Solution equilibrium characteristics of electroless copper deposition on thermally-activated palladium-catalysed polyimide substrates

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Solution equilibrium characteristics of two electroless copper baths containing EDTA and tartrate as the complexing agents were studied as functions of pH. Equilibrium diagrams were constructed for both Cu-tartrate and Cu-EDTA systems. It was determined that copper is chiefly complexed as Cu_2L_2 in acidic conditions and as $Cu(OH)_2L_2^{-4}$ in alkaline conditions in the tartrate bath, and as CuA^{-2} in the EDTA bath, where L and A are the complexing tartrate and EDTA ligands, respectively. Electroless copper deposition rates were studied from a tartrate bath on thermally activated palladium-catalysed polyimide substrates as functions of copper and formaldehyde concentrations, and pH.

Keywords: *electroless copper, solution equilibrium model, deposition rate*

1. Introduction

Electroless deposition of copper is being used for a variety of applications, one of them being the development of seed metallic layers on nonconductive substrates, which are widely used in electronic circuitry [1]. The thickness of the seed layer deposited by electroless plating is usually a fraction of a micrometre; further copper thickness is consequently raised by electroplating. It is of practical importance to know the various parameters that affect the plating rate and quality of an electroless copper deposit. Much work has been done on electroless deposition in general, and electroless deposition on nonconductive substrates in particular [2–4]. However, the deposition parameters vary significantly with solution composition and characteristics, operating conditions and the types of substrate used. To provide an adequate description of the deposition processes, it is necessary to determine the nature and composition of different components present in the solution at equilibrium. It is known that the equilibrium concentrations of the electroless bath constituents depend on the relative strength of the formation constants. The amount of various components present in solution is also a strong function of variables such as pH, nature and strength of the complexing agent, ratio of the concentrations of metal to the complexing ion and operating temperature. It is thus necessary to identify the various complexes in the specific system considered. It is also essential that the limits up to which the bath can function efficiently be determined, thereby aiding the development of an efficient deposition process.

The objective of this study was to determine the equilibrium composition and concentration of two electroless copper deposition baths, one containing EDTA and the other tartrate, as complexing agents. The characteristics of each of these baths were studied using equilibrium equations, material balances, and the electroneutrality criteria. Of the two baths, tartrate was selected for performing the electroless deposition rate studies. Copper deposition rates were determined as functions of copper and formaldehyde concentrations, and pH. An empirical equation for the copper deposition rate was determined as a function of copper concentration in the operating range. The equilibrium concentrations and the copper deposition rate dependencies determined in this paper are being used as a basis for developing a mathematical model for electroless copper deposition, which will be the subject of a future publication.

2. Experimental details

The pH titration experiments were carried out for various copper–tartrate and copper–EDTA baths for the verification of the equilibrium bulk calculations. Copper sulfate, sodium hydrogen tartrate and EDTA were used. Various concentrations of these solutions were titrated against standard NaOH solutions, and the pH was monitored using a Corning-215 pH meter. NaOH was added until a pH value of 12.5 was reached.

Electroless copper deposition was carried out on thermally activated palladium-catalysed Kapton (a polyimide film marketed by Du Pont) substrates. Before plating, the substrate surface was catalysed by following the method disclosed in the US patent by Tokas *et al.* [5]. A catalyst solution comprised of 9% by weight polyamic acid, 5 parts per hundred palladium in *N*-methyl-2-pyrollidone, with aqueous ammonium hydroxide to provide a molar ratio of ammonia to palladium of 5:1, was deposited onto the Kapton substrate. The coated catalyst solution was subsequently dried by heating at $65\,°C$ to provide a polyamic acid/palladium film about $2\,\mu m$ thick. The dried catalyst film was activated by heating at $340\,°C$ for 25 min.

Electroless copper deposition experiments were carried out from baths containing various concentrations of copper, HCHO and NaOH. Tartrate was used as the complexing agent. Thermally activated palladium catalysed polyimide substrates were immersed in these electroless copper baths for time periods varying from 0.5 to 4 h. The samples were taken out, rinsed in distilled water and dried in a nitrogen atmosphere. The thickness of these samples were determined using a Magnaflux, model MR-300 plated through-hole thickness tester. Samples were plated in triplicate and the copper thickness was measured. Copper thickness values were then obtained from proper averaging. Copper concentration ranged from 2–$5\,g\,dm^{-3}$, HCHO from 4–$11\,g\,dm^{-3}$, and pH from 11.5–12.5.

