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Electrochemical investigations of copper etching by $Cu(NH_3)_4Cl_2$ in ammoniacal solutions

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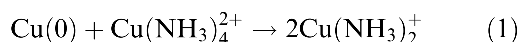
Cyclic voltammetry has been employed to investigate the mechanism of copper etching in ammoniacal buffered solutions of cupric chloride. Experiments involving an increase in the solution copper content (up to 0.5 M) and in the thickness of the copper electrode have been used to obtain a better understanding of the copper oxidation. Whatever the Cu(II) concentration, the reduction occurred in two one-electron stages leading successively to Cu(I) and Cu(0). The concentration of ammonia was an important parameter. Increasing the ratio of Cu : NH_3 favoured the formation of transient solid compounds. The expected two-step oxidation of copper was observed only for thin layers of electroplated copper. The determination of the corrosion current in etching solutions suggests that copper oxidation involves the formation of solid cuprous compounds.

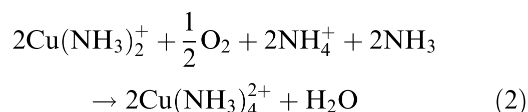
1. Introduction

The anodic behaviour of copper in alkaline solutions has been studied widely. Numerous spectroscopic and electrochemical studies have focussed on the formation of passivating layers [1–4] and on the influence of the anion on the anodic behaviour of the copper [5–7]. However, there is little information [8–11] on copper oxidation in ammoniacal solution, in spite of its practical significance in the electronics industry.

Copper etching in ammoniacal solution is generally used in the manufacture of printed circuit boards. The process involves the oxidation of metallic copper by an ammoniacal cupric complex leading to an ammoniacal cuprous complex (Equation 1). Concomitantly, the cuprous complex is oxidized by oxygen in order to regenerate the starting cupric complex (Equation. 2):



$$Cu(0) + Cu(NH_3)_4^{2+} \rightarrow 2Cu(NH_3)_2^{+} \qquad (1)$$



$$2Cu(NH_3)_2^{+} + \frac{1}{2}O_2 + 2NH_4^{+} + 2NH_3 \rightarrow 2Cu(NH_3)_4^{2+} + H_2O \qquad (2)$$

The concentration of copper in spent solutions is generally large (more than $150\,g\,dm^{-3}$). Several processes [12–14] have been conceived for copper extraction in order to regenerate the etching solution. In this context, it may be interesting to optimize the etching rate of copper and the recycled solution flow.

In the present study, the electrochemical corrosion of copper in ammoniacal cupric complex solutions has been investigated. The main goals were to obtain a better understanding of the mechanism of copper corrosion in these solutions and to validate analytical tools which would be used in research into new recyclable solutions for copper etching.

2. Experimental details

2.1. *Chemicals*

All the solutions were prepared with commercial chemicals (Aldrich) and distilled water. The ammoniacal Cu(II) solutions were prepared by adding $CuCl_2$, $2H_2O$ in ammoniacal buffers (NH_3, H_2O; NH_4Cl). Electroplated copper electrodes were prepared by reduction of cupric sulfate (1 M $CuSO_4$ in 1 M H_2SO_4 solutions) at a platinum electrode.

2.2. *Electrochemical procedures*

Commercial instrumentation (PAR, model 362) was employed for all voltammetry and coulometry experiments. Data were recorded on a Kipp and Zonen X–Y recorder. A conventional three-electrode configuration with an aqueous saturated calomel electrode (SCE) was employed. A Luggin probe was used to minimize resistance effects. The counter electrode was a graphite rod. All the experiments were carried out at room temperature and under nitrogen atmosphere. The potentiodynamic tests were conducted at potential scan rate of $50\ mV\ s^{-1}$.

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The working electrode was either a disc of vitreous carbon (3 mm diam.), platinum (1 mm diam.) or copper (2 mm diam.). The copper electrodes were made from a copper rod (99.99%) embedded in an epoxy resin. The thin layers of electroplated copper were obtained by controlled current electrodeposition at a platinum electrode with a current density of 0.6 mA cm^{-2}. The calculated thickness of the layers was checked for some samples by anodic stripping in 0.5 M H_2SO_4 solutions. A copper wire (2 mm diam.) was used in the study of corrosion. Except for experiments with thin layers of copper, the electrodes were polished with emery-paper up to grade 4000 and then carefully rinsed with distilled water before use.

