

Complex Chemistry & the Electroless Copper Plating Process

by J. Li & P.A. Kohl*

The effects of ethylenediaminetetraacetic acid (EDTA) and triethanolamine (TEA) as complexing agents on the electrochemical reduction of cupric ions and the oxidation of formaldehyde on palladium and copper electrodes have been investigated. A dual-complexing agent electroless copper solution containing EDTA and TEA has also been investigated. The reductive behavior of cupric ions in a strong base depends on the complexing agents because of the formation constant of the complex, which affects the mixed potential and thus the deposition rate of electroless copper. At the mixed potential, the oxidation of formaldehyde is independent of the copper complexing agents, but

can be accelerated by increasing the pH of the bath. The EDTA-based electroless copper solution has a relatively low deposition rate and high bath stability because EDTA forms a strong complex with cupric ions. TEA adsorbs on palladium and can poison the oxidation of formaldehyde and thus inhibit the initial copper deposition on the active palladium. Although TEA forms a weaker complex with cupric ions than EDTA, the TEA-based electroless copper solution achieves a higher deposition rate only after the active palladium surface is covered with fresh copper. The TEA-EDTA dual-complexing agent electroless copper solution provides reasonable deposition rate and bath stability. The deposition rate increases as the mole ratio of TEA to EDTA increases and the bath stability holds. The uneven surface coverage of copper deposition on the palladium activated surface decreases with an increase in the TEA to EDTA mole ratio. It can be improved, however, by adjusting the operating temperature and pH of the bath.

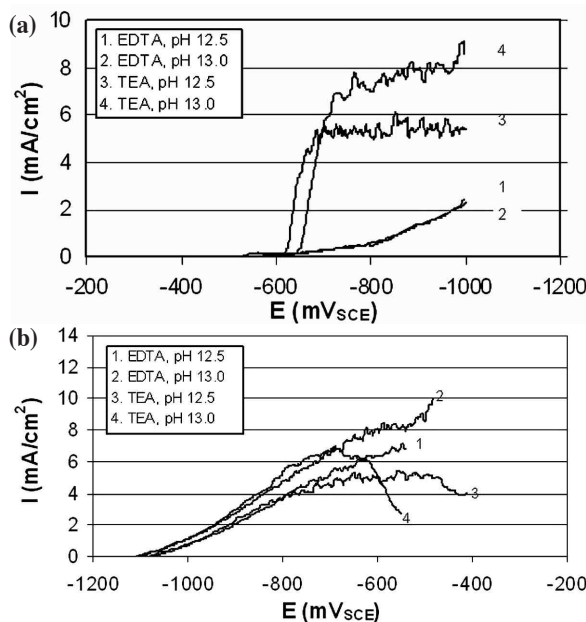


Fig. 1—Current-potential curves for (a) reduction of cupric ions; (b) oxidation of formaldehyde on the palladium electrode in the electrolyte having different complexing agents at 55°C (131°F) and pH 12.5 or 13.0. The electrolyte for (a) contains 0.04M CuSO₄, 0.20M complexing agent. The electrolyte for (b) contains 0.12M formaldehyde and 0.20M complexing agent.

Electroless copper plating is widely used for the fabrication of printed circuit boards and other electronic devices. Electroless copper can provide a seed layer on a dielectric material for subsequent acid copper electroplating.^{1,2} There is renewed interest in copper deposition for ultra-large scale integrated circuits (ULSI) because of the higher conductivity of copper versus aluminum.³⁻⁶ Electroless copper plating is well suited for uniform copper deposition on a variety of substrates.⁷ However, when compared to the electrodeposition of copper, electroless plating has a lower deposition rate (1 to 3 μm/hr; ~40 to 120 μ-in./hr)^{8,9} and the resultant deposit has less desirable metallurgical properties.¹⁰ Furthermore, electroless plating requires more rigorous control because of transient bath changes, and the deposit mechanical properties are highly process-dependent. Thus, further improvements are necessary for the electroless copper plating process to meet the specific needs of ULSI circuitry.

The deposition rate and deposit properties of electroless copper plating depend on the copper complexing agent, reducing agent, bath temperature and pH.¹¹ In addition, additives such as stabilizers, accelerators and brighteners

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In electroless copper plating, there is always a tug-of-war between the deposition rate and bath stability. A stable bath is slow, but a higher rate bath can decompose at the drop of a hat. Here, the authors have studied the effects of a dual-complexed electroless copper bath, using both EDTA and triethanolamine (TEA). The results show a successful compromise.