The concentration analysis of copper and formaldehyde were carried out before and after deposition, and the average values were reported as their existing concentrations. Copper concentration was determined using a conventional EDTA titration using PAN indicator. Formaldehyde concentration was determined using a pH titration for the amount of NaOH formed during the addition of a known amount of sodium sulfite to a sample containing formaldehyde.

3. Equilibrium bulk calculations

For the purpose of modelling an electroless deposition system, it is necessary to know the bulk and surface concentration of the reactive species in order to determine the magnitude of mass transfer effects and reaction rates. The bulk concentrations of different species are calculated by using the equilibrium constants, material balance equations and the electro-neutrality condition. Two widely used electroless copper deposition solutions were considered for the equilibrium computations. The first one consisted of $CuSO_4$, HCHO and sodium hydrogen tartrate as the complexing agent, and the other bath contained $CuSO_4$ and HCHO with EDTA as the complexing agent. In the case of a tartrate bath, Schoenberg [6] suggested that the methylene glycol ion present in very basic solutions containing formaldehyde can enter the first coordination sphere of the copper tartrate complex. However, for the purpose of calculating the equilibrium compositions, it was assumed that form-

aldehyde does not undergo any complexation reaction with tartrate (or EDTA) and is also not chemically reactive in the conditions given above. This assumption is reasonable due to the fact that aqueous formaldehyde does not decompose up to temperatures of $300\,°C$ [7], and since HCHO is also a strong reducing agent, most of these reactions are possible in the presence of catalysts (e.g., palladium metal) only.

3.1. Copper–tartrate system

3.1.1. Determination of initial (mixing) pH. For the copper-tartrate system, the following equilibrium reactions are possible [8]:
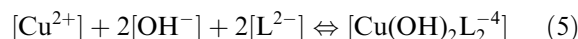
$$[Cu^{2+}] + [OH^-] \Leftrightarrow \lfloor Cu(OH)^+ \rfloor \qquad (1)$$

$$[Cu^{2+}] + 2[OH^-] \Leftrightarrow [Cu(OH)_2] \downarrow \qquad (2)$$

This precipitation reaction has a solubility product value of $2.2 \times 10^{-20}\,(mol\,dm^{-3})^2$. Since a prepared solution with $0.06\,M\,Cu^{2+}$ and $0.35\,M$ tartrate does not produce any precipitate, we can assume that this reaction does not occur at this pH and therefore
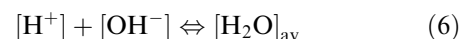
$$[Cu(OH)_2] = 0 \qquad (3)$$

The other possible reactions are

$$2\lfloor Cu^{2+} \rfloor + 2\lfloor L^{2-} \rfloor \Leftrightarrow [Cu_2L_2] \qquad (4)$$

and

$$[Cu^{2+}] + 2[OH^-] + 2[L^{2-}] \Leftrightarrow [Cu(OH)_2L_2^{-4}] \qquad (5)$$

where $[L^{2-}]$ denotes the bulk concentration of the free tartrate ligand. Water equilibrium reaction has to be accounted for

$$[H^+] + [OH^-] \Leftrightarrow [H_2O]_{av} \qquad (6)$$

where $[H_2O]_{av}$ is the concentration of water unionized in the solution. When sulfates are added into the solution, the following equilibrium is necessary:

$$[H^+] + [SO_4^{2-}] \Leftrightarrow \lfloor HSO_4^- \rfloor \qquad (7)$$

A material balance equation for each of the components present in the solution needs to be evaluated. The material balance equation for copper is

$$[CuSO_4]_{ad} = [Cu^{2+}] + \lfloor Cu(OH)^+ \rfloor + [Cu(OH)_2]$$
$$+ 2[Cu_2L_2] + [Cu(OH_2)L_2^{4-}] \qquad (8)$$

where $[i]_{ad}$ is the concentration of species added to the bulk solution.

