, at this and other ammonium hydroxide concentrations, was determined from the slope of such linear plots, the area of the sample and the density of copper.

To understand the dissolution behavior further, polarization curves were recorded with an EG&G Princeton Applied Research Model 273 potentio/galvanostat. An EG&G Princeton Applied Research Model 352 SoftCorr TMII corrosion software was adopted to control the potentio/galvanostat. The measurements were made in a standard corrosion cell in which three electrodes—a working electrode, a counter electrode (platinum electrode), and a reference electrode (saturated calomel electrode, abbreviated as SCE in the following)—were inserted. A rotating copper disk electrode (3.1 mm in diameter) was used as the working electrode. The reference electrode (SCE) was inserted into the corrosion cell through a

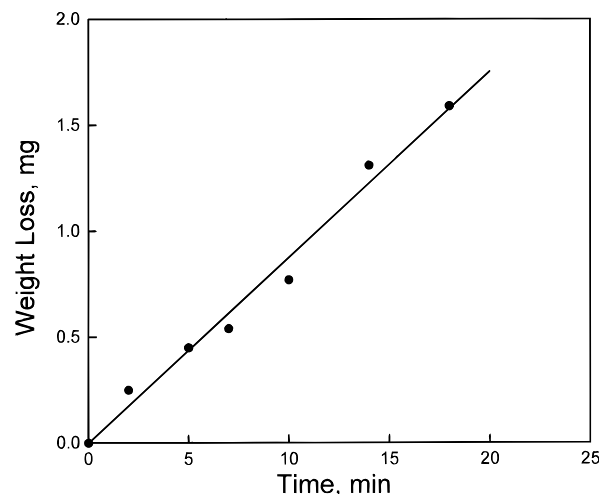



**Figure 1.** Copper weight loss vs immersion time in 6 wt % $NH_4OH$ solution at 25 °C and 95 rpm stirring speed.

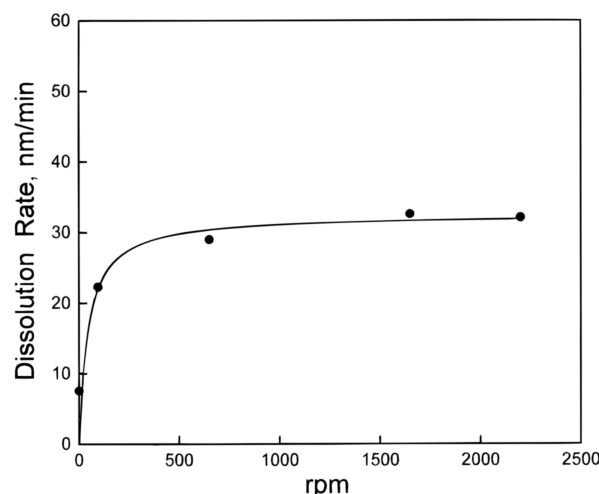



**Figure 2.** Effect of stirring speed on copper dissolution rate in 6 wt % $NH_4OH$ solution at 25 °C.

Luggin bridge whose tip was 1−2 mm from the working electrode. A saturated $Na_2SO_4$ solution was used as the medium in the bridge. The measurements were obtained at different rotational speeds of the working electrode. Polarization curves were recorded by scanning from negative voltage to positive voltage with a voltage scan rate of 0.5 mV/s. The voltage scan was initiated automatically. The corrosion current density ($i_{corr}$) and open-circuit potential ($E_{corr}$) were calculated using the Stern−Geary equation.[17] It was estimated, using the measured solution resistance, that the maximum *IR* drop will be less than 10 mV even at the maximum current density of 0.1 A/cm$^2$ measured in all our experiments. Hence, *IR* compensation was not required.

The dissolution rate of copper in the presence of inhibitors is very low, and the weight loss method is not sufficiently sensitive for short immersion times. Hence, the dissolution rate in the presence of inhibitors, was obtained from the corrosion current density determined by the linear polarization technique with a voltage scan rate of 0.1 mV/s and the scanned voltage range was $E_{corr} \pm 20$ mV.