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Table 1
Complex Formation Equilibrium Constants of Cupric Ion Complex (room temperature)

Complexing Agent	Complex Formation	Formation Constant (log K)	Standard Potential (V_{NHE})
EDTA	CuL	18.8	-0.213
	Cu(OH)L	21.2	-0.283
TEA	CuL	4.23	0.217
	Cu(OH)L	12.5	-0.027

are used.⁹ The use of a complexing agent in the bath is essential because it prevents precipitation of Cu(OH)_2 under alkaline solution conditions. On the other hand, the complexing agent stabilizes the bath, making the selection of the reducing agent critical. It also affects the rate of crystal formation. The higher the formation constant for the copper complex, the more negative is the reduction potential.¹² In addition, the concentration of the complexing agent in the bath often exceeds that of the cupric ions. This is especially true at the electrode surface where the ligand is released as the cupric complex is reduced. The excess complexing agent can adsorb on the electrode surface and affect the electroless plating.¹³

Ethylenediaminetetraacetic acid (EDTA) and sodium potassium tartrate have been widely used as complexing agents in conventional electroless copper plating solutions with formaldehyde as the reducing agent.¹⁴⁻¹⁷ These plating solutions exhibit low deposition rates because of the high formation constants of the cupric complexes and the shift in reduction potential toward negative values with stability constants. Recently, complexing agents such as triethanolamine (TEA) and triisopropanolamine have been used to yield high deposition rates.^{13,18} However, high deposition rates are associated with bath stability and deposit quality problems.

According to the mixed potential theory of electroless plating, the overall reaction of the electroless copper process can be estimated by the two following half-reactions:^{19,20}

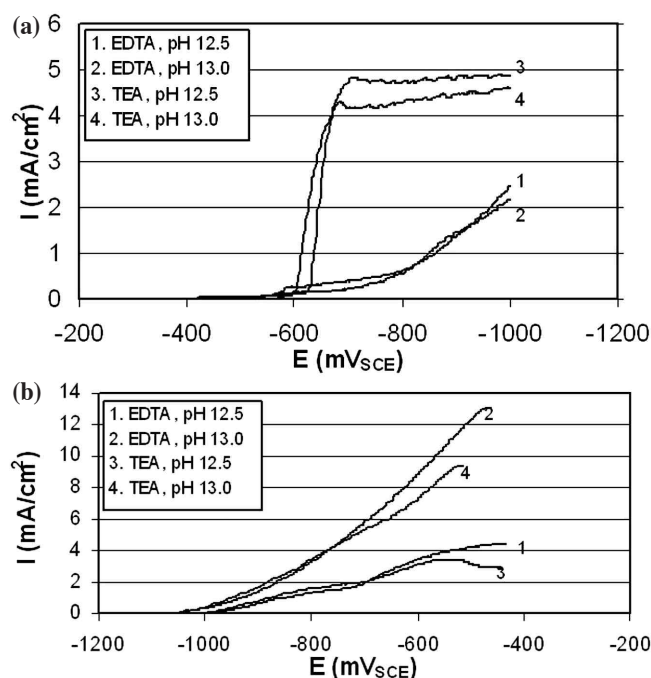
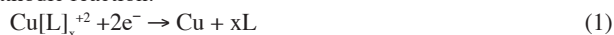


Fig. 2—Current-potential curves for (a) reduction of cupric ions; (b) oxidation of formaldehyde on the copper electrode in the electrolyte having different complexing agents at 55°C (131°F) and pH 12.5 or 13.0. The electrolyte for (a) contains 0.04M CuSO_4 , 0.20M complexing agent. The electrolyte for (b) contains 0.12M formaldehyde and 0.20M complexing agent.

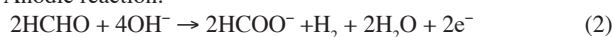
Table 2
Effects of Complexing Agents & pH on the Transfer Coefficients of Cupric Ion Reduction & Formaldehyde Oxidation (55°C; 131°F)

Complexing agent	pH	Electrode	Reduction Reaction α_{Cu}	Oxidation Reaction β_F
EDTA	12.5	Pd	0.112	0.214
EDTA	13.0	Pd	0.108	0.224
TEA	12.5	Pd	0.878	0.204
TEA	13.0	Pd	0.851	0.212
EDTA	12.5	Cu	0.099	0.292
EDTA	13.0	Cu	0.094	0.306
TEA	12.5	Cu	0.740	0.274
TEA	13.0	Cu	0.726	0.280

Cathodic reaction:



Anodic reaction:



During the electroless process, the two reactions occur simultaneously on a catalytic surface. In this paper, the effects of EDTA and TEA on the half-reactions of cupric ion reduction and formaldehyde oxidation were investigated. Based on the use of two complexing agents, an electroless copper plating process with a high deposition rate and good stability was developed.