3. Results

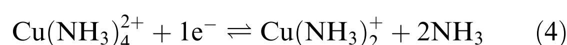
The copper concentration in the etching solutions is large in order to allow fast corrosion rates of metallic copper. This corrosion phenomenon is difficult to study by electrochemical methods. The use of high cupric complex concentrations and copper layers of variable thickness allowed us to investigate copper oxidation.

3.1. *Voltammetry of ammoniacal cupric complex*

The electrochemical behaviour of ammoniacal cupric complex in an ammoniacal buffer was investigated by cyclic voltammetry at vitreous carbon electrodes. Cyclic voltammograms (Fig. 1) exhibited two cathodic monoelectronic peaks C1 and C2 at potentials of −0.22 and −0.84 V vs SCE, respectively. The backward potential scan showed two anodic peaks A2 and A1 at −0.32 and −0.15 V vs SCE. The peak current of A1 corresponded to a one electron process. The higher value of the peak current of A2 was due to the redissolution of copper electrodeposited during the forward potential scan. The two stage reduction of ammoniacal cupric complex has already been observed by polarography or potentiometry [15–21].

3.1.1. Reversible reduction of Cu(II) complex. The redox couple Cu(II)/Cu(I) is a reversible system as shown by the current ratio, i_{pa}/i_{pc} of the peaks A1 and C1 being close to one. The stability constants $\beta 1$ and $\beta 2$ of the ammoniacal cupric and cuprous complexes are known to be $\log \beta 1 = 10.80$ and $\log \beta 2 = 12.59$ [22]. The standard potential of the system $Cu(NH_3)_4^{2+}/Cu(NH_3)_2^+$ is calculated by Equation 3 [23] ($E^\circ_{cal} = +0.053$ V vs ENH or −0.189 V vs SCE with $E^\circ_{Cu^{2+}/Cu^+} = +0.158$ V vs ENH [23]), This value is in good agreement with our experimental observations ($E^\circ_{exp} = -0.185$ V vs SCE ; $E^\circ_{exp} = 0.5\,(E_{pA1} + E_{pC1})$). The peaks C1 and A1 may be attributed to the reversible reaction (Equation 4) as reported elsewhere [21–24].

$$E^\circ_{Cu(NH_3)_4^{2+}/Cu(NH_3)_2^+} = E^\circ_{Cu^{2+}/Cu^+} + \frac{RT}{F}\ln\left(\frac{\beta_1}{\beta_2}\right) \quad (3)$$



$$Cu(NH_3)_4^{2+} + 1e^- \rightleftharpoons Cu(NH_3)_2^+ + 2NH_3 \quad (4)$$

The difference in the number of ammonia ligands in the Cu(I) and Cu(II) complexes suggests that the overall reaction (Equation 4) involves the decoordination of ligands. By investigating the effect of the ammonia concentration on the kinetics, Shumilov *et al.* [21] and Brown *et al.* [24] have concluded that the reduction occurs on the triammine complex $Cu(NH_3)_3^{2+}$.

The linearity between the peak current of C1 and the copper concentration (from 10^{-3} to 10^{-1} M) showed that the Cu(II) reduction was under diffusional mass transport control.

3.1.2. Reduction of Cu(I) complex. At the second cathodic peak C2, the electrodeposition of copper occurred as shown by the redissolution peak A2. The redox system Cu(I)/Cu(0) is slow and its potential depended on the electrode / electrolyte interface. The reduction of cuprous complex to copper began at −0.69 V vs SCE but during the anodic scan the copper electrodeposition continued to −0.5 V vs SCE