## Experimental Results and Discussion

**Dissolution of Copper.** Figure 2 shows the effect of rotational speed of the stirrer on the copper dissolution rate. The ammonia concentration used here was 6 wt % of $NH_4OH$. The copper dissolution rate increases

(17) Stern, M.; Geary, A. L. *J. Electrochem. Soc.* **1957**, *104*, 56.

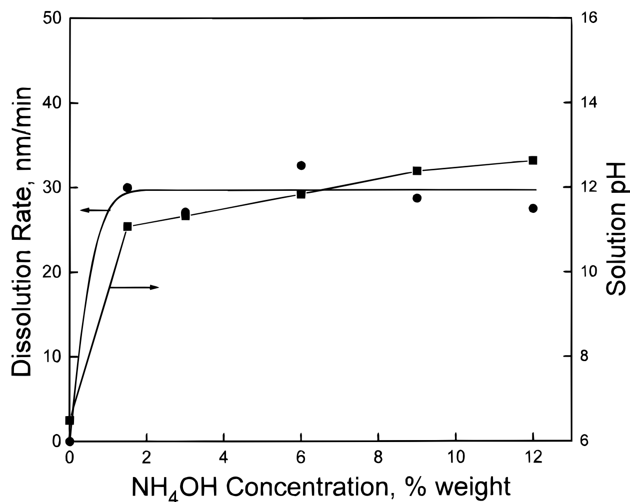



**Figure 3.** Effect of $NH_4OH$ concentration on copper dissolution rate at 1650 rpm and 25 °C. Solution pH changes with $NH_4OH$ concentration.

significantly, from 8 to 22 nm/min, as the rotational speed increases from 0 to 95 rpm. The dissolution rate increases very slowly beyond 650 rpm, reaching a value of 32 nm/min at 1650 rpm. This implies that either the mass transport of oxygen from the solution to the copper surface and/or the diffusion of the dissolution products in the bulk solution are not rate limiting or the maximum oxygen concentration is achieved, i.e., oxygen concentration cannot be increased further by stirring even though the dissolution may be still controlled by oxygen diffusion.

The effect of ammonia concentration (by weight of $NH_4OH$) on the copper dissolution rate was investigated at 1650 rpm and 25 °C. This rotational speed was chosen since at this speed there are no significant effects of the rotational speed on the dissolution rate. The experimental results are shown in Figure 3. The copper dissolution rate increases significantly when a small amount of $NH_4OH$ is added to the solution, reaching 30 nm/min at 1.2 wt % $NH_4OH$ and then levels off within experimental error. Therefore, increasing the $NH_4OH$ concentration beyond 1.2% by weight does not increase the copper etch rate. Since the solution pH varied with $NH_4OH$ concentration as shown in Figure 3, it may affect the copper dissolution rate. To understand this result better, the measurement was repeated, but this time adding 1 M NaOH solution to maintain a constant pH of 11. The results are shown in Figure 4. In this figure, the $NH_4OH$ concentration was varied from 0 to 1.2 wt %. The dissolution behavior at these low $NH_4OH$ concentrations is similar to that shown in Figure 3.

Solution temperature affects the copper dissolution rate significantly as shown in Figure 5. These results were obtained at a fixed $NH_4OH$ concentration of 1.5 wt % and at 1650 rpm. Under these conditions, the copper dissolution rate follows zero order kinetics with $NH_4OH$ concentration (see Figures 3 and 4). The temperatures investigated here were 10, 15, 25, and 35 °C. An Arrhenius expression was used to fit the experimental data yielding an apparent activation energy of 7.2 kJ/mol (Figure 5).

Figure 6 shows the polarization curves at various $NH_4OH$ concentrations under static conditions. The currentpeak at −0.33 V (SCE) in the anodic branch can

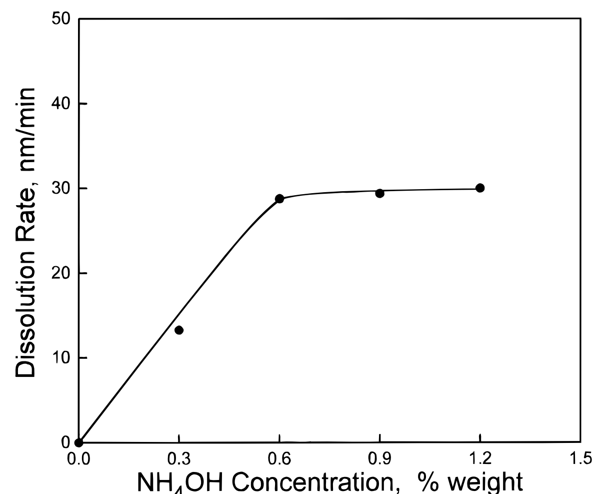



**Figure 4.** Effect of $NH_4OH$ concentration on copper dissolution rate at 1650 rpm and 25 °C. Solution pH is fixed at 11.0 by adding 1 M NaOH.