Tartrate balance gives:

$$[NaHL]_{ad} = [L^{2-}] + 2[Cu_2L_2] + 2[Cu(OH)_2L_2^{4-}] \quad (9)$$

Sulfate is distributed as

$$[CuSO_4]_{ad} = [HSO_4^-] + [SO_4^{2-}] \qquad (10)$$

Oxygen balance yields

$$[H_2O]_{ad} + 4[CuSO_4]_{ad}$$
$$= \lfloor Cu(OH)^+ \rfloor + 2[Cu(OH)_2] + 2[Cu(OH)_2L_2^{4-}]$$
$$+ [OH^-] + 4[HSO_4^-] + 4[SO_4^{2-}] + [H_2O]_{av} \quad (11)$$

and lastly sodium balance gives

$$2[Na_2L]_{ad} = [Na^+] \qquad (12)$$

The electroneutrality constraint, which is to be combined with the above equations, is given by

$$\sum z_i c_i = 0 \qquad (13)$$

The concentrations of the unknown variables above can be obtained by simultaneously solving these algebraic equations, Equations 1, 3–13, using the subroutine NEQNJ from the IMSL library, which uses a modified Powell hybrid algorithm to determine a root of the system of equations.

3.1.2. Determination of pH for Cu(OH)$_2$ precipitation.

In the case of precipitation reactions, only one of the two equations, Equation 2 or Equation 3, holds good at any given pH. So, in order to determine the pH at which the precipitation should occur as given by the set of equations, a trial and error procedure was assumed wherein Equation 2 or Equation 3 was used and coupled with the other equations mentioned above. NaOH was added to the set of equations as a variable, thereby setting the pH as an independent variable. In the system of equations presented above, the only changes with the inclusion of NaOH would occur in the material balance equations for oxygen and sodium, Equations 11 and 12, which would be

$$[H_2O]_{ad} + 4[CuSO_4]_{ad} + [NaOH]_{ad}$$
$$= \lfloor Cu(OH)^+ \rfloor + 2[Cu(OH)_2] + 2[Cu(OH)_2L_2^{4-}]$$
$$+ [OH^-] + 4[HSO_4^-] + 4[SO_4^{2-}] + [H_2O]_{av} \quad (14)$$

and

$$[NaHL]_{ad} + [NaOH]_{ad} = \lfloor Na^+ \rfloor \qquad (15)$$

Solving Equations 1, 3, 4–10 and 13–15 up to the lowest pH at which a solution is obtained, one can determine the pH at which Cu(OH)$_2$ is expected to precipitate.
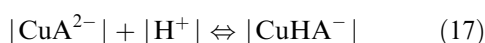
Subsequently, Equation 2 or Equation 3 is used in the corresponding region for the complete equilibrium diagram computation.

3.2. Copper–EDTA system

Unlike tartrate, EDTA is freely ionized to its tetravalent form (A^{4-}) in solution. The EDTA complexes that are assumed for the purpose of this study are as follows [9]:

$$\lfloor Cu^{2+} \rfloor + \lfloor A^{4-} \rfloor \Leftrightarrow \lfloor CuA^{2-} \rfloor \qquad (16)$$

and

$$\lfloor CuA^{2-} \rfloor + \lfloor H^+ \rfloor \Leftrightarrow \lfloor CuHA^- \rfloor \qquad (17)$$

The values for the equilibrium constants for the tartrate and EDTA reactions are given in Table 1.

Data for the equilibrium constituents and constants were obtained from the literature. The formation constants of the reactions forming different compounds and complexes are also temperature de-

Table 1. Equilibrium constants and solubility products

Equation [j]	Constant	Reference
1	1.00×10^{-7} (dm^3 mol^{-1})	Lange [8]
4	0.38×10^9 (dm^3 mol^{-1})^3	IUPAC [9]
5	5.01×10^{20} (dm^3 mol^{-1})^5	IUPAC [9]
6	1.0×10^{14} (dm^3 mol^{-1})^2	CRC [16]
7	97.0 (dm^3 mol^{-1})	Lange [8]
16	5.01×10^{18} (dm^3 mol^{-1})	IUPAC [9]
17	1.0×10^3 (dm^3 mol^{-1})	IUPAC [9]

Equation [j]	Solubility product	Reference
2	2.2×10^{-20} (mol dm^{-3})^2	Lange [8]

pendent. However, there is no sufficient data in the open literature for the formation constants and other thermodynamic properties of such reactions as a function of temperature. Thus, temperature effects have not been taken into account in these calculations.