Experimental

The electroless copper plating bath contained 0.04M cupric sulfate, 0.12M formaldehyde and 0.20M complexing agents. A potenti-

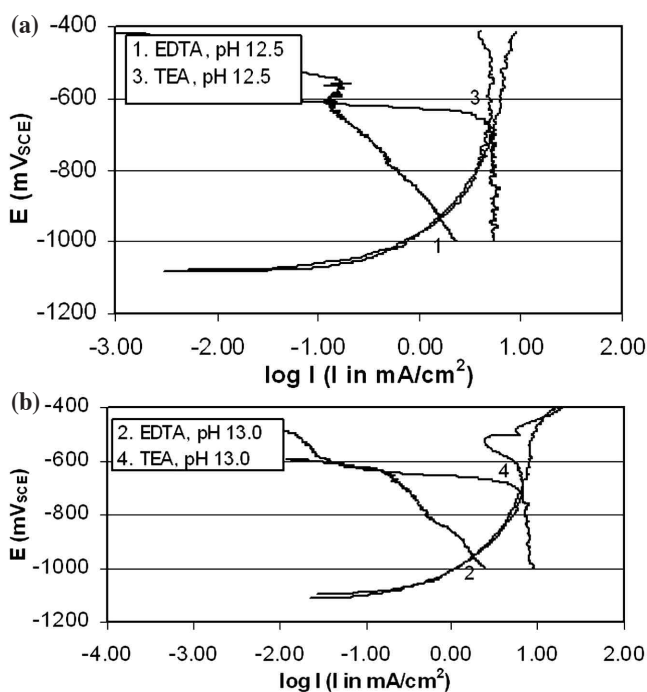


Fig. 3—Combined current-potential curves for the oxidation of formaldehyde and the reduction of cupric ions on the palladium electrode in the electrolyte with two complexing agents at 55°C (131°F): (a) pH 12.5, (b) pH 13.0.

Table 3
Effect of the Complexing Agents on the Mixed Potential
& Predicted Deposition Rate of the Electroless Copper Solution
On the Palladium & Copper Electrodes (55°C; 131°F)

Complexing agents (0.20 M)	EDTA		TEA	
	Pd	Pd	Cu	Cu
Electrode				
Mixed potential (V_{SCE} , pH 12.5)	-0.917	-0.646	-0.843	-0.627
Mixed current density (mA/cm^2 , pH 12.5)	1.774	5.063	1.050	3.069
Calculated deposition rate ($\mu\text{m}/\text{hr}$, pH 12.5)	1.545	6.668	1.400	4.091
Mixed potential (V_{SCE} , pH 13.0)	-0.938	-0.688	-0.881	-0.739
Mixed current density (mA/cm^2 , pH 13.0)	2.041	6.807	1.679	4.721
Calculated deposition rate ($\mu\text{m}/\text{hr}$, pH 13.0)	2.689	8.965	2.238	6.293
Measured mixed potential (V_{SCE} , pH 12.5)			-0.731	-0.606
Measured deposition rate ($\mu\text{m}/\text{hr}$, pH 12.5)			3.36	11.29
Measured mixed potential (V_{SCE} , pH 13.0)			-0.746	-0.652
Measured deposition rate ($\mu\text{m}/\text{hr}$, pH 13.0)			4.08	14.86

Table 4
Characteristic Peak Relative Intensity
& ratio I(111)/I(200) of the As-plated & Vacuum
Annealed (150°C; 302°F) Copper Deposits

Copper deposits	I (111)	I (200)	I (220)	I(111)/I(200)
As-plated	100	37.7	17.1	2.65
150°C (302°F) for 1 hr	100	34.0	12.4	2.94
150°C (302°F) for 2 hr	100	32.0	12.2	3.13
150°C (302°F) for 3 hr	100	32.4	12.1	3.09
150°C (302°F) for 4 hr	100	35.5	2.21	2.82

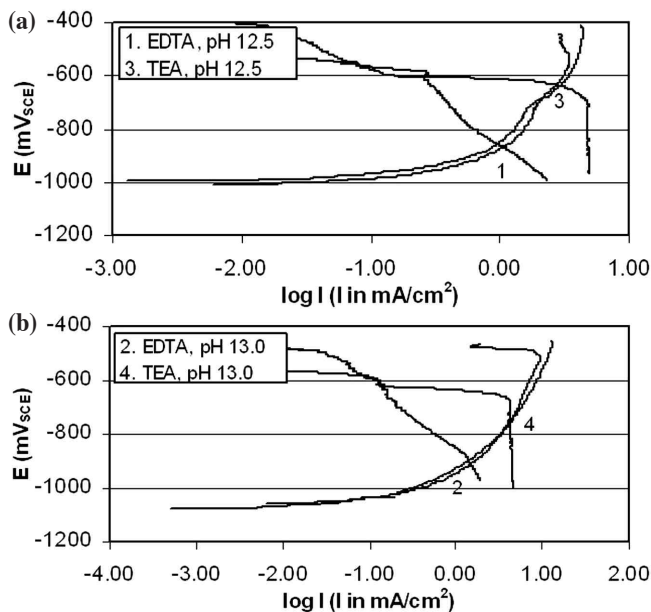


Fig. 4—Combined current-potential curves for the oxidation of formaldehyde and the reduction of cupric ions on the copper electrode in the electrolyte with two complexing agents at 55°C (131°F): (a) pH 12.5, (b) pH 13.0.

