



## The Acceleration of Nonformaldehyde Electroless Copper Plating

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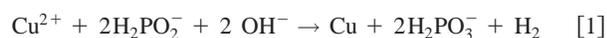
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Nonformaldehyde, low pH (compared to highly alkaline bath) electroless copper plating has been investigated. Thiourea and its derivatives have been shown to increase the deposition rate of electroless copper plating solutions using HEDTA [*N*-(2-hydroxyethyl)ethylenediaminetriacetic acid trisodium salt hydrate] as the complexing agent and sodium hypophosphite as the reducing agent. A thiourea concentration of 1.0 ppm produced a fourfold increase in the deposition rate of copper from about 1 to 4  $\mu\text{m/h}$ . The effect of thiourea on the electrochemical reactions, and the crystal structures and electrical properties of the copper deposits were examined. A small amount of thiourea, or its derivatives, in the electroless copper solution improves the catalytic activity of the copper surface for the oxidation of hypophosphite, resulting in a higher electroless deposition rate. The thiourea also increases the growth colony size of the copper deposits and improves its conductivity. A reaction mechanism is proposed to describe the function of the thiourea and its derivatives on the process.

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Electroless copper plating involves the reduction of  $\text{Cu}^{2+}$  ions to copper metal and the surface catalyzed oxidation of a reducing agent. These processes are widely used in the fabrication of printed circuit boards due to their conformal deposition, low cost, and simple equipmental setup.<sup>1</sup> Commercial electroless copper plating solutions often use formaldehyde or its derivatives as reducing agents because of their high deposition rate and the excellent mechanical properties of the copper deposits.<sup>2,3</sup> However, the catalytic oxidation of formaldehyde increases with hydroxide concentration and is only effective at pH above 11. The high pH is not compatible with some dielectric or photoresist materials. In addition, formaldehyde is a volatile carcinogenic liquid. Several electroless copper solutions using nonformaldehyde reducing agents have been reported.<sup>4-8</sup> Among them, hypophosphite is attractive because it is less costly and relatively safe to use. The overall electroless copper plating reaction using hypophosphite as the reducing agent is given in Eq. 1<sup>9</sup>



However, the inherent drawback for using hypophosphite as the reducing agent is the weak catalytic activity for the oxidation of hypophosphite on copper. While the initial substrate surface is palladium-activated, once it is coated with copper, the reaction slows. One way to compensate for the poor catalytic activity of copper is to add nickel ions to the solution. The codeposited nickel in the copper deposit serves to catalyze the oxidation of hypophosphite, thus increasing the overall deposition rate.<sup>10</sup> Further, the deposition of electroless copper depends on the complexing agents in the solution because they chelate both copper and nickel ions. For example, the electroless copper solution using hypophosphite as the reducing agent and sodium citrate as the complexing agent produces a constant deposition rate with time,<sup>4</sup> however the electrolyte using *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid trisodium salt hydrate (HEDTA) as the complexing agent has a very low deposition rate, and the copper deposit is nearly black in color.

In this study, we report the use of thiourea (tu) and 1,3 diphenyl-2-thiourea (DPTU) to accelerate the electroless copper plating process using HEDTA as the complexing agent and hypophosphite as the reducing agent. These species have previously been used as

stabilizers in formaldehyde electroless copper process.<sup>11</sup> The electrical properties of the copper deposits are also reported.

### Experimental

The composition and operating conditions of the electroless copper plating solution employed in the experiment are summarized in Table I. HEDTA functions as the complexing agent for the cupric ions avoiding  $\text{Cu}(\text{OH})_2$  precipitation, sodium hypophosphite is the reducing agent, boric acid buffers the electrolyte, polyethylene glycol is a surfactant, and nickel sulfate improves the catalytic effect of the deposit. Deionized water was used, and the pH was adjusted using NaOH or  $\text{H}_2\text{SO}_4$ .

Epoxy boards (6  $\text{cm}^2$  area) were used as the substrates for the electroless copper plating. The epoxy boards were activated according to the Shipley process, which is commercially available from Shipley Company, Inc. Plating was performed in a 200 mL electroless copper solution with continuous stirring. Copper deposition rates were determined by the changes in weight of the epoxy boards after 30 min 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 (XRD,  $\text{Cu K}\alpha$  radiation and graphite filter at 40 kV and 30 mA), and the surface morphology was observed by means of scanning electron microscopy (SEM, Hitachi S-800). The chemical composition of the copper deposits at the surface were determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed after a brief sputtering cleaning.