4. Results and discussion

4.1. Copper–tartrate system

Figure 1 shows the comparison between the experimental results for the pH titration and the comparison from the equilibrium model. As one can see from the curves, the experimentally observed initial mixing pH of a solution of 0.06 M CuSO$_4$ and 0.15 M tartrate is 2.2, whereas the pH obtained in the model is 1.5. This discrepancy arises from the fact that the salts are not completely dissolved at this pH. Hence, there might be an error associated with the measurement of the experimental pH under these conditions. On addition of NaOH, the pH increases, and typical of any strong acid–base titration, there is a sudden pH change when all the acid is neutralized. The amount of NaOH that is required to neutralize the acid corresponds to the amount of free H$^+$ ions present in the system, which in turn is determined by the nature of
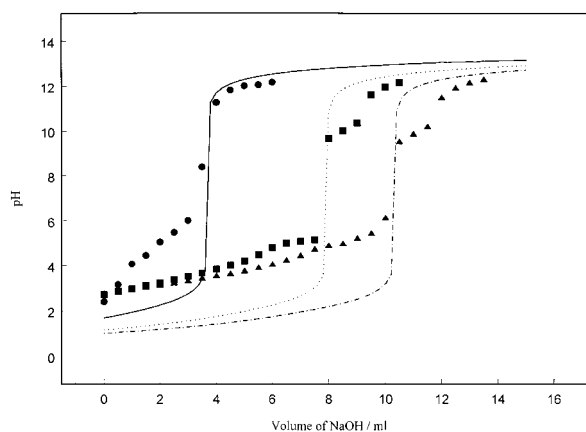

Fig. 1. Experimentally observed and theoretically predicted curves for the pH titration of 0.06 M CuSO$_4$ with various tartrate concentrations: (●) 0.06 M (exptl); (——) 0.06 M (model); (■) 0.12 M (exptl); (·······) 0.12 M (model); (▲) 0.15 M (exptl); (·–·–·–) 0.15 M (model).

the complex formed. As it can be seen here, the model predicts a jump that is in good agreement with the experimentally obtained trend. Experiments carried out with tartrate concentrations lower than 0.06 M, for a copper concentration of 0.06 M did not give consistent results due to copper precipitation. The model predictions also suggest that the copper precipitation occurs under conditions of higher copper concentration than tartrate.

The equilibrium computations for the copper–tartrate system for a concentration of 0.06 M CuSO$_4$ and 0.35 M NaHL are given in Fig. 2. One can see that copper exists as two major complexes, concentrations of which depend on the bath pH. It exists as Cu$_2$L$_2$ under acidic conditions and as a hydroxide complex Cu(OH)$_2$L$_2^{4-}$ under alkaline conditions. The existence of these two complexes have also been postulated by Schoenberg [6], from his experiments using the electron paramagnetic resonance (EPR) technique.

It can be seen from the model that the transition from the first complex to the second occurs due to the pH dependence arising from the nature of the second complex being formed. The presence of a very strong complex of the form Cu(OH)$_2$L$_2^{4-}$ causes the copper to remain in a complexed state at high pH values. The formation of a symmetric complex under low pH values explains the precipitation of copper in solution when its concentration is higher than that of tartrate.

The pH at which the transition occurs between the two above-mentioned complexes is an important region that dictates the availability of a complex of a given form for electroless deposition. For example, if the complex Cu$_2$L$_2$ is available in significant quantities in the pH conditions under which electrodeposition is carried out, the kinetics will differ significantly because of the availability of a different reactive species. Figure 3 shows the effect of this transition pH on the copper and tartrate concentrations. As the tartrate concentration increases, the transition pH goes towards a more acidic value. This can be explained by taking into account the expression for the equilibrium constant for the complex formation re-
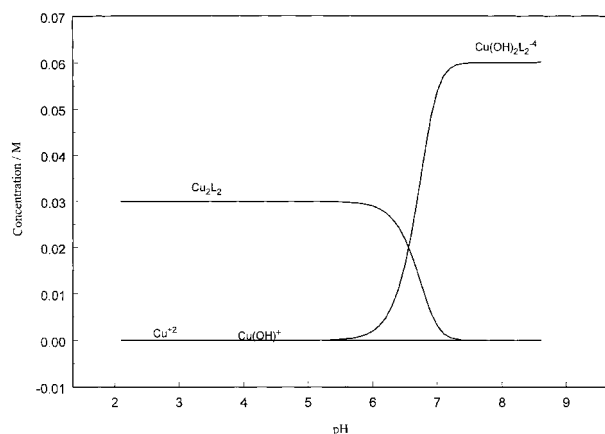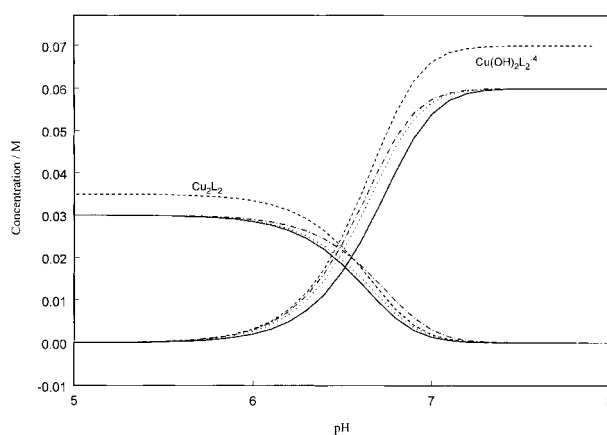