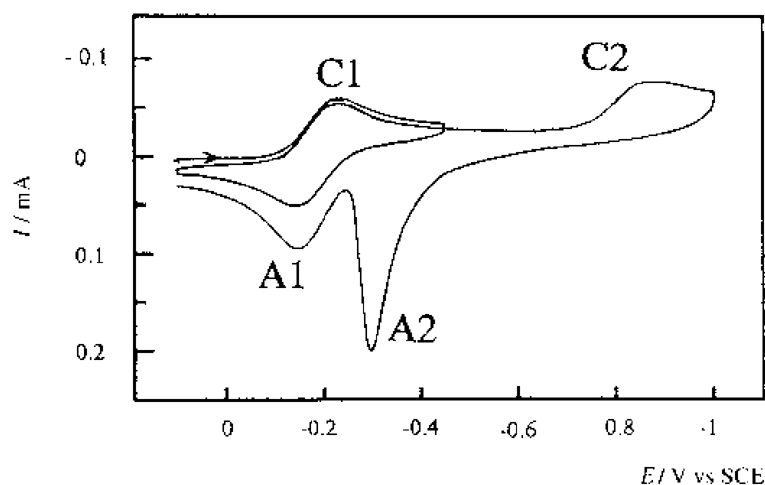


Fig. 1. Cyclic voltammetry of cupric ammoniacal complex at a vitreous carbon electrode, (0.5 M NH_3, H_2O; 0.5 M NH_4Cl; 5×10^{-2} M Cu (II)).

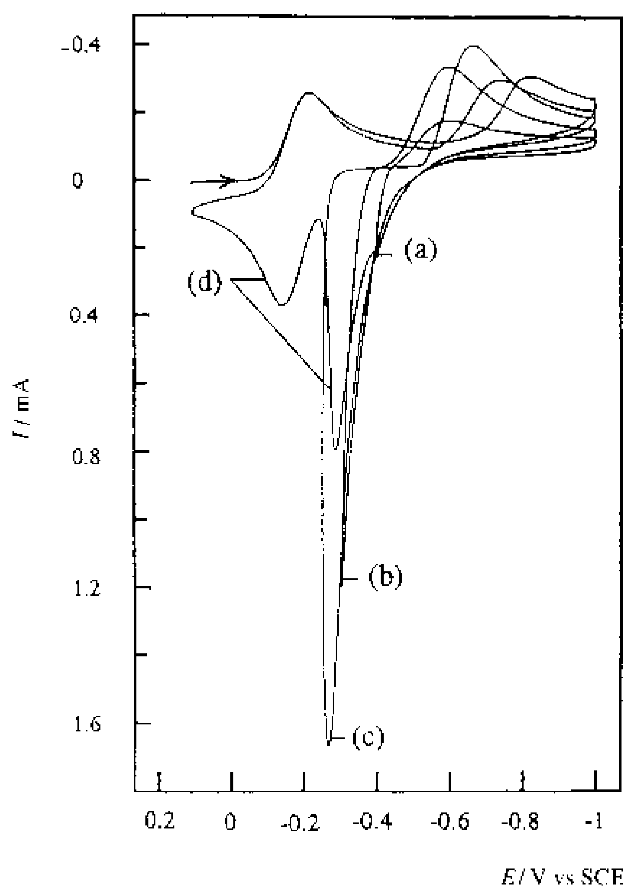


Fig. 2. Cyclic voltammetry of cupric ammoniacal complex (vitreous carbon electrode, 0.5 M NH_3, H_2O; 0.5 M NH_4Cl; 10^{-2} M Cu (II)) with various reversal potentials during the anodic scan: (a) −0.4, (b) −0.3, (c) −0.25 and (d) 0.1 V vs SCE.

(Fig. 1) showing that the electron transfer was faster at a copper electrode than at vitreous carbon.

The cathodic peak potential of $Cu(NH_3)_2^+$ depended on the remaining copper at the cathode as shown in Fig. 2, after reversing the anodic scan before the oxidation was complete. During the first scan the reduction potential of the ammoniacal cuprous complex was −0.84 V vs SCE and when the cathode was covered by the copper, the reduction became easier and occurred at −0.60 V vs SCE.

3.2. *Oxidation of copper*

3.2.1. Oxidation of bulky copper electrode. The electrochemical oxidation of a bulky electrode was investigated by cyclic voltammetry in 0.5 M ammoniacal buffer solutions (Fig. 3). The copper oxidation was characterized by three peaks. The first peak A2, which appeared at −0.13 V vs SCE, may be attributed to oxidation leading to the cuprous complex. The peak A3 at 0.05 V vs SCE was sharp and characteristic of a surface reaction. The third peak A4 occurred at 0.17 V vs SCE and was followed by a current limitation.