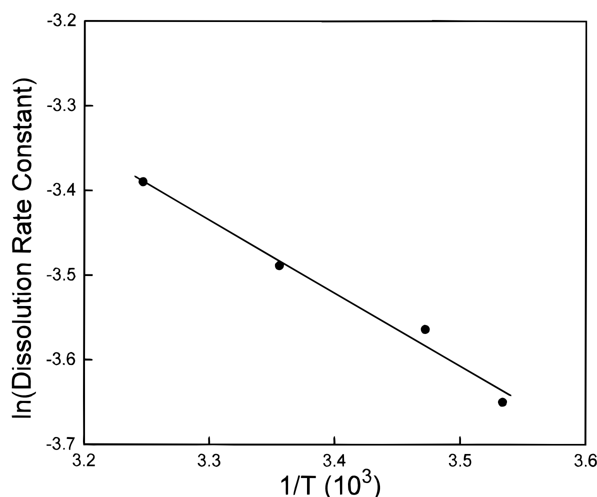



**Figure 5.** Arrhenius plot for the copper dissolution rate constants in 1.5 wt % $NH_4OH$ solution (pH ~ 10.5) at 1650 rpm. The dissolution follows zero-order kinetics with respect to $NH_4OH$ under these conditions. The apparent activation energy is 7.2 kJ/mol.

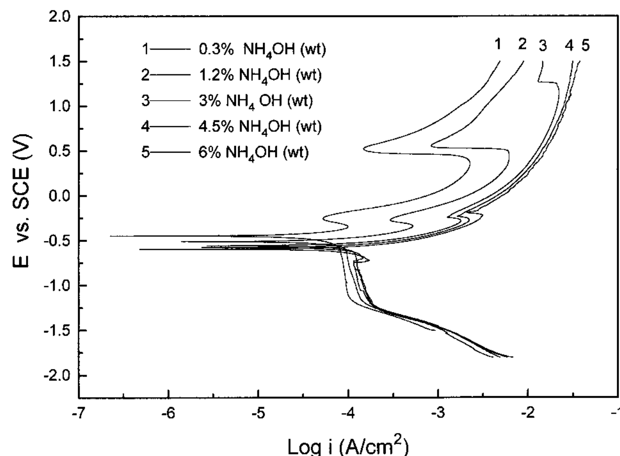



**Figure 6.** Polarization curves at various concentrations of $NH_4OH$ in stagnant solutions.

be ascribed to the formation of $Cu_2O$[8] and the current peak at 0.3 V (SCE) is due to the formation of CuO film. At higher $NH_4OH$ concentrations, the second peak is either absent or shifted to much higher voltages. In the cathodic branch, the reduction of oxygen is at its

**Table 1. Solution pH's and $E_{corr}$ Values in Figure 6**

| $NH_4OH$ concn (%) | 0 | 0.3 | 0.6 | 0.9 | 1.2 | 3 | 4.5 | 6 |
|---|---|---|---|---|---|---|---|---|
| solution pH | 6.5 | 10.9 | 11.2 | 11.4 | 11.5 | 11.9 | 12.2 | 12.4 |
| $E_{corr}$ (vs SCE) | −0.19 | −0.44 | −0.47 | −0.49 | −0.51 | −0.55 | −0.57 | −0.59 |
| $i_{corr}$ (mA/cm$^2$) | 0.00049 | 0.10 | 0.09 | 0.18 | 0.18 | 0.38 | 0.42 | 0.44 |