An EG&G PARC model 263A potentiostat was used to conduct the electrochemical measurement. The working electrode was a copper plate (99.9% purity) with 1  $\text{cm}^2$  surface area; the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). Prior to each test, the electrodes were immersed in the solution for 5 min to reach a steady open circuit potential (OCP). The pH of the solutions was 9.3, and the temperature was maintained at 70°C.

**Table I. Composition of the electroless copper plating solution and operating conditions.**

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.04 M
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	0.12 M
HEDTA	0.08 M
$\text{H}_3\text{BO}_3$	0.48 M
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	500 ppm
Polyethylene glycol	200 ppm
pH	9.3
<i>T</i> (°C)	70 °C

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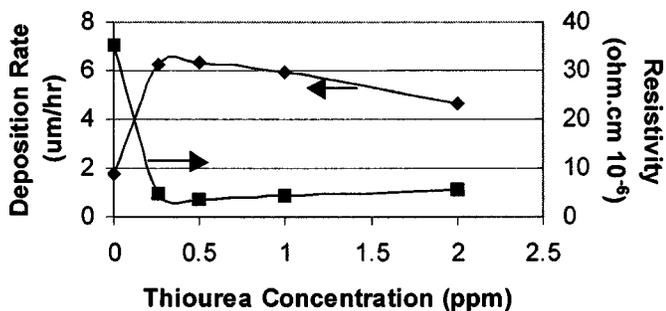


Figure 1. Effects of the thiourea concentration in the electroless copper plating solution on the deposition rates and resistivity of the copper deposits.

Results and Discussion

The effect of tu and DPTU on deposition rates.—Thiourea has been used as the stabilizer in formaldehyde-based electroless copper solutions to inhibit spontaneous decomposition. However, when only a small amount of tu was added to the electroless copper plating solution with HEDTA as the complexing agent and hypophosphite as the reducing agent, the deposition rate of copper plating increased significantly, as shown in Fig. 1. The color of the deposits changed from black in the absence of tu in the solution to semibright at 0.5 ppm tu. In addition, the resistivity of the copper deposits decreased due to changes in the structure of the deposits. The darker deposits were rougher and more porous. Unfortunately, as the tu concentration was increased, the plating rate decreased slightly. When the tu concentration was more than 1.0 ppm, the copper deposit became brittle and appeared black in color, similar to when there was no tu.

DPTU, Fig. 2, had similar beneficial effects on the deposition rate as tu in the electroless copper plating solution. Figure 3 shows the average deposition rate of the electroless copper plating solution and resistivity of the deposit as a function of DPTU concentration.

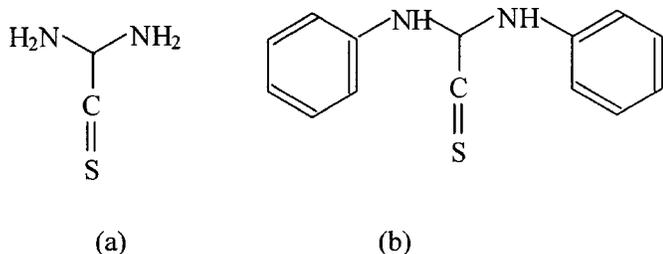


Figure 2. Structures of (a) thiourea and (b) 1,3-diphenyl-2-thiourea.

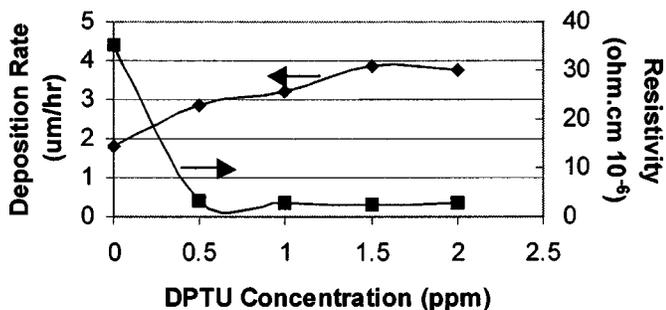


Figure 3. Effects of the DPTU concentration in the electroless copper plating solution on the deposition rates and resistivity of the copper deposits.