* EG&G PAR 273 Potentiostat, Princeton Applied Research, Division of AMETEK, Paoli, PA 19301

stat* was used to measure the current-potential curves for the reduction of cupric ions and the oxidation of formaldehyde. The working electrode was a copper plate or a palladium wire (99.9% purity), the counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). Potential sweeps were performed at a rate of 1 mV/sec. Prior to each test, the electrodes were immersed in the solution for five minutes to reach a steady open circuit potential (OCP). All solutions were prepared with analytical grade reagents and deionized water. The pH of the solutions was adjusted in the range of 11 to 13 using NaOH or H₂SO₄ and temperature was maintained in the range of 45 to 70°C (113 to 158°F).

Epoxy boards (6.0 cm²; 0.93 in² in area) were used as the substrates for electroless copper plating. Since electroless copper plating is a catalytic process,^{21,22} palladium seeding is required on the epoxy boards in order to initiate copper deposition.

The epoxy boards were activated with palladium in the sequence described in the process literature.²³ Plating was performed in a 200 mL electroless copper solution with strong nitrogen agitation. The copper deposition rate was determined by the change in weight of the epoxy boards after 1 hr of plating, assuming uniform plating and bulk density.

The resistivity of the copper was measured using a four-point probe. The crystal structures of the copper deposits were investigated using X-ray diffraction (Cu K_α radiation and graphite filter at 40 kV and 30 mA). The thermal annealing of the deposits was conducted at 150°C (302°F) under vacuum.

Results & discussion

Electroless Copper Plating Using a Single Complexing Agent

Electroless copper plating is catalyzed by an active palladium surface, and continues to deposit autocatalytically on the freshly reduced copper. The deposition rate depends on the half-reaction activity of cupric ion reduction and formaldehyde oxidation on the active palladium and copper surfaces. Complexing agents can change the behavior of the half-reactions by stabilizing the cupric ion through complexation and by surface adsorption.

The potential and kinetics of the cupric ion reduction reaction, Equation 1, in an aqueous solution depend on the formation constant of the cupric-ligand complex. The equilibrium potential E_{Cu} for cupric ion reduction reaction, is given by the Nernst equation,²⁴

$$E_{Cu} = E_{Cu}^0 - \frac{0.059}{2} \log \beta \quad (3)$$

where E_{Cu}^0 is the standard potential for cupric ion reduction, which is 0.342V vs. the normal hydrogen electrode (NHE) at 25°C (77°F) and β is the formation constant. Table 1 lists the formation constants of two cupric complexes²⁵ and the equilibrium potential for the reduction reactions of the cupric complexes. The pH of the solution influences the reduction potential through protonation of the ligand or by hydroxide acting as a ligand. The participation of hydroxide in the TEA complex gives it a pH dependence, whereas EDTA is fully deprotonated at high pH values. The equilibrium potential for the formaldehyde oxidation in Equation 2 at room temperature can also be given by the Nernst equation,^{11,26}