By waiting for different periods of times at a potential situated between peak A3 and A2, ($E = -0.08$ V vs SCE) and then reversing the potential scan, the shape of peak C2 was modified. There was a significant change in the cathodic current after peak C2 (Fig. 3). The current decreased more slowly when the waiting time was increased. This suggests a slow dissolution of an oxidized copper compound leading to reducible cuprous complex.

When copper was oxidized in a 3 M ammoniacal buffer solution, analogous behaviour was observed but with larger oxidation currents, showing that the anodic oxidation was dependent on the composition of the solution.

3.2.2. Oxidation of electrogenerated copper. In bulky copper electrodes the oxidable substrate is unlimited and this does not facilitate the interpretation of the voltammograms. By electrogenerating copper layers of different thicknesses and oxidizing them in the same solution, the anodic behaviour of copper would be analysed with more accuracy. The use of electrogenerated copper layers avoids the contribu-

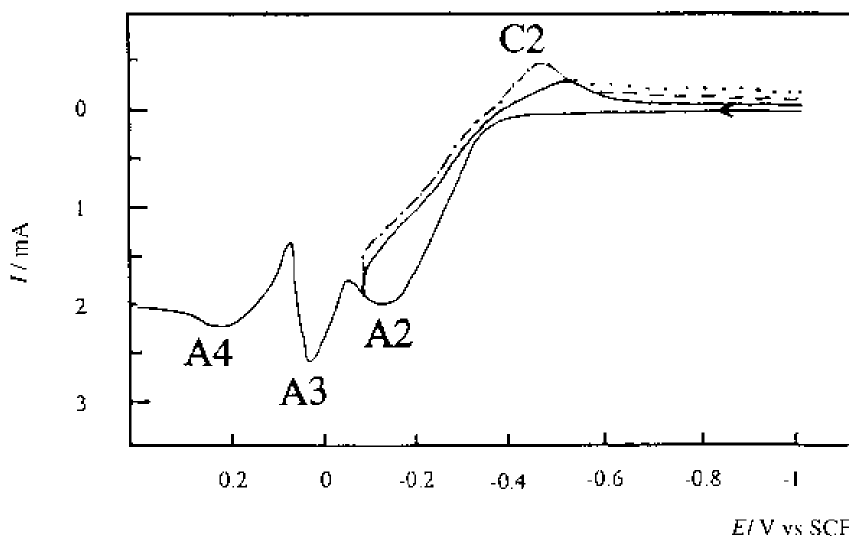


Fig. 3. Oxidation of a bulky copper electrode in 0.5 M ammoniacal buffer solution with increasing times of halt at −0.08 V vs SCE: (a, —) 0, (b, – –) 2 and (c, · · ·) 4 min.

tion of unlimited substrate in the electrochemical oxidation.

Some research has made use of electroplated copper electrodes to study copper oxidation in KOH or NaOH solutions [25] and there has been work using variable thickness of the copper layer [26, 27]. De Medina *et al.* [27] have demonstrated that by keeping the oxidation product for different times at zero current potential, the Cu(OH) initially formed is chemically transformed into the more stable Cu_2O.

When the electrode potential was held at −0.6 V vs SCE in order to thicken the electrodeposited copper, the voltammetric scans revealed the influence of increasing quantities of copper on its oxidation. The Cu(I) species provided by the anodic oxidation may be analysed by their anodic (Fig. 4) and cathodic (Fig. 5) behaviour.

Whatever the duration of copper electrodeposition, the expected anodic peaks A2 and A1, were observed (Fig. 4) but with a potential shift to less negative values when the copper quantity increased. The peak A1, which may be attributed to the overall oxidation of $Cu(NH_3)_2^+$ to $Cu(NH_3)_4^{2+}$ cannot be measured with accuracy. However, when the peak current A2 increased, the peak C1 which corresponds to the reduction of Cu(II) complex to Cu(I) complex, increased continuously.

When the electrode potential was held at −0.6 V vs SCE during growth times and then the anodic potential scan was reversed after the copper redissolution peak A2, the cyclic voltammogram (Fig. 5) showed that the cathodic peak corresponding to cuprous complex did not increase continuously with the thickness of the electrodeposited copper layer.