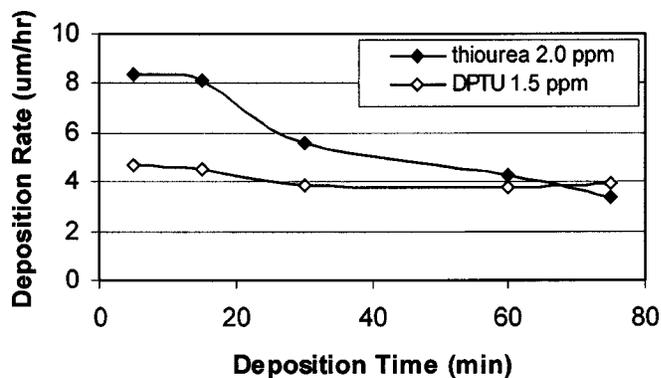
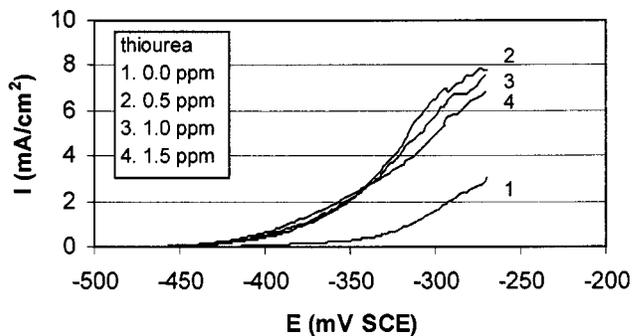


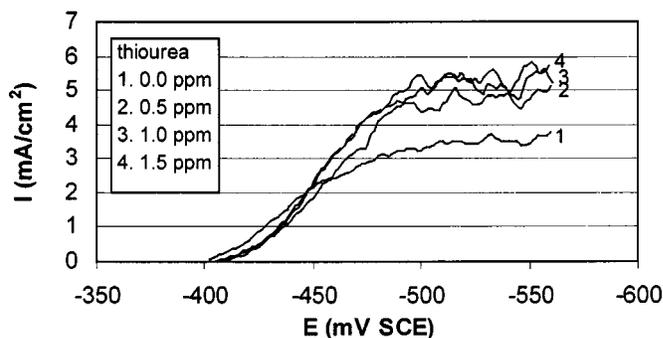
Figure 4. Dependence of the average deposition rate of the electroless copper plating solution containing thiourea additives on plating time.

Although the deposition rate with DPTU was less than that with tu, the resistivity of the copper deposit was lower and nearly the same as that obtained with formaldehyde-based electroless copper solutions.<sup>12</sup> Furthermore, the deposition rate increased slightly with DPTU concentration, and the deposit appeared semibright at all DPTU concentrations.

Tu and DPTU both improve the temporal uniformity of the electroless process. The deposition rate of the electroless copper solution in the absence of tu drops quickly with time once the palladium catalyst on the substrate surface is covered by deposited copper, even when nickel ions are present in the solution. The change in deposition rate with time using tu and DPTU in the solution is

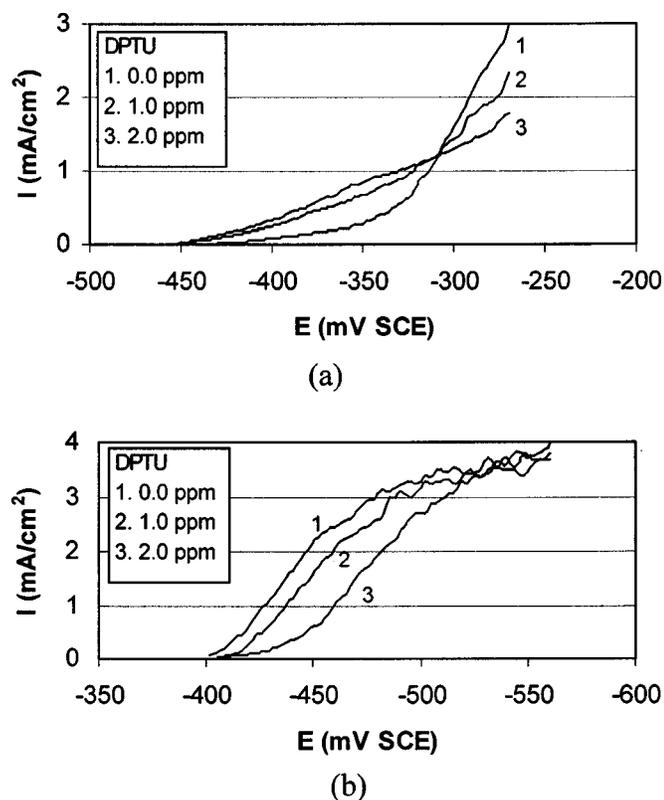


(a)



(b)

Figure 5. Current-potential curves for (a) oxidation of hypophosphite and (b) reduction of cupric ions with different thiourea concentration. The electrolyte for (a) contains 0.12 M NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O, 0.08 M HEDTA, 0.48 M H<sub>3</sub>BO<sub>3</sub>; the electrolyte for (b) contains 0.04 M CuSO<sub>4</sub>, 0.08 M HEDTA, and 0.48 M H<sub>3</sub>BO<sub>3</sub>.