$$E_F = E_F^0 - 0.118\text{pH} \quad (4)$$

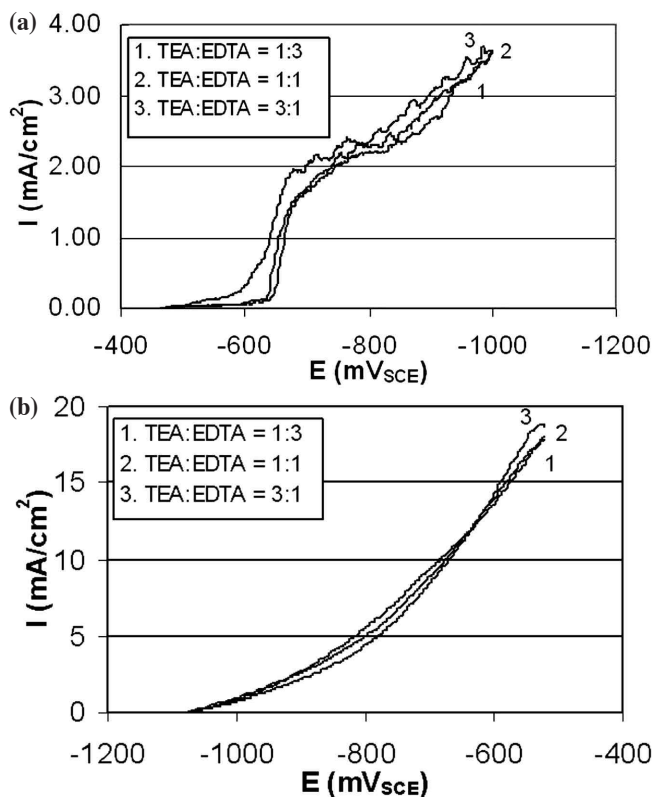


Fig. 5—Current-potential curves for (a) reduction of cupric ions; (b) oxidation of formaldehyde on the copper electrode in the electrolytes having different TEA:EDTA mole ratios at 55°C (131°F) and pH 13.0. The electrolyte for (a) contains 0.04M CuSO_4 , 0.20M total complexing agents. The electrolyte for (b) contains 0.12M formaldehyde, 0.20M total complexing agents.

where E'_F combines the standard electrode potential E^0_F and the concentration term in the Nernst equation. The equilibrium potential for the formaldehyde oxidation becomes more negative with increasing pH.

Figure 1 shows the current-potential curves for the reduction of cupric ions (Fig. 1a) and the oxidation of formaldehyde (Fig. 1b) on a palladium electrode with the two complexing agents at two pH values at 55°C (131°F). In strong basic solution, the reduction of the EDTA cupric complex occurred at potential of -0.60V and the reduction current increased slowly with potential. The reduction current for TEA-complexed cupric ions increased rapidly with potential and reached a diffusion-limited current at -0.64V. The reduction current for cupric ions in the TEA solution was higher than that in the EDTA solution. The oxidation of formaldehyde depended on pH and the nature of the electrode surface. The change in the pH of the solution from 12.5 to 13.0 affected the current-potential curves as expected by the Nernst equation. The onset potential for the formaldehyde oxidation shifted toward the negative value and the oxidation current increased with increasing pH. At more negative potentials (low currents), the oxidation current of formaldehyde was independent of the complexing agent and the magnitude of the current increased steadily with potential. However, small changes in the oxidation of formaldehyde at high potentials could be seen. This may have been caused by the adsorption of the complexing agents on the electrode which would inhibit the oxidation of formaldehyde.¹³ The adsorbed species could block the surface and impede electron transfer, resulting in higher overpotentials.

Figure 2 shows the current-potential curves for the reduction of cupric ions and the oxidation of formaldehyde on the copper electrode under the same conditions used in Fig. 1. The reduction

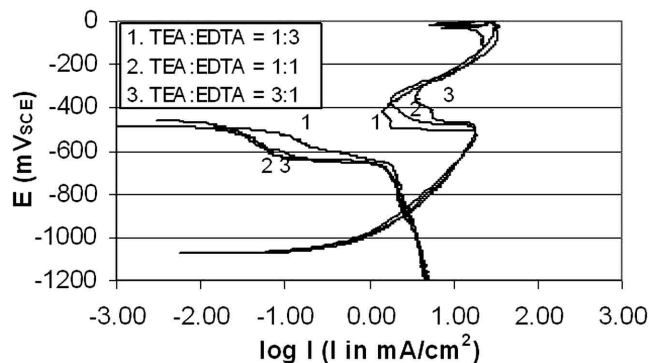


Fig. 6—Combined current-potential curves for the oxidation of formaldehyde and the reduction of cupric ions on the copper electrode in the dual complexing agent electrolytes with different TEA:EDTA mole ratios at 55°C (131°F) and pH 13.0.

of cupric ions on the copper electrode showed trends similar to the reduction of cupric ions on the palladium electrode. The oxidative current of formaldehyde on the copper electrode also increased with pH from 12.5 to 13.0 and was higher for EDTA than for the TEA ligand.

The transfer coefficients for cupric ion reduction (α_{Cu}) and formaldehyde oxidation (β_F) can be calculated from the Tafel region of the logarithmic current-potential curves¹¹ according to Equations 5 and 6, respectively,

$$\eta_{Cu} = -\frac{2.3 RT}{2\alpha_{Cu} F} \log i_{Cu}^0 + \frac{2.3 RT}{2\alpha_{Cu} F} \log I_{Cu} \quad (5)$$

$$\eta_F = -\frac{2.3 RT}{\beta_F F} \log i_F^0 + \frac{2.3 RT}{\beta_F F} \log I_F \quad (6)$$

where η_{Cu} and η_F are the overpotentials for the cupric ion reduction and formaldehyde oxidation, respectively, I_{Cu} and I_F are the reduction and oxidation current densities related to the overpotentials, i_{Cu}^0 and i_F^0 are the exchange current densities of the reduction and oxidation, F is Faraday's constant and T is absolute temperature.