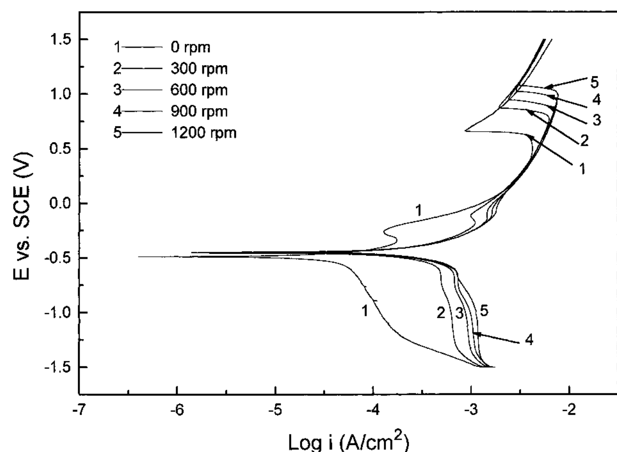



**Figure 7.** Polarization curves at various rotational speeds of the copper disk electrode. The concentration of $NH_4OH$ is 0.6 wt %.

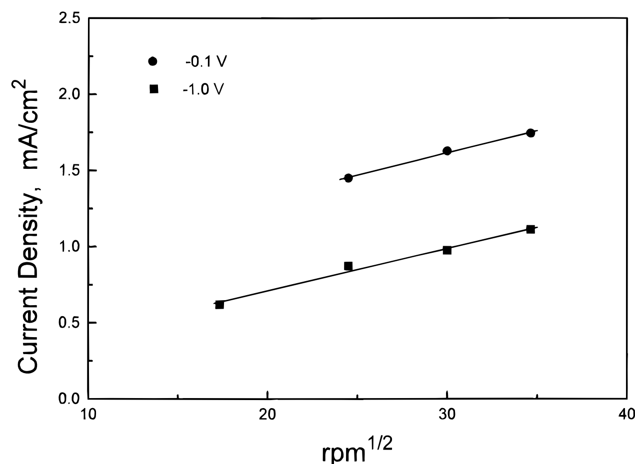



**Figure 8.** Plot of current density vs rpm$^{1/2}$ at various potentials.

limiting value prior to intersecting the anodic branch on the activation potential region of the copper oxidation, indicating that the rate of dissolution of copper in aerated aqueous ammonia (at least above 1.2 wt % $NH_4OH$) is controlled by oxygen diffusion. The solution pHs and $E_{corr}$ are listed in Table 1 for these solutions. In this table, a 0.1 M $Na_2SO_4$ solution is used when the $NH_4OH$ concentration is zero. It can be seen from this table that the current density ($i_{corr}$) increases with $NH_4OH$ concentration. At low $NH_4OH$ concentrations such as 0.3 wt %, considering both the anodic and cathodic branches, it appears that the copper removal is controlled by the dissolution of the oxide film formed on copper surface as well as the diffusion of oxygen or dissolution products or both (curve 1, controlled by mixed kinetics). $E_{corr}$ decreases with increasing $NH_4OH$ concentration due to the increased dissolution rate of the copper oxide film.

This explanation can be further verified by rotating the copper disk electrode. The results obtained using 0.6 wt % of $NH_4OH$ are shown in Figure 7. The current density is increased by rotating the electrode. The plot of current density vs (rpm)$^{1/2}$ at various voltages, as shown in Figure 8, is linear, confirming that the copper dissolution in this solution is controlled by the oxygen diffusion. Therefore, at $NH_4OH$ concentrations higher than 0.6 wt %, the copper dissolution is oxygen diffusion-controlled.

At high $NH_4OH$ concentrations ([$NH_3$] + [$NH_4^+$] = 1.0 M), Guan and Han[16] reported that the dissolution is controlled by oxygen diffusion. This conforms to the results shown in Figure 6 at high $NH_4OH$ concentrations. Figure 9 shows the effect of $NH_4OH$ concentration on the polarization behavior of copper with a constant $NaClO_3$ concentration (0.1 M) under static conditions and can be compared with Figure 6, obtained in the absence of $NaClO_3$. The anodic current density in this stagnant solution again increases significantly with $NH_4OH$ concentration while $E_{corr}$ decreases slightly. The smaller drop in the current in the anodic branches