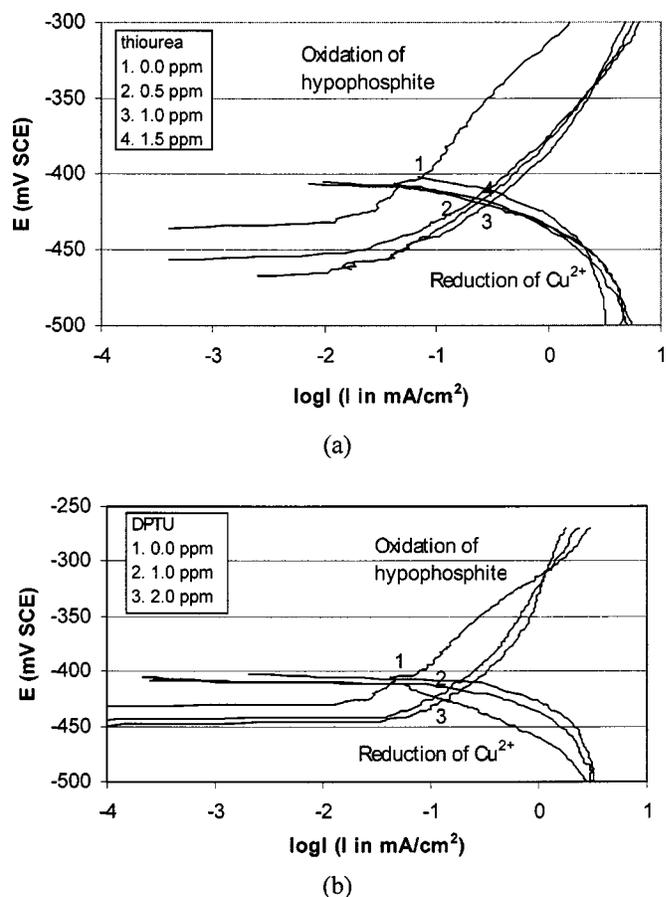


**Figure 6.** Current-potential curves for (a) oxidation of hypophosphite and (b) reduction of cupric ions with different DPTU concentration. The electrolyte for (a) contains 0.12 M  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 0.08 M HEDTA, 0.48 M  $\text{H}_3\text{BO}_3$ ; the electrolyte for (b) contains 0.04 M  $\text{CuSO}_4$ , 0.08 M HEDTA, and 0.48 M  $\text{H}_3\text{BO}_3$ .

shown in Fig. 4. The deposition rate with 2 ppm tu decreased steadily with time, whereas the deposition rate with 1.5 ppm DPTU was more constant.

*The effects of tu and DPTU on the oxidation of hypophosphite and reduction of cupric ions.*—According to the mixed potential theory of electroless plating,<sup>13-15</sup> the overall reaction of the electroless process is determined by the two half-reactions on the same electrode, *i.e.*, the reduction of cupric ions and the oxidation of the reducing agent. Obviously, the anodic and cathodic current must be equal at a common potential (mixed potential), and the current density at the mixed potential can be used to predict the deposition rate of the electroless plating. Consequently, studying the effects of tu and DPTU on the half-reactions can help elucidate the electroless plating mechanism even though the anodic and cathodic half-reactions in the electroless process are interdependent.<sup>16</sup>

Linear sweep voltammetry (LSV) of the oxidation of hypophosphite on the copper electrode was carried out in an electrolyte containing 0.12 M  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 0.08 M HEDTA, 0.48 M  $\text{H}_3\text{BO}_3$ , Fig. 5a. The scan rate was at 1 mV/s going positively from OCP to  $-0.27$  V at  $70^\circ\text{C}$ . It can be seen that the addition of 0.5 ppm (or greater) tu to the electrolyte caused a significant increase in magnitude of the current and shift in potential to more negative values for the oxidation of hypophosphite on the copper electrode. There was little difference in current at higher tu concentrations (more than 0.5 ppm), especially at low currents which correspond to those used in electroless plating. The improvement in the catalytic activity of the copper surface is reflected in the shift in potential to more negative values.<sup>15</sup> The reduction of cupric ions on the copper electrode was also studied by LSV in an electrolyte containing 0.04 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 0.08 M HEDTA, 0.48 M  $\text{H}_3\text{BO}_3$  at 1 mV/s from OCP negatively to  $-0.56$  V at  $70^\circ\text{C}$ , Fig. 5b. The presence of tu had



**Figure 7.** Combined current-potential curves for the oxidation of hypophosphite and the reduction of cupric ions with different (a) thiourea concentrations and (b) DPTU concentrations

no effect on the onset potential of cupric ion reduction, but decreased slightly the reduction current at low current densities and increased the reduction current at higher current densities. Higher concentrations of thiourea had little effect on the reduction of cupric ions, especially at less negative potentials.