Fig. 3. Effect of copper and tartrate concentrations on the transition pH. Concentrations: (—) 0.06 M (CuSO$_4$), 0.35 M (NaHL); (·····) 0.06 M (CuSO$_4$), 0.45 M (NaHL); (−·−·−) 0.06 M (CuSO$_4$), 0.5 M (NaHL); (- - - -) 0.07 M (CuSO$_4$), 0.5 M (NaHL).

action, Equation 5. The equilibrium constant is written as

$$k_5 = \frac{[\mathrm{Cu(OH)_2\ L_2^{4-}}]}{[\mathrm{Cu}][\mathrm{OH^-}]^2\ [\mathrm{L^{2-}}]^2} \qquad (18)$$

An increase in tartrate concentration must correspondingly increase the complex concentration to maintain the equilibrium constant at a constant value. Hence an increased tartrate concentration would cause the formation of the complex at an earlier pH. One would expect a similar relationship of the transition pH with the copper concentration, which is what one observes with an increase in copper concentration as shown in Fig. 3.

The overall reaction of copper deposition from an electroless tartrate bath can be written as

$$\mathrm{CuX + 2\ HCHO + 4\ OH^-}$$
$$\rightarrow \mathrm{Cu + 2\ HCOO^- + H_2 + 2H_2O + X^{2-}} \qquad (19)$$
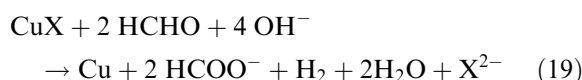
where X is a bivalent complexing molecule, which might be the complexing agent or its hydrated form. This reaction suggests that raising bath pH can increase the rate. Hence, an operation under highly alkaline conditions is desirable. Since, in the presence of the hydrated copper complex Cu(OH)$_2$ L$_2^{4-}$, the tartrate does not precipitate even under highly alkaline conditions, the more alkaline the solution, the faster will be the rate of the above reaction. However, an increase in the pH causes the copper to be complexed more strongly as dictated by the equilibrium Equation 18. Hence, according to this study, there must exist a maximum in the rate of electroless deposition as a function of bath pH. Indeed, a maximum has been recorded for the electroless copper deposition rate experimentally by several researchers [6, 10]. This maximum as a function of pH has been explained as being due to the dissociation of methylene glycol [6] and also the change in the transfer coefficient of the formaldehyde oxidation reaction [11]. Our study suggests that the maximum in the rate of copper deposition as a function of pH might also be

Fig. 2. Equilibrium diagram for the copper–tartrate system. $c_{\mathrm{CuSO_4}}$: 0.06 M, c_{NaHL} : 0.35 M.

due to the competition between copper complexation and reduction rates as a function of pH. A kinetic model taking this complexation equilibrium into account needs to be developed in order to shed more light on the effect of copper complexation on the rate as a function of pH.

