EQUILIBRIUM CHARACTERISTICS OF TARTRATE AND EDTA-BASED ELECTROLESS COPPER DEPOSITION BATHS

M. Ramasubramanian, B. N. Popov and R. E. White
Department of Chemical Engineering
University of South Carolina
Columbia, SC-29208
K. S. Chen
Engineering Sciences Center
Sandia National Laboratories
Albuquerque, NM 87185-0826

Abstract

Solution equilibrium characteristics of two electroless copper baths containing EDTA and tartrate as the complexing agents were studied as functions of pH, chelating agent and metal ion concentrations. Equilibrium diagrams were constructed for both Cu-tartrate and Cu-EDTA systems. It was determined that copper is chiefly complexed as Cu(OH)_2L_4 in the tartrate bath, and as CuA^-2 in the EDTA bath, where L and A are the complexing tartrate and EDTA ligands, respectively. The operating ranges for electroless copper deposition were identified for both baths. Dependence of Cu(OH)_2 precipitation on the pH and species concentrations was also studied for these systems.

Introduction

Electroless deposition of copper is being used for a variety of applications, one of them being the development of seed metallic layers on non-metals, which are widely used in electronic circuitry. Thickness of the base or seed layer electrolessly plated is usually on the order of a micron; further copper thickness is consequently raised by electroplating. It is of practical importance to know the various parameters that affect the thickness and quality of an electroless copper deposit. There has been a lot of work done on electroless deposition in general, and electroless deposition on non-metals in particular. However, the deposition parameters vary significantly with the solution composition and characteristics, operating conditions and the types of substrate used. This paper aims at describing the effect of solution composition on the copper electroless plating rate from a Cu-EDTA and Cu-tartrate bath. In order to provide an adequate description of the processes occurring during deposition, it is necessary to determine the nature and composition of different components in the solution present 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 certain variables such as the pH, nature and

---

1 This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, A Lockheed Martin Company, for the United States Department of Energy.
strength of the complexing agent, ratio of the concentrations of metal to the complexing ion, and operating temperature. It is hence necessary to identify the various complexes that can be formed 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.

**Equilibrium Calculations**

Two widely used electroless copper deposition solutions were considered for the equilibrium computations. The first one consists of CuSO₄, HCHO and di-sodium tartrate as the complexing agent, and the other bath contains CuSO₄ and HCHO with EDTA as the complexing agent. Both EDTA and tartrate complexing agents are being used for the electroless copper plating systems. It is assumed that HCHO does not undergo any complexation reaction with EDTA (or tartrate) and also is not oxidized in the conditions given above. Aqueous formaldehyde does not decompose up to temperatures of 300°C. The decomposition of formaldehyde to methanol and formic acid in the presence of water occurs only at elevated temperatures, e.g. > 300°C. Since HCHO is a strong reducing agent, most of the reactions are possible in the presence of catalysts only. In the presence of EDTA, HCHO does not undergo any reactions (HCHO is used to commercially produce EDTA in the presence of CN⁻). Hence in our electroless deposition solution at equilibrium, formaldehyde is assumed to be present in an unreacted form.

**Copper-Tartrate System**

**Determination of Initial (mixing) pH.**- The initial pH can be determined by solving a set of simultaneous equations consisting of the equilibrium expressions for the various equilibrium reactions and the material balance equations along with the electroneutrality constraint. The data for the equilibrium constituents and constants are obtained from the literature. However, caution must be exercised in adopting the data from the literature due to the high sensitivity of the equilibrium results to these data. The formation constants of the reactions forming different compounds and complexes are also temperature dependent. However, there is no sufficient data for the formation constants and other thermodynamic properties of such reactions. For the copper-tartrate system, the following equilibrium reactions are possible:

\[
[\text{Cu}^{2+}] + [\text{OH}^-] \leftrightarrow [\text{Cu(OH)}^+] \quad [1],
\]

\[
[\text{Cu}^{2+}] + 2[\text{OH}^-] \leftrightarrow [\text{Cu(OH)}_2] \downarrow \quad [2].
\]

This precipitation reaction has a solubility product value of \(2.2 \times 10^{-20}\) (mol/liter)². Since a prepared solution with 0.06 M Cu⁺² and 0.25 M tartrate does not produce any precipitate, we assume that this reaction doesn't occur at this pH and therefore:

\[
[\text{Cu(OH)}_2] = 0 \quad [3].
\]
The other possible reactions are:

\[
[Cu^{+2}] + 2[OH^-] + 2 L^{-2} \leftrightarrow Cu(OH)_2 L^{-2}
\]  

where \( L^{-2} \) is the free tartrate ligand. The water equilibrium reaction has to be accounted for:

\[
[H^+] + [OH^-] \leftrightarrow [H_2O]_{av}
\]

and, when sulfates are added into the solution, the following equilibrium is necessary:

\[
[H^+] + [SO_4^{2-}] \leftrightarrow [HSO_4^-]
\]