The effect of the complexing agents and pH on the rate of cupric ion reduction and formaldehyde oxidation at the palladium and copper electrodes can be expressed in terms of the transfer coefficients, α_{Cu} and β_F , which is shown in Table 2. The transfer coefficient for cupric ion reduction in the solution containing TEA ligand was much higher than that containing EDTA ligand. The transfer coefficient for formaldehyde oxidation depended on the pH, increasing with increasing pH. In addition, the transfer coefficient for formaldehyde oxidation in the solution containing EDTA ligand was a little higher than that containing TEA ligand. Under the same conditions, the transfer coefficient for cupric ion reduction on the palladium electrode was larger than that on the copper electrode. However, the transfer coefficient for formaldehyde oxidation on the palladium electrode was smaller than that on the copper electrode.

The net rate of deposition of electroless copper plating occurs at the mixed potential when the cathodic and anodic currents are equal. The logarithmic current-potential curves for the oxidation of formaldehyde and the reduction of cupric ions on the palladium and copper electrodes were combined in Fig. 3 and Fig. 4, respectively. The mixed potential occurs at the intersection of the oxidation and reduction curves on the same electrode surface. At the mixed potential, the cathodic (or anodic) current density represents the electroless deposition rate in the absence of secondary effects of one half-reaction on the other. The predicted mixed potential and calculated deposition rate of the electroless copper plating solutions from the half-reactions on the palladium and copper elec-

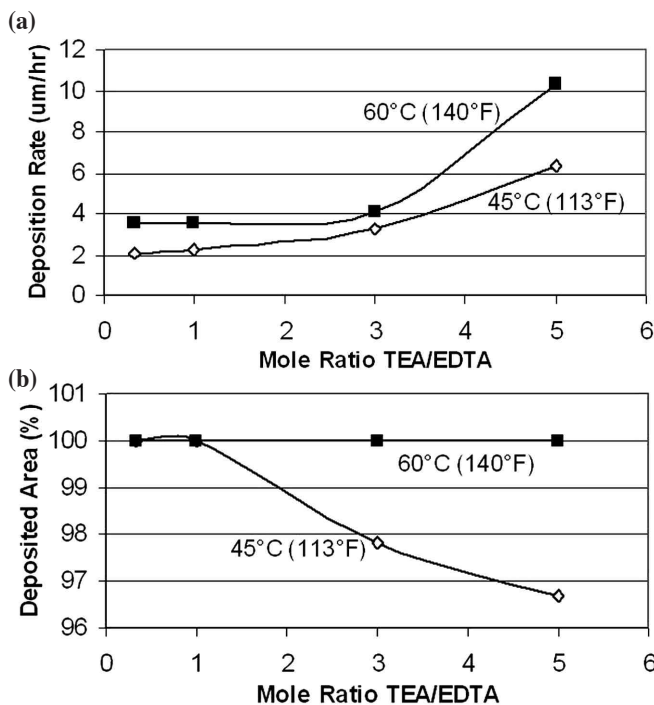


Fig. 7—Dependence of deposition rate (a) and deposited area (b) on various TEA:EDTA mole concentration ratios in the bath containing: 0.04M CuSO_4 , 0.12M formaldehyde, 0.20M TEA and EDTA, and 0.5 mL/L polyethylene glycol at pH 12.5.

trodes are listed in Table 3. It can be seen that the mixed potentials of the electroless copper plating systems lay between -0.60 and -0.94V. At the same pH, the mixed potential and deposition rate of the electroless copper plating were dependent on the complexing agent and the electrode. The higher the formation constant for the copper-ligand complex, the lower was the deposition rate for electroless copper plating. Hence, the electroless copper solution with EDTA as the complexing agent should have a lower deposition rate than that containing TEA. Increasing the pH of the solution from 12.5 to 13.0 increased the transfer coefficient of formaldehyde oxidation, thus increasing the deposition rate of the electroless copper solution. The deposition rate on the palladium electrode was higher than that on the copper electrode, indicating that the initial copper deposition on the activated palladium surface easily occurred in the overall process.

Table 3 also lists the measured copper deposition rate and the mixed potentials of the electroless copper plating process using EDTA and TEA as complexing agents at 55°C (131°F). Consistent with the current-potential curves, the EDTA-based electroless copper process had a lower deposition rate and better stability than the TEA-based process. There was no reaction in the TEA-based electroless copper plating on the palladium-activated surface. However, when the palladium-activated surface was coated with a thin layer of copper in the EDTA-based electroless copper solution and then inserted into the TEA-based electroless copper solution, an increased deposition rate of about 15 $\mu\text{m/hr}$ was realized. This phenomenon has been previously observed.¹⁸ One explanation for this phenomenon is that the adsorption of TEA could poison the catalytic oxidation of formaldehyde on the active palladium surface, and thus inhibit copper deposition. During copper deposition, the two half-reactions occur simultaneously on the same electrode. However, there is often an induction time where each of the half-reactions strive to reach the mixed potential and contamination or air oxidation of the catalytic palladium layer can delay or terminate the copper deposition.⁷ In addition, the copper deposition rate is seen to be much higher than predicted from mixed potential theory.