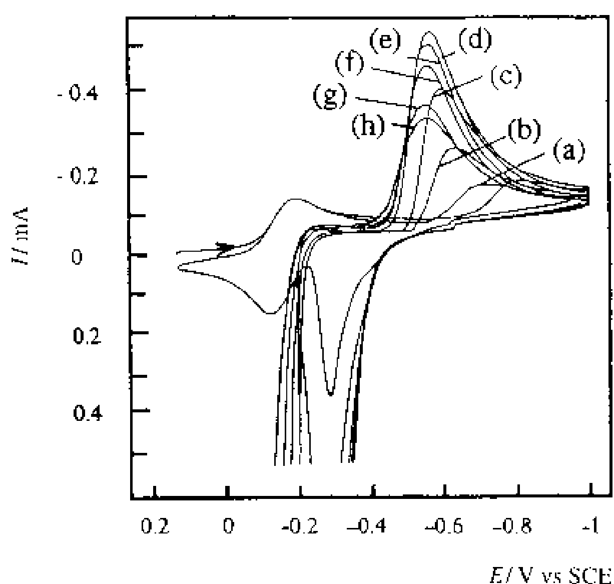


Fig. 5. Oxidation of copper electrodeposited at −0.6 V vs SCE (vitreous carbon electrode, 0.5 M NH_3, H_2O; 0.5 M NH_4Cl, 10^{-2} M Cu (II)) with increasing times of halt: (a) 0, (b) 1, (c) 2, (d) 4, (e) 5, (f) 7, (g) 8 and (h) 9 min.

Thicker copper layers were prepared at platinum electrode (1 mm diam.). In a 5×10^{-2}M ammoniacal cupric solution (Fig. 6), when the layer thickness was increased to 1.1 μm, the copper oxidation still showed the two oxidation peaks A2 and A1, but the shape of peak A1 changed. The current decreased rapidly to the null value as for a passivation phenomenon. The oxidation at peak A1 is not the cuprous complex oxidation to cupric complex which has been observed during the oxidation of thinner layers (Fig. 4). Indeed, during the following potential cathodic scans

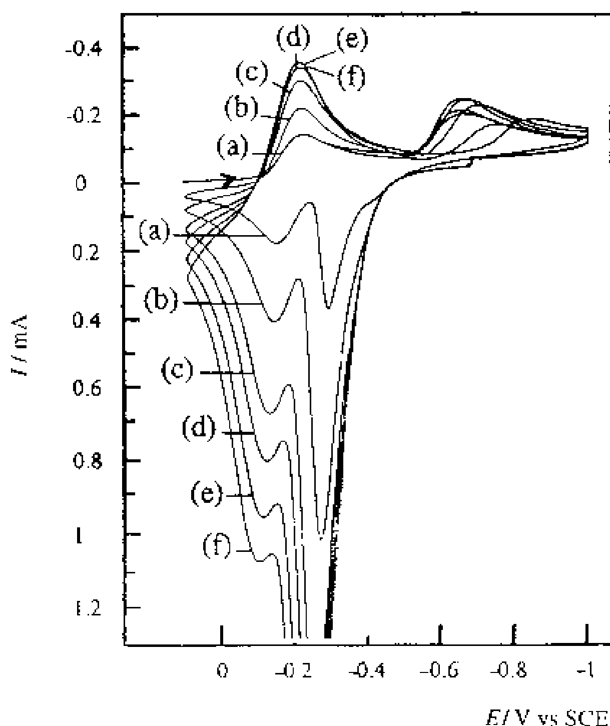


Fig. 4. Oxidation of copper electrodeposited at −0.6 V vs SCE (vitreous carbon electrode, with different times of electrodeposition: (a) 0, (b) 1, (c) 2, (d) 3, (e) 4 and (f) 5 min.