The formation constants and solubility products are presented in Table-I. A material balance equation for each of the components present in the solution needs to be evaluated. The material balance equation for copper is:

\[
[CuSO_4]_{ad} = [Cu^{+2}] + [Cu(OH)^+] + [Cu(OH)_2] - [Cu(OH)_2 L^{-2}]
\]

Tartrate balance gives:

\[
[Na_2L]_{ad} = [L^{-2}] + 2[Cu(OH)_2 L^{-2}]
\]

Sulfate is distributed as:

\[
[CuSO_4]_{ad} = [HSO_4^-] + [SO_4^{2-}]
\]

Oxygen balance yields:

\[
[H_2O]_{ad} + 4[CuSO_4]_{ad} = [Cu(OH)^+] + 2[Cu(OH)_2] + 2[Cu(OH)_2 L^{-2}]
+ [OH^-] + 4[HSO_4^-] + 4[SO_4^{2-}] + [H_2O]_{av}
\]

and lastly sodium balance gives:

\[
2[Na_2L]_{ad} = [Na^+]
\]

where \([i]_{ad}\) is the concentration of species added to the bulk solution and \([H_2O]_{av}\) is the concentration of water unionized in the solution. The electroneutrality equation to be combined with the above equations is:
\[ \sum z_i c_i = 0 \quad [12]. \]

The concentrations of the unknown variables above can be obtained by simultaneously solving these set of algebraic equations (Eqs. [1], [3]-[12]) using MAPLE, a commercially available symbolic solver package.

*Determination of pH of Cu(OH)\(_2\) Precipitation.* In the case of precipitation reactions, only one of the two equations Eq. [2] or Eq. [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 Eq. [2] or [3] was used 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 Eqs. [10] and [11] which would be:

\[
\begin{align*}
[H_2O]_{ld} + 4[CrSO_4]_{ld} + [NaOH]_{ld} &= [Cr(OH)^+] + 2[Cr(OH)_2] + 2[Cr(OH)_2L^+] \\
&+ [OH^-] + 4[HSO_4^-] + 4[SO_4^{2-}] + [H_2O]_{ev}
\end{align*}
\]

and

\[
2[Na_2L]_{ld} + [NaOH]_{ld} = [Na^+] \quad [14].
\]

Solving Eqs [1], [3], [4]-[9] and [12]-[14] 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, Eq. [2] or [3] is used in the corresponding region for the complete equilibrium diagram computation.

**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:

\[
[Cu^{2+} + A^{4-}] \leftrightarrow [CuA^{2-}] \quad [15]
\]

and

\[
[CuA^{2-} + H^+] \leftrightarrow [CuHA^-] \quad [16].
\]

The values for the equilibrium constants are given in Table. I. Using these equations, one can constitute a set of independent algebraic equations for the EDTA system and solve it to obtain the equilibrium diagram.

**Results and Discussion**
Cu-Tartrate System

A solution containing 0.06 M CuSO₄ and 0.25 M Na₂L was calculated to have a pH of 1.67. The experimentally measured pH of such a system was 1.8. Fig. 1 shows the equilibrium diagram for a system containing the aforementioned concentration of CuSO₄ and Na₂L. It can be seen that free copper is present only under acidic conditions and its presence decreases significantly under alkaline conditions. It can also be seen that the copper is in a complexed form throughout the pH range 7.0-14.0. The copper complex with tartrate is strong enough that the free copper available is less than the amount required to cause precipitation. Hence, for such a system, in which the tartrate concentration is in excess, the copper deposition does not need to have an upper limit for the deposition pH. The overall reaction of copper deposition from an electroless tartrate bath goes through the following steps:

\[
\text{CuX} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + 2\text{HCOO}^- + \text{H}_2 + \text{H}_2\text{O} + \text{X}^- \quad [17]
\]

where X is a bivalent complexing molecule, which might be the complexing agent or its hydrated form. This reaction suggests that the rate can be increased by raising bath pH. Hence, an operation under highly alkaline conditions is desirable.

As mentioned earlier, there are a large number of complex species and corresponding rate constants available in the literature for the Cu-tartrate system. It is necessary to choose the species that are more relevant to the type of solution considered. For the Cu-tartrate system, the formation constant for the reaction

\[
[Cu^{+2}] + [L^{-2}] \leftrightarrow [CuL] \quad K_1 = 3.10 \quad [18]
\]

\[
2[Cu^{+2}] + 2[L^{-2}] \leftrightarrow [Cu_2L_2] \quad K_2 = 8.58 \quad [19].
\]

The equilibrium constants for these two reactions are comparably small which suggests that copper forms a relatively weak symmetric complex with tartrate. Calculating the equilibrium concentrations after assuming these to be the only complexed species existing in the system, it can be shown that copper precipitates as its hydroxide at a pH of 6.2. Experimentally, copper precipitation doesn't occur up to pH values of 13.0 from a tartrate bath, which suggests the existence of a stronger species which complexes copper from its bivalent form. The inclusion of Cu(OH)₂L₂⁻ gives a reasonable explanation of the experimentally observed phenomena.