The effect of DPTU on the current-potential curves of the two half-reactions are shown in Fig. 6a and b. The effects of DPTU on the oxidation of hypophosphite and the reduction of cupric ions are similar to tu. The oxidation of hypophosphite on the copper electrode, Fig. 6a, was shifted to more negative values. The magnitude of the oxidative current was higher in the low-current region as the DPTU concentration increased. The magnitude of the reduction current for cupric ions decreased slightly with the DPTU concentration. Thus, tu and DPTU facilitate the oxidation of hypophosphite and depress the reduction of cupric ions. The presence of nickel ions in the electrolyte had no effect on the electrochemical oxidation of hypophosphite and reduction of cupric ions on the copper electrode (current-voltage curves) with and without tu or DPTU additions. To confirm the improved catalytic activity of the copper electrodes by tu and DPTU, the deposition rate of the electroless copper solution containing 1.0 ppm DPTU (no nickel ions) was measured. A deposition rate of  $1.85 \mu\text{m/h}$  was achieved, and the copper deposit was semibright.

The current-potential curves for the oxidation of hypophosphite and the reduction of cupric ions as a function of tu or DPTU concentration were combined in Fig. 7a and b, respectively. The mixed potential occurs at the intersection of the oxidation and reduction curves, and the current density represents the rate of the electroless deposition in the absence of secondary effects, such as nickel ions and the effect of one half-reaction on the other. The mixed potential

**Table II. Effects of the thiourea concentration on the mixed potential and deposition rate of the electroless copper solution.**

Thiourea concentration (ppm)	0.0	0.5	1.0	1.5
Mixed potential (mV vs. SCE, Fig. 7a)	-406	-419	-419	-417
Measured mixed potential (mV vs. SCE)	-404	-407	-407	-405
Mixed current density (mA/cm <sup>2</sup> , Fig. 7a)	0.043	0.236	0.317	0.253
Calculated deposition rate (μm/h)	0.056	0.311	0.418	0.333
Measured deposition rate (μm/h)	1.790	6.361	5.952	5.387

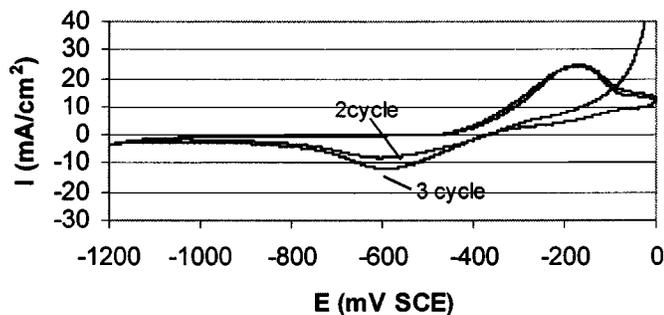
**Table III. Effects of the DPTU concentration on the mixed potential and deposition rate of the electroless copper solution.**

DPTU concentration (ppm)	0.0	1.0	2.0
Mixed potential (mV vs. SCE, Fig. 7b)	-406	-416	-427
Measured mixed potential (mV vs. SCE)	-404	-404	-407
Mixed current density (mA/cm <sup>2</sup> , Fig. 7b)	0.043	0.158	0.153
Calculated deposition rate (μm/h)	0.056	0.208	0.201
Measured deposition rate (μm/h)	1.790	3.211	3.774

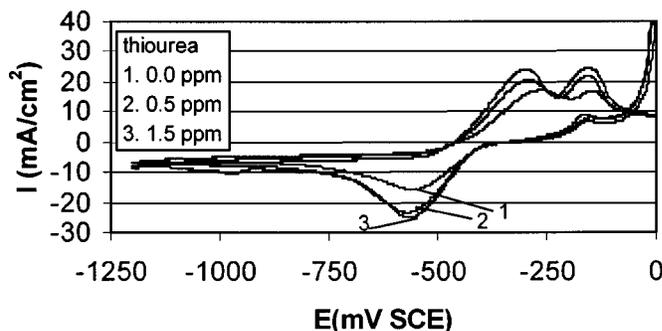
and calculated deposition rate of the electroless copper solutions as a function of tu and DPTU concentration are listed in Tables II and III, respectively. The actual potentials for the copper electrode in the electroless copper plating solutions are also listed in Tables II and III. It can be seen that the mixed potential in this electroless copper solution without tu or DPTU is nearly the same as the measured one. Thiourea and DPTU have very little effect on the measured mixed potential. The values of the calculated deposition rates based on Fig. 7 are much lower than the actual values obtained with tu and DPTU. This can occur if the products from one half-reaction change the magnitude of the current for the other half-reaction. The existence of the nickel ions in the solution can also facilitate higher deposition rates.