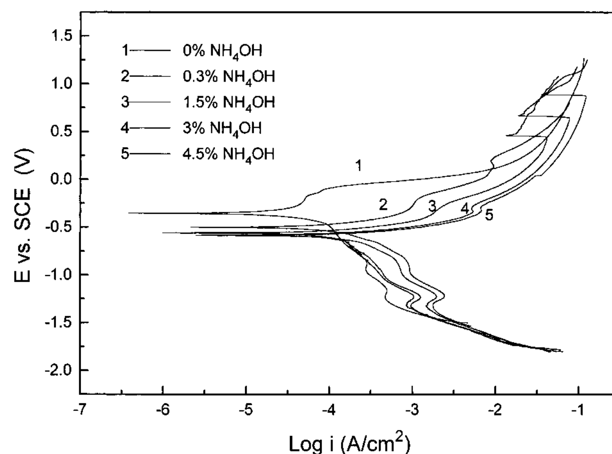



**Figure 9.** Polarization curves at various concentrations of $NH_4OH$ in the presence of 0.1 M $NaClO_3$ under static conditions.

corresponding to the two peaks, seen in Figure 6, indicates that only a very thin copper oxide film remains on copper surface. When $NH_4OH$ concentration is increased beyond 4.5 wt % (not shown in the figure), the current density increases only very slightly, implying that the dissolution is controlled by the reaction on the copper surface, and oxide film does not exist. The corresponding second peak appears at lower voltages, suggesting the easy formation of copper oxide film due to the presence of $NaClO_3$ at high $NH_4OH$ concentration.

It is necessary to have a high copper to silicon dioxide selectivity during the CMP of copper. However, a high pH will result in a high silicon dioxide polish rate[18] and, hence, a low polish selectivity of copper to silicon dioxide. To improve the polish selectivity, an alternative is to use ammonium salts instead of ammonia to lower solution pH, while maintaining a reasonable copper removal rate. To test the feasibility of this

(18) Cook, L. *J. Non-Cryst. Solids* **1990**, *120*, 152.

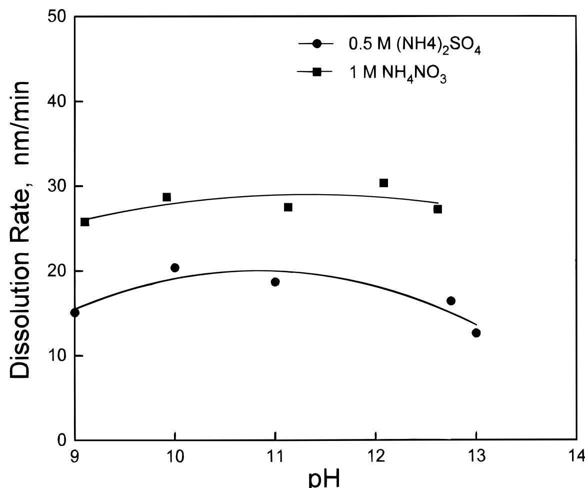
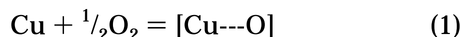



**Figure 10.** Copper dissolution rate in solutions containing ammonium salts at various pH's at 1650 rpm and 25 °C.

alternative, ammonium sulfate and ammonium nitrate were investigated. The rotational speed was fixed at 1650 rpm, and the total ammonium ion concentration was chosen as 1 M for both $(NH_4)_2SO_4$ and $NH_4NO_3$ solutions. The measured dissolution results are shown in Figure 10. The dissolution rates are lower than those obtained using aqueous ammonia directly. Interestingly, the dissolution rate in $(NH_4)_2SO_4$ is lower than that in $NH_4NO_3$. Since the surface oxidation is not the rate-determining step as stated earlier, the etch rate difference of $(NH_4)_2SO_4$ and $NH_4NO_3$ may be ascribed to $SO_4^{2-}$, which is a complexing agent,[19] inhibiting the reduction of the oxidizers on copper surface, or the extra oxidizing power of $NO_3^-$, or a combination of the two.

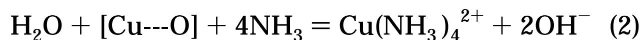
**Dissolution Mechanism.** Halpern[14] suggested many years ago the following mechanism for copper dissolution in ammonia solutions.

