



## The Deposition Characteristics of Accelerated Nonformaldehyde Electroless Copper Plating

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The deposition process of an electroless copper plating solution using sodium citrate as the main complexing agent and sodium hypophosphite as the reducing agent has been investigated. The deposit composition, structure, and catalytic activity for the oxidation of hypophosphite during the process have been investigated. Formamidine disulfide (fd) has been shown to accelerate the deposition rate of the electroless plating just as it does with electroless plating solutions using *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid trisodium salt hydrate (HEDTA) as the complexing agent. For solutions with the Cu<sup>2+</sup>/Ni<sup>2+</sup> mole ratio of 42, the deposition rate decreased with time and terminated after 90 min plating because the surface catalytic activity of the deposit had decreased with thickness. A copper deposit with total thickness of 6.48–6.59 μm was obtained after 90 min plating. The decrease in the deposition rate with time was mitigated by decreasing the Cu<sup>2+</sup>/Ni<sup>2+</sup> mole ratio, holding the concentration of copper ions constant. An optimized electroless copper plating process with sustained deposition rate with time and high metal conductivity was developed. The bath was used in a fully additive high density wiring process.  
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Electroless copper plating is widely used for metallization in the fabrication of printed circuit boards and other electronic devices because of the ease of fabrication and high conductivity of copper.<sup>1–4</sup> Commercial electroless copper plating solutions often use formaldehyde or its derivatives as reducing agents and are operated at pH values above 11. Since the high pH is not compatible with some low-*k* dielectric or photoresist materials and formaldehyde is a volatile carcinogenic liquid, previous papers have investigated low pH electroless copper solutions using nonformaldehyde reducing agents such as dimethylamine borane (DMBA),<sup>5</sup> sodium hypophosphite,<sup>6,7</sup> glyoxylic acid,<sup>8</sup> and cobalt(II)-ethylenediamine complex.<sup>9</sup> Among them, sodium hypophosphite is especially attractive because of its low cost and relative safety.

Sodium hypophosphite has been widely used as a reducing agent for electroless nickel plating.<sup>10</sup> However, the electroless copper plating process is more complicated than electroless nickel plating because copper is not as good a catalyst as nickel for the oxidation of hypophosphite. Nickel ions (or other metal ions) can act as mediators in copper electroless plating. A very small amount of co-deposited nickel in the copper deposit serves to catalyze the oxidation of hypophosphite enabling continuous copper deposition.<sup>6</sup> Therefore, the deposits obtained often consist of Cu-Ni alloy rather than pure copper.<sup>1</sup> In the Cu-Ni plating solution, the concentration of nickel ions and the selection of the complexing agent are important because they effect the role of deposition. Higher nickel ion concentration could lower the solution stability and increase the nickel content in the deposit, resulting in higher deposit resistivity. Honma *et al.* reported that the optimum mole ratio between copper(II) and nickel ions is approximately 13:1.<sup>11</sup> Copper(II) and nickel ions have different standard redox potentials (Cu/Cu<sup>2+</sup> = 0.34 V vs. NHE and Ni/Ni<sup>2+</sup> = -0.25 V vs. NHE).<sup>6</sup> The use of a complexing agent not only stabilizes the solution, but can also bring the deposition potential of the two ions closer together by shifting the potentials different amounts, making codeposition possible. It has been found that citrate is an appropriate complexing agent for electroless copper plating using hypophosphite as the reducing agent, leading to a substantial plating rate.<sup>6,12</sup>

We previously reported that thiourea and its derivatives accelerate the electroless copper plating process using *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid trisodium salt hydrate (HEDTA) as the complexing agent and hypophosphite as the reducing agent at a Cu<sup>2+</sup>/Ni<sup>2+</sup> mole ratio at 21. It was found that thiourea

could be oxidized to formamidine disulfide (fd) in the solution.<sup>13</sup> In this study, the deposition process of electroless copper plating using sodium citrate as the complexing agent and fd as the accelerator has been investigated. The composition, structure, and properties of the copper deposits and the catalytic characteristics for the oxidation of hypophosphite with deposition time are reported.

### Experimental

The electroless copper plating solution contained 0.04 M copper sulfate, 0.00095 to 0.0057 M nickel sulfate, 0.17 M sodium hypophosphite, 0.051 M sodium citrate, 0.015 M HEDTA, 0.485 M boric acid, 200 ppm polyethylene glycol, and 0.5 ppm fd. Deionized water was used to prepare the solution. The pH was adjusted using NaOH or H<sub>2</sub>SO<sub>4</sub> to a final value of 9.0 to 9.3. The temperature was held at 72.5°C. Sodium citrate is the complexing agent for chelating the copper(II) and nickel ions, and HEDTA was added to maintain the stability of fd. The functions of other chemicals are the same as described previously.<sup>13</sup>

Epoxy boards (6 cm<sup>2</sup> area) were used as the substrates for the electroless copper plating. The epoxy boards were activated by palladium in the sequence as described in the Shipley process.<sup>13</sup> 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 different plating times 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, 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 was determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed after a brief sputter cleaning.

An EG&G PAR model 263A potentiostat was used to conduct the electrochemical measurement. The working electrode was deposited copper with 1 cm<sup>2</sup> surface area, the counterelectrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). Prior to each test, the electrolyte was deaerated with nitrogen gas and the electrodes were immersed in the electrolyte until a steady open-circuit potential (OCP) was reached.