To investigate possible interactions, cyclic voltammetry (CV) of a copper electrode in the electroless copper plating solution was performed at a scan rate of 100 mV/s between 0.00 and -1.20 V vs. SCE. In order to identify the reaction corresponding to each peak, the CV in a blank electroless copper plating solution without sodium hypophosphite, copper sulfate, and nickel sulfate was measured. The results are presented in Fig. 8. On the positive going sweep, the copper was oxidized at -0.18 V (peak potential) and re-reduced at -0.60 V on the reverse sweep. When 0.12 M NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O was added, a second oxidation peak was observed at -0.24 V (Fig. 9), corresponding to the oxidation of hypophosphite.

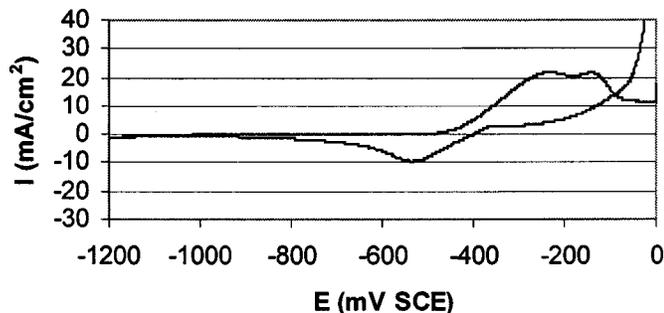
The effects of tu and DPTU on the CVs in the electroless copper solutions are shown in Fig. 10 and 11, respectively. The peak current



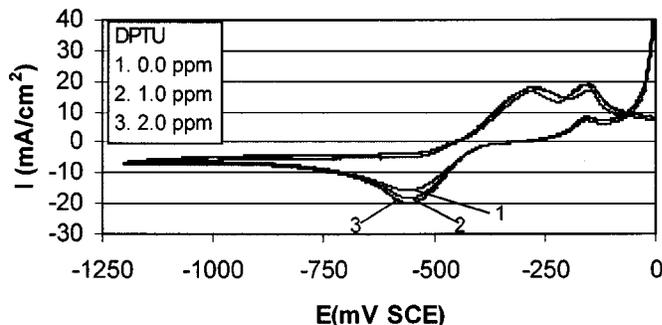
**Figure 8.** Cyclic voltammograms for a copper electrode in the blank electroless copper plating solution containing 0.08 M HEDTA, 0.48 M H<sub>3</sub>BO<sub>3</sub>, and 200 ppm polyethylene glycol (the second and third cycle).



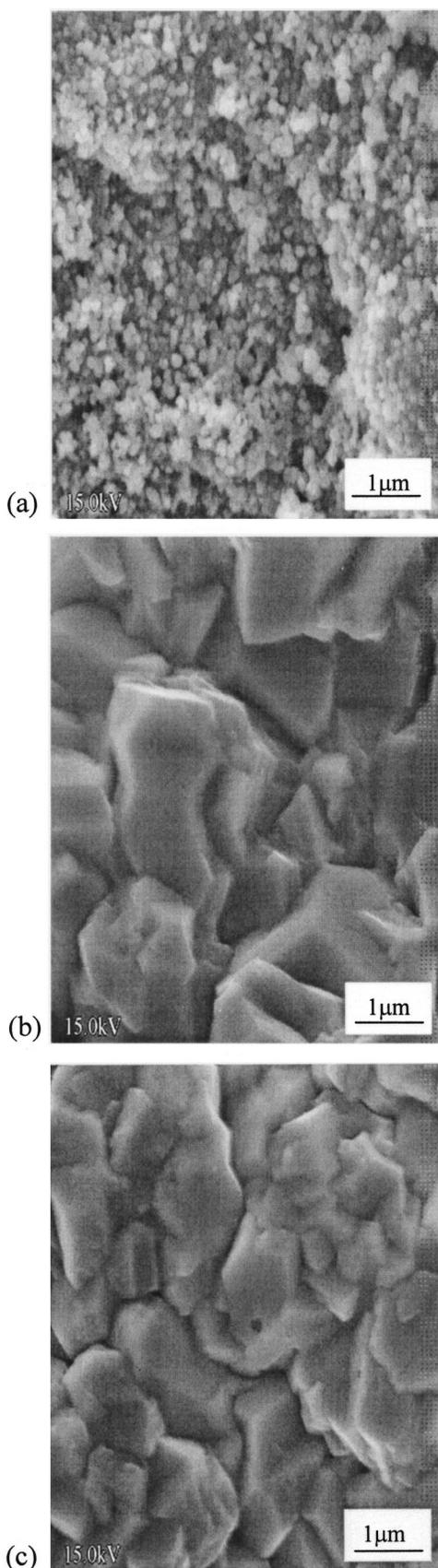
**Figure 10.** Cyclic voltammograms for a copper electrode in the basic electroless copper plating with different thiourea concentration.