4.2. Copper–EDTA system

Figure 4 shows the results obtained for the experiments carried out with various concentrations of CuSO$_4$ and EDTA. Unlike the tartrate case, the experimental curve obtained from an EDTA titration does not show a significant shift in pH at the equivalence point, which is typical of a strong acid–strong base titration. In this case, the EDTA behaves like a weak acid with different levels of dissociation. It has been shown in the literature [10] that apart from existing as EDTA^{4-}, EDTA might exist in acidic solutions as H–EDTA^{3-}, and (H$_2$–EDTA)$^{2-}$. In such a case, the pH that actually exists in the solution will be more alkaline than that would exist if it were completely dissociated. For the purpose of this study, the partial dissociation of EDTA was not taken into consideration while developing the model, since the electroless deposition experiments were to be carried out under highly alkaline conditions under which one would expect very low free H$^+$ ion concentrations. One can also see from the graph that the model predicts the equivalence point reasonably well. The model also accurately predicts the change in equivalence point with a change in concentration. In the presence of excess EDTA, the pH of the system is dependent to a negligible extent on the amount of copper present in the system. For example, the curves traced by the model and experiment are almost identical for two different copper concentrations with the same EDTA concentration. This is unlike the tartrate system, which showed a change in the transition pH with a change in copper concentration
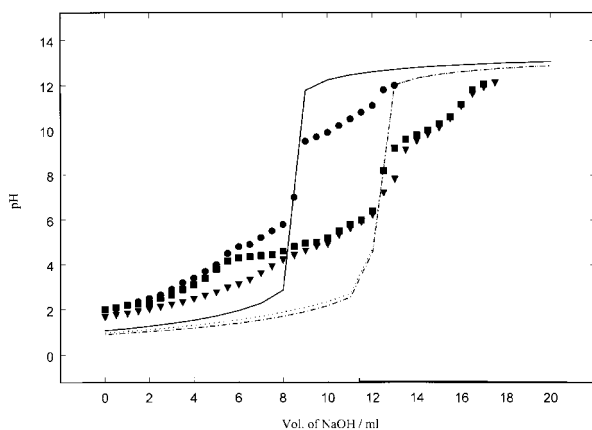
(Fig. 3). The literature data for EDTA complexation with copper shows a very high value for the equilibrium constant for the formation of a symmetric complex CuA^{2-}. This complexation reaction rate is not directly affected by the pH, and neither does the concentration of the complex formed directly affect the pH of the bath. On the other hand, in a tartrate system, a higher copper concentration for a fixed tartrate concentration causes more of the complex Cu(OH)$_2$L$_2^{4-}$ to form, thereby making the bath more acidic. In the case of EDTA, the stationary nature of the titration curve with varying copper concentration serves as an additional criterion for assuming CuA^{2-} to be the primary complexed form.

The equilibrium diagram of a copper EDTA system with a copper concentration of 0.06 M and EDTA concentration of 0.5 M is given in Fig. 5. In highly acidic conditions, the copper is present in an ionized form. At significantly low pH values (about 2.0), complete complexation of copper occurs. The copper stays as a complex until high pH values (around 12.0), where Cu(OH)$_2$ starts to precipitate.

4.3. Electroless deposition experiments

Figure 6 shows the electroless-copper thickness as a function of plating time for solutions of different pH. The copper concentration was maintained at 3.5 ± 0.1 g dm^{-3} and formaldehyde at 6.7 ± 0.2 g dm^{-3} throughout the experiments. Tartrate concentrations were maintained at high levels to minimize their influence on the copper deposition rate. The electrodeposition area to solution volume ratio was kept as low as possible ($\simeq 0.008$ cm^{-1}) in order to ensure that the concentration variations in the bulk of the electrolyte are negligible during prolonged deposition. The results obtained here show that the electrodeposition rate is nearly linear in time. The rate increases with an increase in pH, starting from a value of 0.53 mm h^{-1} during deposition with a solution of initial pH 11.75 up to 1.03 mm h^{-1} in the case of a solution with a pH of 12.25. A pH value lower than this produced a dull and non-uniform deposit.
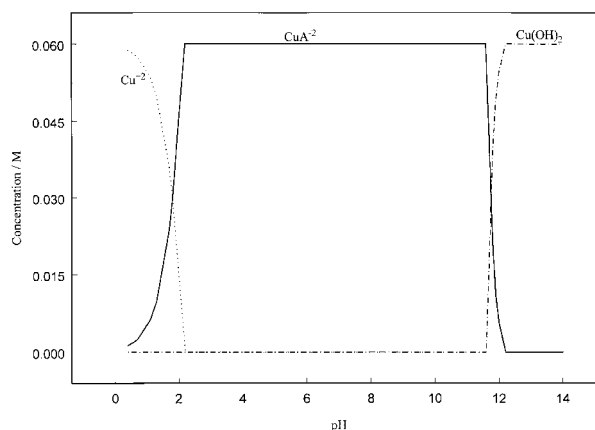

Fig. 4. Experimentally observed and theoretically predicted curves for the pH titration of various copper–EDTA concentrations: (●) 0.04 M (Cu), 0.06 M (EDTA) exptl; (——) 0.04 M (Cu), 0.06 M (EDTA) model; (■) 0.04 M (Cu), 0.08 M (EDTA) exptl; (·—·—·—) 0.04 M (Cu), 0.08 M (EDTA) model; (▼) 0.06 M (Cu), 0.08 M (EDTA) exptl; (······) 0.06 M (Cu), 0.08 M (EDTA) model.