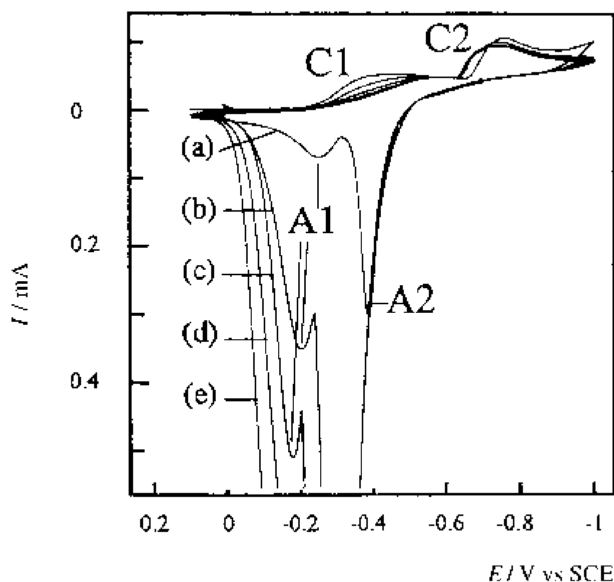


Fig. 6. Oxidation of copper electrodeposited at −0.7 V vs SCE (platinum electrode, 3 M NH_3, H_2O; 3 M NH_4Cl; 5×10^{-2} M Cu (II)) at different holding times. (a) 0, (b) 2, (c) 4, (d) 6 and (e) 8 min.

the reduction at peak C1 did not show an increase of the cathodic current.

3.2.3. Oxidation of copper layers. The oxidation of electrogenerated copper layers in ammoniacal cupric solution gave valuable but limited information, because the electrodeposited copper was not controlled and the electrochemical behaviour of cupric complex affected the copper layer oxidation. The use of copper layers electrodeposited *ex situ* allowed a quantitative analysis of copper oxidation without interference from the electrochemical behaviour of the cupric complex.

The oxidation of thin copper layers gave rise to voltammograms similar in shape to those obtained previously (Fig. 7(a)). The typical redissolution peak A2 appeared at −0.28 V vs SCE followed by a second peak A1 at −0.09 V vs SCE. For very thin layers (around 0.03 μm) the copper oxidation to cuprous complex was complete as indicated by current integration, Q_A.

For thicker layers, the redissolution yield decreased with increase in thickness (Table 1). This observation indicated that the electrodeposited copper was not completely oxidized at peak A2. When the layer depth reached around 0.40 μm, the voltammogram was similar to that of a bulky copper electrode (Fig. 7(b)). The first anodic peak A2 appeared at −0.19 V vs SCE and lost the typical shape of a redissolution peak. The sharp second peak, which occurred at −0.04 V vs SCE corresponded to a surface phenomenon (like A3 in Fig. 3) and a third peak emerged at 0.05 V vs SCE. However, in contrast to bulky copper oxidation, there was no current limitation after the third peak and the current decreased to the null value. By adding concentrated ammonia to this solution and oxidizing a copper layer of 0.40 μm thickness, the voltammogram presented two anodic peaks A2 and A1 at potentials of −0.22 and −0.10 V vs SCE before the current decreased to the null value.

Table 1. Coulometric measure of the anodic oxidation of thin layers of electrodeposited copper

Media		*Electrodeposited copper layer*		*Oxidation*[*]	*Ratio*
NH_3,H_2O(M);	NH_4Cl(M)	$10^{-4}Q_C$/C	e/μm	$10^{-4}Q_A$/C	Q_A/Q_C
0.5	0.5	3.10	0.029	3.20	1
0.5	0.5	6.06	0.057	4.34	0.72
0.5	0.5	12.12	0.113	6.80	0.56
0.5	0.5	24.19	0.227	11.80	0.49
0.5	0.5	48.06	0.452	†	–
1.4	0.5	48.04	0.452	18.70	0.39
3	3	48.13	0.452	13.50	0.28

[*] Integration of the current of peak A1.
† Overlap of peaks A1 and A2.

By oxidizing thick copper layers in a 3 M buffer ammoniacal solution, the two anodic peaks A2 and A1 appeared at potentials of −0.27 and −0.17 V vs SCE. The addition of concentrated ammonia to the solution did not modify the shape of the voltammogram. A negative displacement of the peak potentials occurred. Although the concentration of ammoniacal solution was high, the copper oxidation was not complete at peak A2.