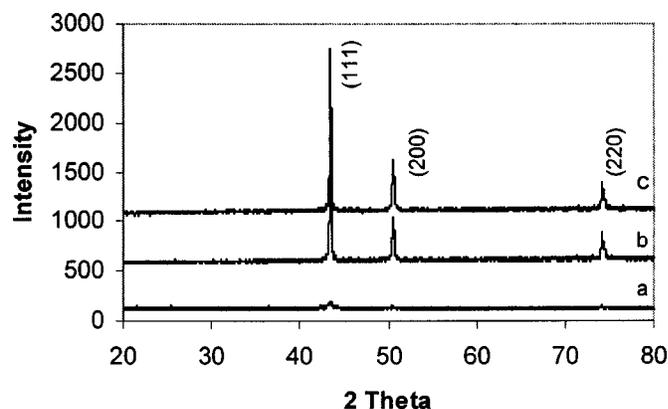
**Figure 9.** Cyclic voltammogram for a copper electrode in the blank electroless copper plating solution containing 0.12 M NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O, 0.08 M HEDTA, 0.48 M H<sub>3</sub>BO<sub>3</sub>, and 200 ppm polyethylene glycol.



**Figure 11.** Cyclic voltammograms for a copper electrode in the basic electroless copper plating with different DPTU concentrations.



**Figure 12.** Surface morphologies of the copper deposited from (a) basic electroless copper solution, (b) electroless copper solution containing 0.5 ppm thiourea, (c) electroless copper solution containing 1.0 ppm DPTU.



**Figure 13.** XRD patterns of the copper deposited from (a) basic electroless copper solution, (b) electroless copper solution containing 0.5 ppm thiourea, (c) electroless copper solution containing 1.0 ppm DPTU.

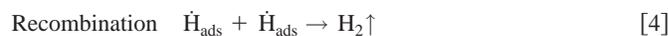
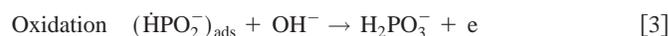
for the oxidation of hypophosphite and oxidation-dissolution of copper increased with the addition of tu (Fig. 10) or DPTU (Fig. 11). A similar effect on the dissolution of Au was found.<sup>17</sup> The peak potential for the oxidation of hypophosphite shifted to less positive values and is consistent with the catalytic effect obtained in Fig. 5 and 6. The peak current for the reduction of cupric ions and nickel ions also increased with tu and DPTU. Further additions of tu and DPTU had only a small influence on the peak current for the reduction process.

*Surface morphologies of copper deposits.*—Figure 12 shows the surface morphologies of the copper deposits from the electroless solutions with the without tu or DPTU additions. The topography of the copper deposited from the hypophosphite electroless copper plating solution was relatively rough with small growth colonies. This resulted in higher resistivity, as shown previously. When tu and DPTU were added in the solution, the copper deposits became more uniform and the growth colony size increased. The growth colonies of the copper from the tu solutions were larger than those from DPTU. The XRD patterns of the copper deposits are shown in Fig. 13. Tu and DPTU did not change the crystallographic orientation of the copper deposits. All deposits exhibited strong (111) texture. The diffraction peak intensities of the copper deposited from the solution without tu or DPTU were much lower because of the thinness of the deposit. No nickel was detected in the copper deposits from the solutions with and without tu or DPTU additions, via XPS analysis.

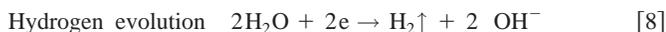
*Mechanism.*—Thiourea and DPTU has been shown to act as catalysts in the electroless copper process. However, previous experiments have shown that a small amount of tu in the electroless copper solution had little effect on the deposition rate and coating properties if sodium citrate was used as the complexing agent in place of HEDTA.<sup>7</sup>

A reaction mechanism has been proposed to account for the electroless processes by Van Den Meerakker.<sup>18</sup> In this mechanism, the dehydrogenation of the reducing agent is the first step in the reaction.