Fig. 5. Equilibrium diagram for the copper–EDTA system. c_{CuSO_4} : 0.06 M, c_{EDTA} : 0.5 M.
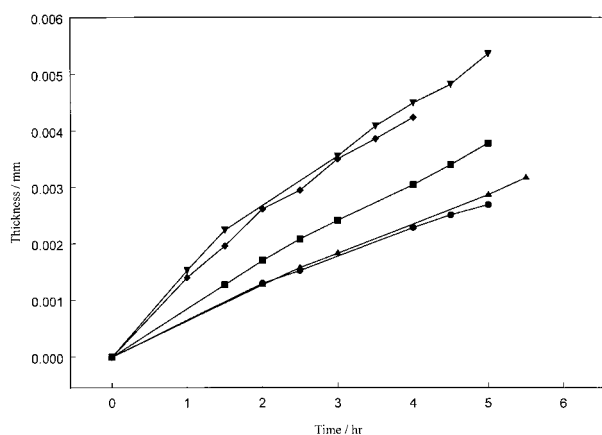
Fig. 6. Copper deposition thickness as a function of time for various bath pH. Cu: 3.5 g dm^{-3}; HCHO: 6.7 g dm^{-3}. pH: (●) 11.75, (▲) 11.9, (■) 12.02, (◆) 12.2, and (▼) 12.25.

At higher pH values than 12.25 the rate of electroless deposition does not vary appreciably suggesting that the hydroxide ion might not be the limiting component under those conditions. Between a pH of 11.9 and 12.2, there appears to be a mixed control for the occurrence of the electroless deposition reaction.

The rate of electroless copper deposition as a function of various copper concentrations in the electrolyte is given in Fig. 7. Copper concentration was varied between 2.1 and 4.4 g dm^{-3}. As one can see from the plot, there is a significant influence of copper concentration on its deposition rate. The concentration dependence of the deposit thickness on copper concentration can be written in an empirical rate form as

$$r = [Cu]^x \qquad (20)$$

where r denotes the rate of copper deposition g cm^{-2} h^{-1} and [Cu] refers to the concentration of copper as determined by quantitative chemical analysis. Figure 8 shows a plot of the log rate of copper deposition plotted against the log of copper concentration. The slope of such a plot gives the value x in Equation 20. The graph is plotted for deposits taken at different times, one after 3.5 h of deposition and the other after 4 h. Both these sets of data were averaged to deter-
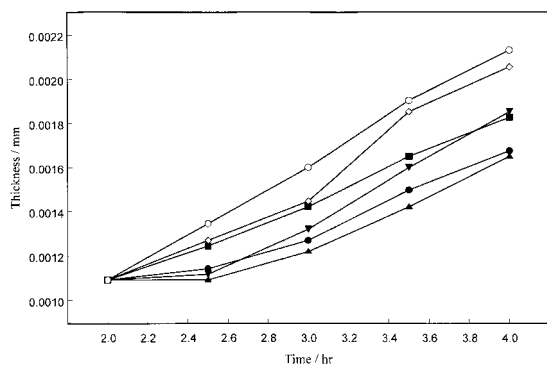
mine the deposition rate per hour, and subsequently plotted in Fig. 8. The plot shows a reasonably straight-line dependence at both these deposition conditions. The slopes were calculated to be 0.37 and 0.43, respectively. An average value can be calculated and used in the empirical rate relationship for the copper deposition rate as a function of copper concentration as

$$r = [Cu]^{0.4} \qquad (21)$$

This result for the rate dependence on the copper concentration in solution is in good agreement with the results obtained for a similar study by El-Raghy and Abo-Salama [13] on methyl methacrylate polyelectrodes and by Shippey and Donahue [14] in tartrate baths.

Figure 9 shows the dependence of the formaldehyde concentration on the electroless copper deposition thickness. Formaldehyde concentrations were varied between 4.3 and 10.5 g dm^{-3}. Copper concentration was maintained at 3.5 g dm^{-3} and the pH at 12.2. Based on the overall reaction of copper electroless deposition, Equation 19, one would expect this formaldehyde concentration range to be in excess of the requirement, and that the change in concentration would not have a significant effect on the rate. It can be seen from the graph that, as expected, the rate of copper deposition depends to a very small extent on the formaldehyde concentration. Experiments carried out for determining the rate of electroless copper deposition by El-Raghy and Abo-Salama [13] and Shippey and Donahue [14] also show that the electroless deposition rate depends on formaldehyde concentration to a much smaller extent than it does on copper and hydroxide concentration. Donahue [15] has also carried out a detailed study of the mechanisms of formaldehyde oxidation and has determined the dependence of plating rate as a function of formaldehyde concentrations over a larger range of formaldehyde concentrations. However, since the experiments carried out in this study were for a narrower range in formaldehyde concentrations (0.15–0.35 M), no appreciable change in the