The reverse scan gave two cathodic peaks C1 and C2 at −0.35 and −0.6 V vs SCE for the thinnest layers but no activity for the thickest ones. However, a detailed voltammogram showed that there was always reduction at −0.6 V vs SCE of the compound obtained at the peak A2 (Fig. 7(c)). The electrode inactivity during the backward scan run from 0.2 V vs SCE may be attributed to the fact that there was no metallic copper remaining on the platinum electrode. In order to research passivated copper, the electrode was rinsed in deoxygenated ammoniacal solution and a further anodic stripping was carried out in ammoniacal buffer solution. The electrode showed no activity, which proved that there was no remaining metallic copper at the electrode.

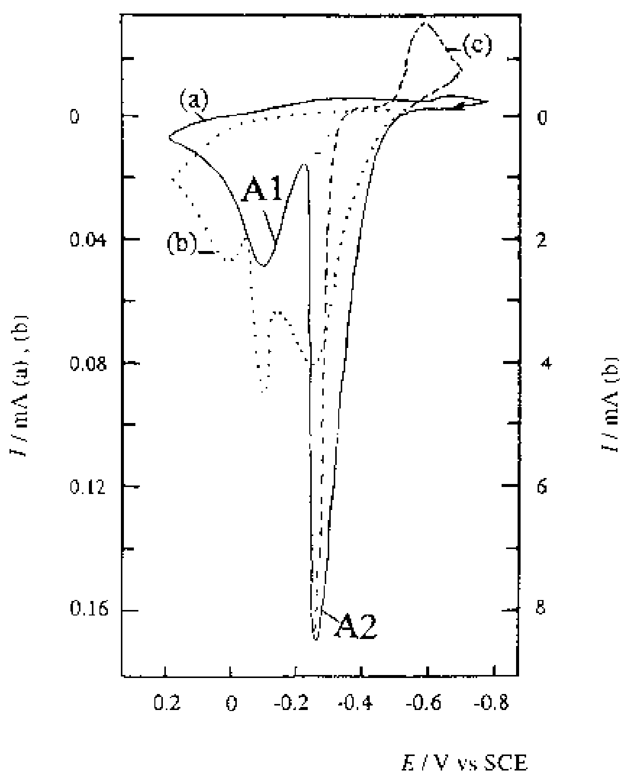


Fig. 7. Oxidation of electrodeposited copper layer in 0.5 M buffer ammoniacal solution. (a, —) 0.03 μm copper layer depth, reverse scan from 0.2 V vs SCE; (b, ····) 0.40 μm copper layer depth.; (c, – – – –) 0.03 μm copper layer depth, reverse scan from −0.23 V vs SCE.

3.3. *Corrosion potential of Cu(0) in $Cu(NH_3)_4Cl_2$ solutions*

The corrosion of bulky copper electrodes was carried out in cupric ammoniacal solutions. The corrosion potential was measured and the corrosion current density (i_{corr}) was calculated from weight loss. The current (i_c) of cupric reduction to cuprous complex at

Table 2. Corrosion parameters of the copper etching in cupric ammoniacal solutions

Media		E_{corr} vs SCE/V	i_c / mA cm^{-2}	i_{corr} / mA cm^{-2} $t = 4$ min	$t = 6$ min	$t = 8$ min
Cu (II) NH_3, H_2O NH_4Cl	1.1 M 4.9 M 2.9 M	−0.374	22.5	35.9	30.8	23.6
Cu (II) NH_3, H_2O NH_4Cl	0.5 M 3 M 3 M	−0.315	12.5	21.1	18.3	11.7
Cu (II) NH_3, H_2O NH_4Cl	0.05 M 3 M 3 M	−0.423	1.2	*	*	*
Cu (II) NH_3, H_2O NH_4Cl	0.05 M 0.5 M 0.5 M	−0.295	1.3	*	*	*

* Etching was too low and i_{corr} was not calculated.

a stationary carbon vitreous electrode was measured at the corrosion potential. Data are shown in Table 2.

The corrosion potential decreased with time and stabilized within a few seconds but returned to its initial value when the electrode was shaken. As expected, when the cupric complex concentration was increased in the ammoniacal buffer solution, the corrosion potential shifted positively. The current density of the cupric reduction to cuprous complex reached a steady value within a few seconds.