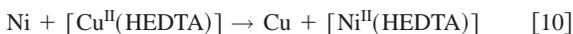
Anodic process



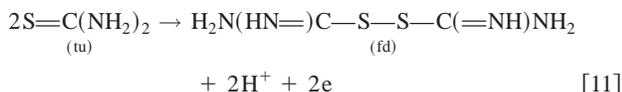
Cathodic process



The codeposited nickel in Eq. 7 can be replaced by cupric ions in the solution<sup>6,7</sup>



It has been shown that tu can be oxidized by the complex  $[\text{Cu}^{\text{II}}(\text{HEDTA})]$ .<sup>19-21</sup> In addition, studies of the electrochemical oxidation of thiourea in acidic, aqueous solutions with relatively low thiourea concentrations ( $\sim 10^{-3}$  M) have found that thiourea was oxidized to formamidine disulfide (fd),<sup>17,22,23</sup> as shown in Eq. 11



The oxidation of tu has been proposed to proceed via intermediates.<sup>22</sup> Thiourea is first oxidized to a free radical tu  $[\dot{\text{S}}\text{C}(=\text{NH})\text{NH}_2]$ , followed by reaction with tu forming tutu, and finally oxidized to fd<sup>17</sup>



Thus, when a small amount of tu was added into the electroless copper solution, some of the tu adsorbed on the copper electrode could be oxidized to fd electrochemically or by the complex  $[\text{Cu}^{\text{II}}(\text{HEDTA})]$  at the copper-solution interface via the same process

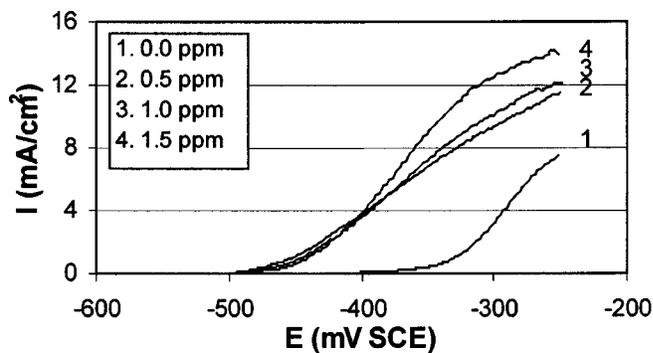


To investigate the role of fd on the process,<sup>17</sup> fd was added to the electroless solution in place of tu or DPTU. Figure 14 shows the current-potential behaviors of hypophosphite oxidation (Fig. 14a) and cupric ion reduction (Fig. 14b) as a function of fd concentration. Fd appears to serve the same function as tu on these two half-reactions. The oxidation of hypophosphite was shifted to a more negative potential and current density for cupric ion reduction increased at high current densities. Thus, one could conclude that the surface catalytic effects of fd may be the same as tu (if it adsorbed in a similar way) or the beneficial effect of tu only occurred once oxidized (forming fd).

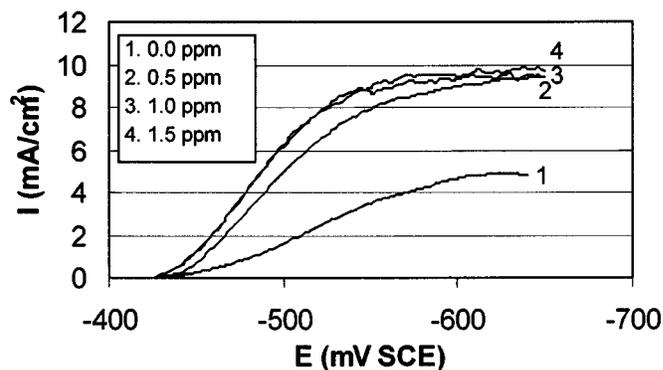
### Conclusions

Thiourea and diphenylthiourea increase the deposition rate of electroless copper plating solutions that use HEDTA as the complexing agent and sodium hypophosphite as the reducing agent. The conductivity of deposited copper was significantly improved compared to no additive. Electrochemical measurements show that small amounts of tu or DPTU in the solution can improve the catalytic activity of copper for the oxidation of hypophosphite and decrease the polarization of the oxidation of hypophosphite, resulting in higher deposition rates.

A proposed reaction mechanism suggests that a small amount of thiourea in the solution could be oxidized by the  $[\text{Cu}^{\text{II}}(\text{HEDTA})]$



(a)



(b)

**Figure 14.** Current-potential curves for (a) oxidation of hypophosphite, (b) reduction of cupric ions with different fd concentrations. The electrolyte for (a) contains 0.12 M  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 0.08 M HEDTA, 0.48 M  $\text{H}_3\text{BO}_3$ ; the electrolyte for (b) contains 0.04 M  $\text{CuSO}_4$ , 0.08 M HEDTA, and 0.48 M  $\text{H}_3\text{BO}_3$ .

complex. The effect of thiourea was to accelerate the oxidation of hypophosphite in the electroless plating process, thus increasing the deposition rate of the electroless plating.

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