Figure 2. shows the equilibrium diagram for the Cu-tartrate system under conditions where the copper concentration is higher than the concentration of tartrate required for complete complexation. In such a case it can be seen that most of the copper precipitates at pH values 7.0 and higher. Cu(OH)₂ takes predominance over the tartrate complex because of the increased availability of Cu^{+2} ions. However, there is still a significant quantity of copper in the complexed form, which depends on the relative strength of the solubility product and the rate constant for the complexation reaction.
Figure 3. shows the effect of tartrate concentration on the formation of $\text{Cu(OH)}_2\text{L}_2^{-4}$ complex for a specified concentration of $\text{CuSO}_4$ (0.06 M). As it can be expected, the precipitation of $\text{Cu(OH)}_2$ is predominant when the concentration of tartrate is lower than the stoichiometric amount necessary. The stoichiometric amount necessary being 0.12 M in this case, concentrations of 0.05 and 0.1 M produce a partially complexed mixture. On the other hand, at higher concentrations of tartrate, it is seen that the complex formation occurs at a lower pH as compared to those at lower concentrations, and all the copper is complexed by tartrate. Fig. 4 shows the effect of copper concentration on the formation of the copper complex $\text{Cu(OH)}_2\text{L}_2^{-4}$ for a constant concentration of $\text{Na}_2\text{L}$ (0.12 M). In order to facilitate easier interpretation of the graph, a stoichiometric factor for the formation of $\text{Cu(OH)}_2\text{L}_2^{-4}$ can be defined as:

$$\zeta = \frac{[\text{L}^{-2}]}{2[\text{Cu}^{+2}]} \quad [20]$$

This factor $\zeta$ is greater than 1 if the tartrate ion is in excess when compared to the copper ions in the system, and less than unity when tartrate is the limiting reactant. Under conditions where $\zeta$ is greater than or equal to unity, it can be seen that copper completely forms the complex. For values of $\zeta<1$ the system undergoes partial precipitation. It is interesting to note that, for values of $\zeta<1$, the amount of copper present in a complexed form does not depend on the copper concentration any further. One would expect that, for $\zeta<1$, the fraction of copper complexed would depend on the stoichiometric fraction $\zeta$. The observation of identical amounts of $\text{Cu(OH)}_2\text{L}_2^{-4}$ at $\text{pH}>7.0$ for various values of $\zeta<1$ shows that it is independent of the copper concentration. It can also be seen from Fig. 3 that this precipitation fraction depends on $\text{L}^{-2}$ concentration when $\zeta<1$. This is due to the following reason. Under precipitating conditions, the amount of free copper available is dictated by the solubility product of the $\text{Cu}^{+2}$ ion. Hence, $[\text{Cu}^{+2}]\times[\text{OH}^-]^2$ is a constant. Therefore, the equilibrium equation for the formation of copper complex, i.e. Eq. [8], reduces to:

$$K_{sp}K_8[\text{L}^{-2}]^3 \leftrightarrow \text{Cu(OH)}_2\text{L}_2 \quad [21]$$

where, $K_{sp}$ is the solubility product of copper ions, and $K_8$ is the equilibrium constant for the above complexation reaction. It can be seen from the above equations that the amount of complex formed is independent of the free copper and dependant on the free tartrate available under precipitating conditions.

Cu-EDTA System:

For a solution containing 0.06 M $\text{CuSO}_4$, 0.01 M EDTA and 0.045 M HCHO, the pH at which the solution stabilizes was calculated to be 1.83. It is to be noted here that HCHO is assumed to remain in an unionized form and does not contribute towards the pH. An experimental solution prepared in the laboratory showed a pH of 2.0. However, in such a solution, EDTA dissolution takes around 72 hrs. The pH for $\text{Cu(OH)}_2$ precipitation was found to be 11.34 according to the calculations. Figure 5. shows the composition of
various components as a function of pH. It can be seen from the plot that at a pH of 2.5 up to a pH of 11.34, copper ions are present in the complex form with EDTA. Most of the copper is in a complex of the form CuA^2-, and a significant amount is in the form CuHA at low pH values. As the pH increases from 2.5 to 11.34, the composition of the monovalent complex decreases, as expected. This is due to the lesser availability of H^+ ions in the solution thereby causing the equilibrium in Eq. [16] to shift to the left. The remaining EDTA is available as a tetravalent (A^4-) ion. Cu(OH)2 starts precipitating at a pH of 11.34. Thus, in a pH range between 11.34 and 12.12, the solution is in a transition stage with most of the copper ions in the form of Cu(OH)2 while some are in the other forms of copper considered including the CuA^2- form.