(1) Adsorption of dissolved oxygen onto the copper surface:



$$Cu + {}^1/_2O_2 = [Cu\text{---}O] \quad (1)$$

(2) Reaction of an $NH_3$ molecule or $NH_4^+$ with the copper−oxygen complex on the surface:



$$H_2O + [Cu\text{---}O] + 4NH_3 = Cu(NH_3)_4^{2+} + 2OH^- \quad (2)$$

or

$$[Cu\text{---}O] + 4NH_4^+ = Cu(NH_3)_4^{2+} + H_2O + 2H^+ \quad (3)$$

The cyclic polarization curve, shown in Figure 11, reveals the possible existence of copper−amine species in the dissolution process in a 0.3 wt % $NH_4OH$ solution. In Figure 11, peak A can again be ascribed to the oxidation of Cu(I) to Cu(II).[8] Peak B may be due to the formation of Cu(II) oxide phase. The existence of an oxide film on copper surface in 0.3% $NH_4OH$ solution was also reported by Carprio et al.[8] Therefore, the oxidation of copper to $Cu^+$ should be included as a separate step in the dissolution mechanism in aqueous ammonia solutions.

Step 1: the adsorption of dissolved oxygen onto copper surface.

(19) Liddell, K. C.; Bautista, R. G. *Metall. Trans. B* **1991**, *12B*, 627.

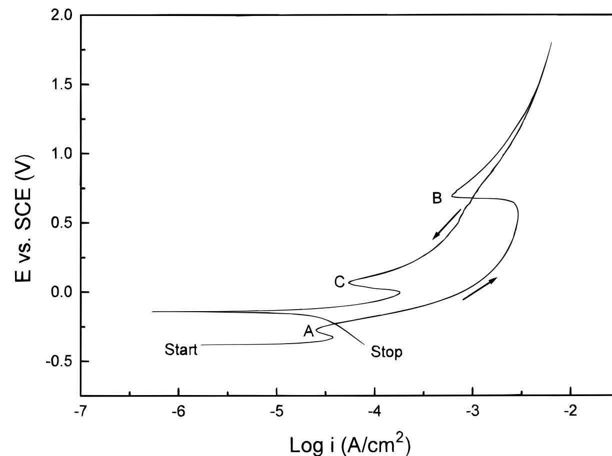



**Figure 11.** Cyclic polarization curve of copper in 0.3% $NH_4OH$ solutions. The voltage scan rate was 2 mV/s.

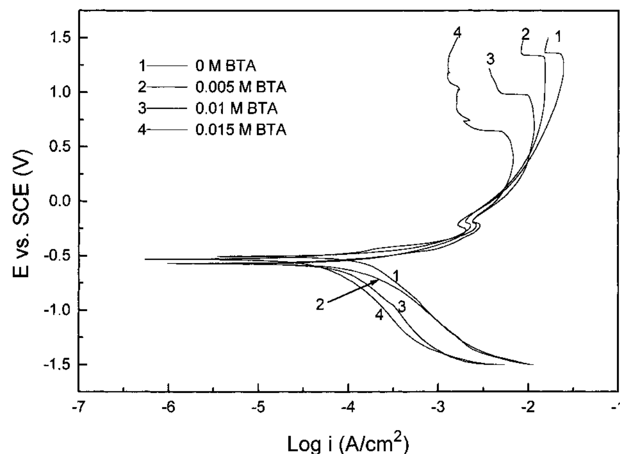



**Figure 12.** Effect of BTA concentration on the dissolution of copper in 3% $NH_4OH$ solutions under static conditions.

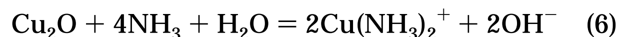
Step 2: the formation of a copper oxide film:

$$2Cu + {}^1/_2O_2 = Cu_2O \quad (4)$$

and/or

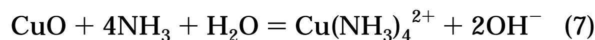
$$Cu + {}^1/_2O_2 = CuO \quad (5)$$

Step 3: Dissolution of the copper oxides:



$$Cu_2O + 4NH_3 + H_2O = 2Cu(NH_3)_2^+ + 2OH^- \quad (6)$$

and/or



$$CuO + 4NH_3 + H_2O = Cu(NH_3)_4^{2+} + 2OH^- \quad (7)$$

This mechanism will be discussed in more detail in a subsequent paper.