Fig. 7. Copper deposition thickness as a function of time for various copper concentrations HCHO: 7.0 g dm^{-3}, pH 12.2. Cu^{2+} concentration: (▲) 1.8, (●) 2.5, (▼) 2.8, (■) 3.0, (◇) 3.5 and (○) 4.0 g dm^{-3}.
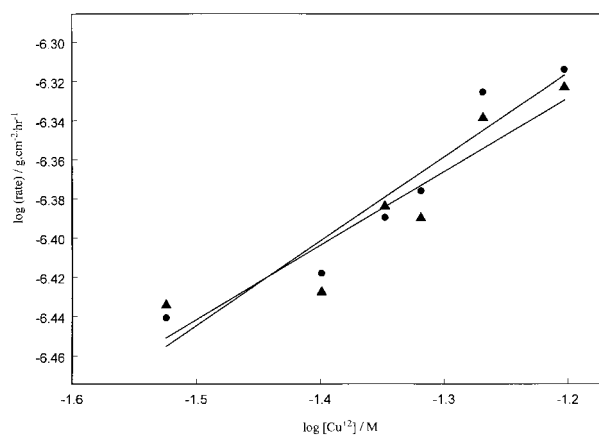

Fig. 8. Copper deposition rate as a function of copper concentration in solution.
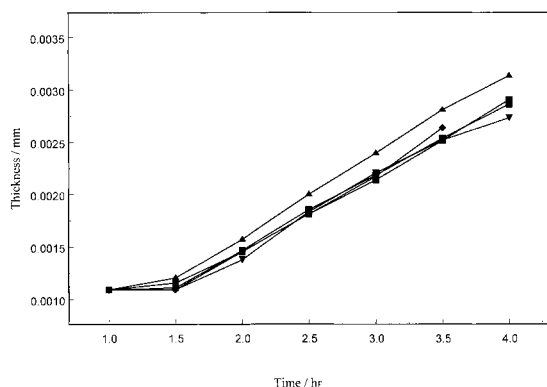
Fig. 9. Copper deposition thickness as a function of time for various formaldehyde concentrations. Cu^{2+}: 3.5 g dm^{-3}, pH 12.2. HCHO concentration: (▲) 4.38, (■) 6.57, (◆) 8.44, (■) 9.69 and (▼) 10.57 g dm^{-3}.

deposition rate was determined with a change in formaldehyde concentrations.

5. Conclusion

The solution equilibrium characteristics of two widely used electroless copper baths, namely Cu–EDTA and Cu–tartrate baths, were studied for identification and quantification of the various complexed species. Equilibrium diagrams were constructed for both Cu–tartrate and Cu–EDTA systems. It was determined that copper is chiefly complexed as Cu_2L_2 under acidic conditions and as $Cu(OH)_2L_2^{4-}$ in alkaline conditions in the tartrate bath, and as CuA^{2-} in the EDTA bath. The pH titration experiments were carried out for various concentrations of electroless copper bath constituents. The pH change was estimated from a model describing the equilibrium equations and compared with the experimentally observed pH change. Both systems predict changes in equivalence point very reasonably. The complexation constant of EDTA was much higher than that of tartrate; thereby suggesting that EDTA forms a stronger complex than compared to tartrate. The tartrate bath was used in order to study the electroless copper deposition rate since it forms an easier complex to dissociate as compared to EDTA. The experiments carried out for the rate of copper deposition showed that the deposit thickness was dependent on the pH up to a value of 12.2 above which there was negligible increase in the deposition rate

with increased alkalinity. Formaldehyde concentrations in the bath were maintained at high levels such that the rate of copper deposition was not influenced by a change in formaldehyde concentration. An empirical rate expression was determined for the copper deposit thickness as a function of copper concentration in the solution. The best deposit was obtained for a tartrate bath containing 4.4 g dm^{-3} Cu^{2+} and 5.0 g dm^{-3} HCHO at a pH of 12.2. A higher pH did not cause an appreciable change in the deposition rate and quality, whereas a lower pH caused dull deposits.

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