Figure 6. shows the equilibrium diagram for a system in which EDTA is the limiting component. It can be seen from this plot that, unlike Fig. [3], the complex Cu(EDTA)^2- is formed to a stoichiometric amount (the EDTA concentration in this case), and remains stable even after Cu(OH)2 starts to precipitate. This suggests that a stronger complex is formed for the EDTA system when compared to the tartrate system. Up to a pH of 6.6, there is some amount of free copper, which causes Cu(OH)2 to precipitate. CuA^2- is still present up to a pH of 10.5 where the precipitation starts to occur. It is also worth noting that an increase in the copper concentration to a value higher than the stoichiometric coefficient (which in this case is defined as the ratio of the A^4 ion to the Cu^2+ ion) does not change the precipitation pH. This can be explained by a similar argument as for the Cu-tartrate system. Figure 7. gives the effect of EDTA concentration on the formation of CuA^2- complex at constant copper concentrations. A higher concentration of EDTA causes the complex formation to occur at more acidic value and the precipitation to occur at a more alkaline value of the pH.

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 components present in them. The systems were studied as functions of pH, chelating agent and metal ion concentrations. Equilibrium diagrams were constructed for both Cu-tartrate and Cu-EDTA systems. It was determined that copper is chiefly complexed as Cu(OH)2L^2- in the tartrate bath, and as CuA^2- in the EDTA bath. For the tartrate bath under alkaline conditions, as long as the concentration of tartrate is stoichiometrically in excess of the amount for complete copper complexation, pH has no further effect. On the other hand, under alkaline conditions and conditions where tartrate is the limiting reactant, an increase in copper concentration does not affect the amount of Cu(OH)2L^2- formed. Cu(OH)2 precipitates from an Cu-EDTA bath around a pH of 11.5 for a bath containing 0.06 M CuSO4, 0.1 M EDTA and 0.04 M HCHO. The pH at which the bath starts precipitating depends on the EDTA concentration. A higher EDTA concentration causes the precipitation to occur at a more alkaline pH. An increase in the copper concentration to values higher than the stoichiometric requirement for complete complexation, does not affect the pH of precipitation any further. The effect of increasing bath temperature can be incorporated into the system if reliable data for the equilibrium constants are available as a function of temperature.
<table>
<thead>
<tr>
<th>Equation [j]</th>
<th>Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.00 \times 10^{-7}$ (liter/mol)</td>
<td>Lange (6)</td>
</tr>
<tr>
<td>4</td>
<td>$5.01 \times 10^{20}$ (liter/mol)$^5$</td>
<td>IUPAC (7)</td>
</tr>
<tr>
<td>5</td>
<td>$1.0 \times 10^{14}$ (liter/mol)$^2$</td>
<td>CRC (8)</td>
</tr>
<tr>
<td>6</td>
<td>97.0 (liter/mol)</td>
<td>Lange (6)</td>
</tr>
<tr>
<td>15</td>
<td>$5.01 \times 10^{18}$ (liter/mol)</td>
<td>IUPAC (7)</td>
</tr>
<tr>
<td>16</td>
<td>$1.0 \times 10^{3}$ (liter/mol)</td>
<td>IUPAC (7)</td>
</tr>
<tr>
<td>Equation [j]</td>
<td>Solubility Product</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>2</td>
<td>$2.2 \times 10^{-20}$ (mol/liter)$^2$</td>
<td>Lange (6)</td>
</tr>
</tbody>
</table>
References

Fig. 1 Equilibrium Diagram for the Cu-Tartrate System

$\text{CuSO}_4=0.06 \text{ M, } \text{Na}_2\text{L}=0.25 \text{ M}$
Fig. 2 Equilibrium Diagram for the Cu-Tartrate System under Precipitating Conditions
CuSO₄=0.06 M, Na₂L=0.05 M
Fig. 3 Effect of Tartrate Concentration on Cu(OH)$_2$L$_2$ Formation

CuSO$_4$=0.06 M
Fig. 4 Effect of Copper Concentration on Cu(OH)$_2$L$_2^{-4}$ Formation

Na$_2$L = 0.12 M
Fig. 5 Equilibrium Diagram for a Cu-EDTA System

Na₂EDTA = 0.2 M, CuSO₄ = 0.06 M
Fig. 6 Equilibrium Diagram for an EDTA Limited Cu-EDTA System

\[ \text{Na}_2\text{EDTA} = 0.05 \text{ M}, \text{CuSO}_4 = 0.06 \text{ M} \]
Fig. 7 Effect of EDTA Concentration on CuL$_2^-$ Formation

CuSO$_4$ = 0.06 M
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.