Surprisingly, the mean etching rate calculated from weight loss depended strongly on the immersion duration of the copper electrode in the ammoniacal cupric solutions. The rate, calculated from the weight loss during the two last minutes of different immersion durations (4, 6 and 8 min) revealed that the etching rate did not reach a steady value, as did the potentials.

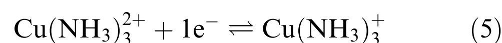
When the Cu(II) concentrations were 1.1 M or 0.5 M, the i_{corr} values determined for 4 and 6 min immersion were higher than the i_c values. After oxidation of copper electrodes in ammoniacal solutions, the presence of metallic copper was previously detected in the anodic deposits[10]. The difference between i_c and i_{corr} might be due to loss of metallic copper during the etching, increased by the convection phenomenon.

In order to prove the loss of copper, controlled current oxidations of a bulky copper electrode were carried out. When copper wires were oxidized in 3 M ammoniacal buffer solutions, a dense film was produced on the electrode. This material ran down the electrode and dropped into the solution where it slowly dissolved. Weight losses were close to the values calculated by Faraday's law for a one electron oxidation leading to cuprous compound.

4. Discussion

The voltammetric behaviour of ammoniacal cupric solutions shows that copper is oxidized in two steps and that its oxidation by Cu(II) complex leading to ammoniacal cuprous complex may be thermodynamically possible. Indeed the corrosion potentials of copper in etching solutions correspond to the first oxidation peak (A2) of copper and to the first reduction of cupric complex.

The couple Cu(II)/Cu(I) is reversible and previous research [24] have established that the triamine species (Equation 5) is an intermediate in the redox reaction.



$$Cu(NH_3)_3^{2+} + 1e^- \rightleftharpoons Cu(NH_3)_3^{+} \quad (5)$$

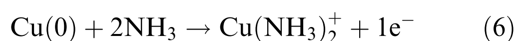
Owing to this reaction, the initial cupric complex cannot supply all the ammonia ligands consumed by the oxidized copper. During the copper oxidation, various coordinating species (NH_3, Cl^-, H_2O) in the solution are implicated in the process. Thus, when the ammonia concentration is low with respect to the quantity of oxidized copper, the formation of different cuprous compounds may be expected. Such compounds are not directly detected by their oxidation or reduction probably because they are solid products. However, many observations agree with the hypothesis. (i) Whereas thin copper layers are oxidized with quantitative coulombic yield, thicker layers are not fully oxidized at the potential of the first anodic peak A2, in agreement with a passivation phenomenon. (ii) Reversing the potential scan after the first anodic peak reveals a slow decrease of the cathodic current of the peak C2, in agreement with a slow dissolution of solid cuprous compound. (iii) When a copper wire is oxidized in ammoniacal buffer solution, dense products run down the electrode before dissolving in the solution.

The anodic behaviour of copper confirms the role of ammonia in etching processes: (i) during oxidation of a bulky copper electrode, there is a partial passivation which decreases when the ammonia concentration is increased; (ii) during oxidation of copper layers of increasing thickness, the shape of the dissolution peak A1 changes and the current tends rapidly to the null value. The oxidation leading to cupric compounds is accompanied by the consump-

tion of ammonia arising from the solution and cuprous complex. When the ammonia is fully consumed, copper oxidation occurs with a sharp peak which may be attributed to the formation of Cu_2O and CuCl. The competitive formation of cuprous hydroxide, oxide and chloride is generally postulated for copper oxidation in alkaline solutions without ammonia [25–28].

5. Conclusion

The role of the ammonia in the anodic behaviour of copper during the copper etching shows that in the conditions studied, the oxidation of metallic copper to cuprous complex does not follow the single Equation 6.



$$Cu(0) + 2NH_3 \rightarrow Cu(NH_3)_2^+ + 1e^- \qquad (6)$$

In the present conditions the etching reaction (Equation 1) cannot be applied to copper etching. Copper etching is not controlled by diffusional mass transport of cupric complex, as shown by the values of i_{corr} and i_c.

The present conditions of copper oxidation does not correspond to those used in copper etching in the manufacture of printed circuits where the temperature is around 50 °C and the etching is carried out under sprinkling process. However, the study has revealed some characteristics of copper oxidation in ammoniacal solutions which can be used in research into new etching solutions.

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