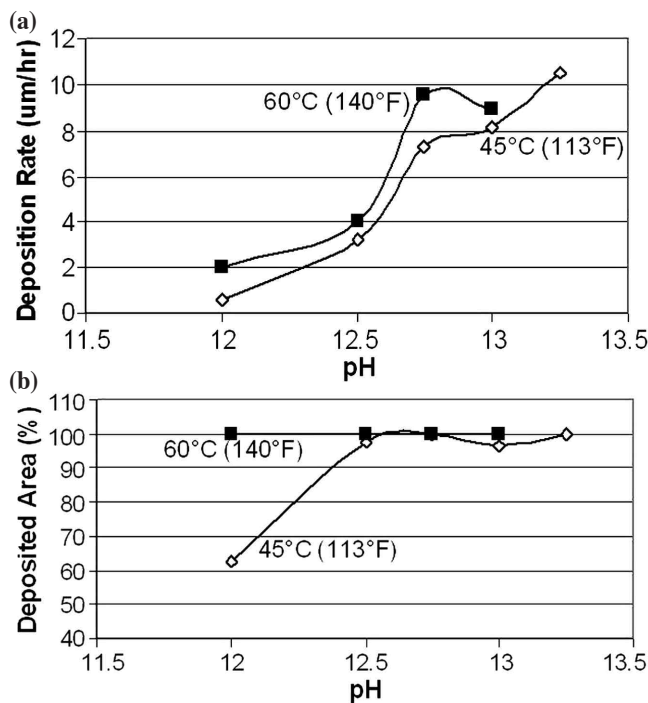


Fig. 8—values of the bath containing: 0.04M CuSO_4 , 0.12M formaldehyde, 0.15M TEA, 0.05M EDTA, and 0.5 mL/L polyethylene glycol.

This may result from the impact of one half reaction on the other half reaction. Many studies have shown that formaldehyde can facilitate cupric ion reduction and this catalysis is critical to the operation of the electroless copper bath.^{14,22,27,28}

Electroless Copper Plating Using Dual-complexing Agents

The effect of a dual-ligand solution was investigated. Figure 5 shows the effect of the mole ratio of TEA to EDTA on the current-potential curves for the reduction of cupric ions and the oxidation of formaldehyde on the copper electrode at 55°C (131°F) and pH 13.0. The total concentration of complexing agents was maintained at 0.20M. From Fig. 5a, it can be seen that the reduction behavior of the cupric ions in the dual-complex bath was between that in the TEA and EDTA solutions. Polarization of the cupric ion reduction decreased slightly with increasing TEA:EDTA ratio. The TEA:EDTA ratio had no significant effect on the oxidation of formaldehyde (Fig. 5b), for the ratios tested.

The mixed potential and deposition rate of the dual-complexing agent electroless copper solution expected from the two half-reactions are shown in Fig. 6. The mixed potential of the dual-complexing agent process occurred at -0.852V. At this potential, the calculated deposition rate was about 5.31 $\mu\text{m/hr}$, and was independent of the TEA:EDTA ratio over the range investigated. From the electrochemical half-reactions, the deposition rate of the dual-complexed electroless copper was higher than that of the single EDTA ligand solution.

The deposition rates for actual TEA:EDTA dual-complexed electroless copper baths at pH 12.5 in a temperature range of 45 to 60°C (113 to 140°F) are shown in Fig. 7. The deposition rate increased with the increasing TEA:EDTA ratio. The plating process was stable with time and more stable than the single ligand electroless copper baths. Some reports have suggested that this high stability results from the formation of a mixed ligand complex of cupric-EDTA-TEA.²⁹ However, the copper deposits were not uniform when the mole ratio of TEA:EDTA in the bath was greater than 1 at 45°C (113°F). There was uneven surface coverage

on the activated palladium, which could be related to poisoning of the formaldehyde oxidation reaction on the active palladium layer which would inhibit the initial copper deposition by TEA. This nonuniformity increased with higher TEA:EDTA ratios. However, the initial copper deposition on the active palladium surface was improved by raising the temperature from 45 to 60°C (113 to 140°F). The nonuniformity was also improved by increasing the pH of the bath, as shown in Fig. 8. These effects were likely caused by an acceleration of the oxidation of formaldehyde. However, the stability of the bath deteriorated with increasing pH and temperature. At 60°C (140°F) and pH 13.5, the bath reacted spontaneously, resulting in catastrophic failure.