**Effect of Inhibitors on Copper Dissolution.** Three inhibitors, resorcinol, 8-hydroxyquinoline,[20] and BTA,[20,21] have been tested for their effectiveness in protecting copper in the recessed regions. The measurements were made under static conditions with a constant concentration of $NH_4OH$ (3 wt %). Resorcinol and 8-hydroxy-

(20) Fontana, M. G.; Staehle, R. W. *Advances in Corrosion Science and Technology*; Plenum Press: New York, 1970; Vol. 1, pp 147−218.

(21) Brusic, V.; Frisch, M. A.; Eldridge, B. N.; Novak, F. P.; Kaufman, F. B.; Rush, B. M.; Frankel, G. S. *J. Electrochem. Soc.* **1991**, *138*, 2253.

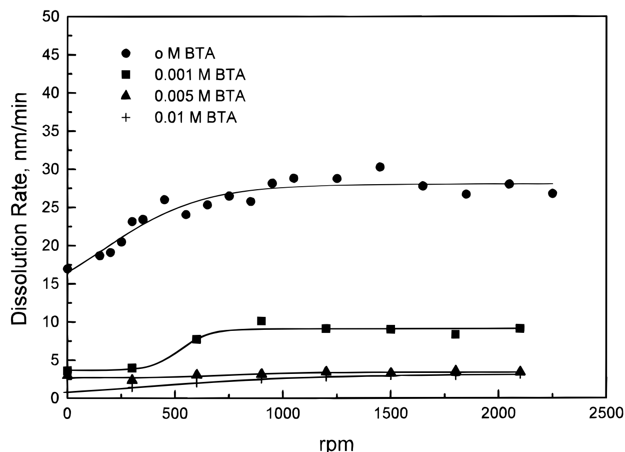



**Figure 13.** Effect of the rotational speed of the copper disk electrode on copper dissolution in the presence of BTA in 3 wt % $NH_4OH$ solution at 25 °C. The dissolution rates have been determined from the linear polarization data obtained with a voltage scan rate of 0.1 mV/s.

quinoline proved to be ineffective, and hence, only the results obtained with BTA are shown in Figure 12. Indeed, BTA demostrated the most positive corrosion potential $E_{corr}$ and the smallest corrosion current density $i_{corr}$, i.e., dissolution rate. BTA also is a very effective inhibitor under acidic conditions.[3,4] Therefore, only BTA was tested and evaluated further.

The effect of BTA concentration on copper dissolution is shown in Figure 13. An $NH_4OH$ concentration of 3 wt % was used for these measurements. As shown in Figure 13, the copper dissolution rate, obtained from the linear polarization data, increases slightly with the rotational speed of the electrode. In the absence of BTA, the maximum dissolution rate is about 29 nm/min, which is very close to the value shown in Figure 3, indicating that the electrochemical method and the weight loss method are in good agreement in determining the dissolution rate. More importantly, it is clear that even a small amount of BTA reduces the copper dissolution rate significantly. The maximum copper dissolution rate is reduced from 29 nm/min in the absence of BTA to 8 nm/min at 0.001 M BTA, and the maximum dissolution rate is further reduced to 3 nm/min as the BTA concentration is increased to 0.005 M. Further increase of BTA concentration does not enhance the protection of copper.

## Conclusions

Copper is etched in $NH_4OH$ solutions at high pH by dissolving the copper oxide film formed on the copper surface. However, the copper dissolution rate is low in various $NH_3$-containing media, ranging from about 8 to 30 nm/min. The copper dissolution rate in $NH_4NO_3$ and $(NH_4)_2SO_4$ solutions does not vary significantly with solution pH at the same concentration of $NH_4^+$, and $NH_4NO_3$ results in a higher dissolution rate. In the stagnant solution, the copper dissolution in aqueous ammonia media is controlled by mixed kinetics (surface reaction of $NH_4OH$ with copper oxides on copper surface and diffusion of oxygen and dissolution products) at low $NH_4OH$ concentrations ($NH_4OH$ concentration $\leq$ 0.3 wt %). However, at high $NH_4OH$ solutions, the dissolution is controlled by the oxygen diffusion to the copper surface.

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