An optimized electroless bath containing 0.04M CuSO₄, 0.12M HCHO, 0.15M TEA, 0.05M EDTA and 0.5 mL/L polyethylene glycol was made up and operated at 55°C (131°F) and pH 12.8. The bath was stable and the average deposition rate during 1 hr of plating was 6.0 μm/hr. The resistivity of the as-plated and vacuum annealed (150°C; 302°F) deposits versus time is shown in Fig. 9. The copper deposit had good conductivity which could be improved by vacuum annealing at 150°C (302°F). Figure 10 shows the XRD patterns of the as-plated and vacuum annealed (150°C; 302°F) copper deposits. The characteristic peaks of crystalline copper could be clearly seen. The relative peak intensities and the I(111)/I(200) ratio are listed in Table 4. It can be seen that copper deposits from the dual-complexed electroless copper solution had a strong (111) texture. After annealing at 150°C (302°F), the (111) texture was slightly enhanced. This indicates that higher annealing temperature resulted in higher crystallization, defect recovery and stress release in the copper deposits.⁶ Such defect reduction could reduce the electrical resistivity of the copper deposits.

Conclusion

The reduction behavior of cupric ions in alkaline solutions depends on the nature of the complexing agents used. This is because of the different complexing abilities as evidenced by their formation constants with cupric ions. At the mixed potential, the oxidation of formaldehyde is independent of the complexing agents used, but can be accelerated by increasing pH of the bath. EDTA has a high formation constant with cupric ions, and thus an EDTA-based electroless copper process has a lower deposition rate and better bath stability. The complexing ability of TEA is much lower than that of EDTA, but could poison the active palladium layer and inhibit the initial copper deposition. The TEA-based electroless copper process with the highest deposition rate occurred only when the active palladium surface was covered with copper.

The TEA-EDTA dual-complexing agent electroless copper bath provided a compromise between the deposition rate and bath stability of the single ligand baths. The deposition rate increased with the mole ratio between TEA and EDTA, and the bath had very good stability. Although uneven surface coverage of the copper on activated palladium worsened with an increase in the TEA:EDTA mole ratio, it could be improved by adjusting the operating temperature and pH of the bath. By optimizing the operating conditions and the TEA:EDTA mole ratio, a stable electroless copper plating with a deposition rate of 6.0 μm/hr was obtained. The copper deposits had good conductivity and could be improved with thermal annealing.

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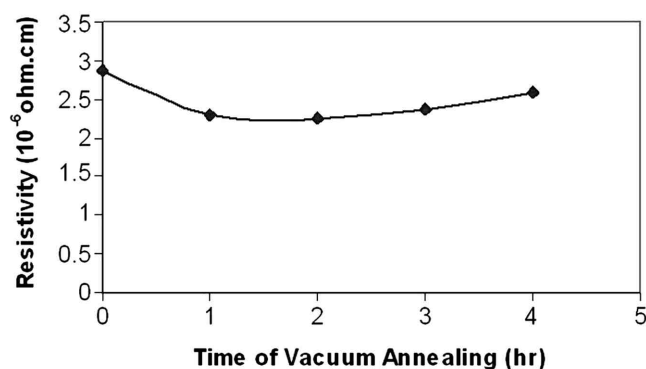


Fig. 9—Dependence of copper deposit resistivity on the time of vacuum annealing at 150°C (302°F).

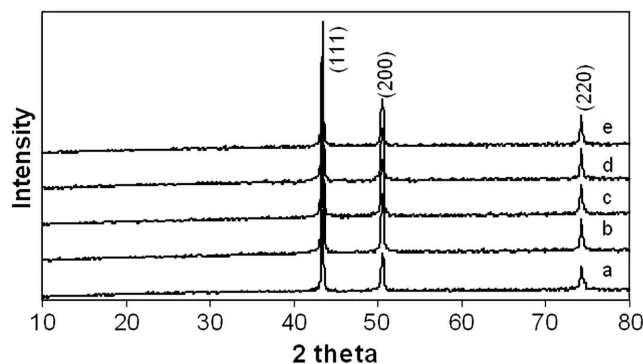


Fig. 10—XRD patterns of the as-plated and thermal annealed copper deposits: (a) as-plated; (b) 1 hr at 150°C (302°F), (c) 2 hr at 150°C (302°F), (d) 3 hr at 150°C (302°F) and (e) 4 hr at 150°C (302°F)

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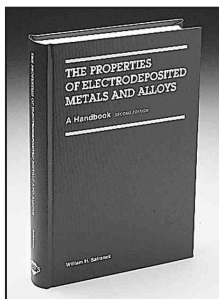
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