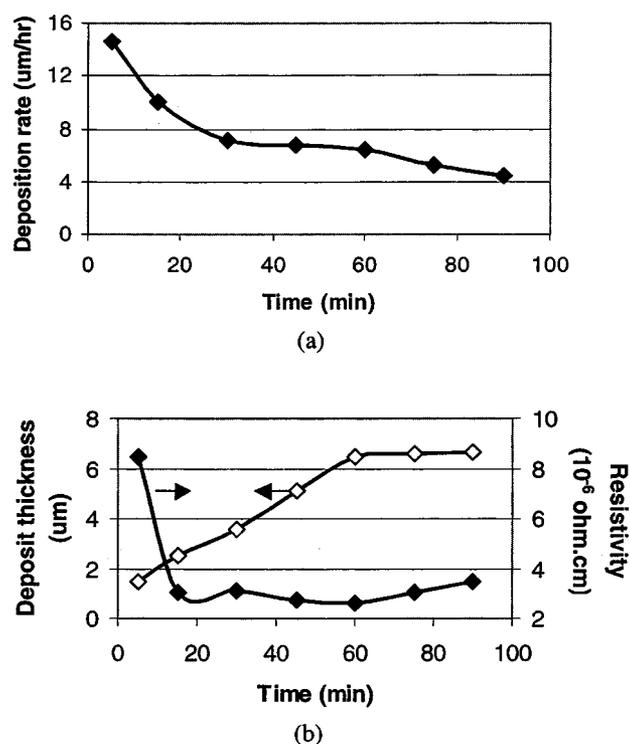
### Results and Discussion

Thiourea and its derivatives accelerated the deposition rate in the electroless copper solution using HEDTA as the complexing agent.<sup>13</sup> They had little effect on the deposition rate and coating properties if sodium citrate was used as the complexing agent in place of HEDTA.<sup>13</sup> Previously, it was shown that fd had the same function as

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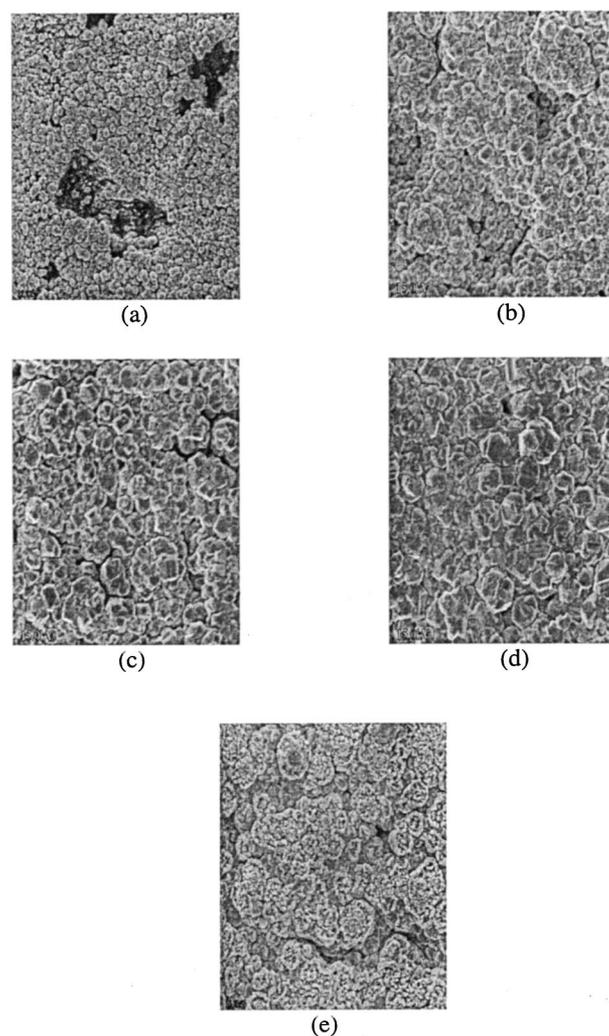


**Figure 1.** Deposition process of the citrate-based electroless copper plating (with 0.5 ppm fd): (a) dependence of the deposition rate on plating time; (b) dependence of the deposit thickness and resistivity on plating time.

thiourea in HEDTA-based electroless copper solution. It was also shown that thiourea is oxidized to fd in an HEDTA-based electroless copper solution. The question at hand is the role of fd as an accelerator in citrate-based electroless solutions. It is possible that only fd can serve as the accelerator (not thiourea) and thiourea is not oxidized to fd in citrate-based electroless solutions. A copper deposit with a pink tint was obtained in a citrate-based electroless copper solution with 0.5 ppm fd. The change in deposition rate of the electroless copper plating with deposition time is shown in Fig. 1. The average deposition rate for 30 min plating (7.15 µm/h) was higher than that in the HEDTA-based electroless copper solution using thiourea or fd as accelerators (5.78-6.36 µm/h). The resistivity of the copper deposit was nearly the same as that obtained with formaldehyde-based electroless copper solutions.<sup>14</sup> At the Cu<sup>2+</sup>/Ni<sup>2+</sup> mole ratio of 42, the citrate-based electroless copper solution had a low deposition rate in the absence of fd (1.27 µm/h for 30 min) and the copper deposit was dark once the palladium catalyst on the substrate surface was covered with copper. This shows that fd accelerates the deposition process in the citrate-based electroless copper plating solution. The function of fd in the solution has been studied previously.<sup>13</sup> The fd accelerates both half reactions, the oxidation of hypophosphite and the reduction of copper(II).

In Fig. 1, it is shown that the deposition rate of the electroless copper plating decreased steadily with time. After 90 min plating, the reaction was almost stopped and the color of the copper deposit changed from pink to dark brown. The total copper deposit thickness was 6.48 to 6.59 µm. Obviously, the catalytic activity of the copper deposit for the oxidation of hypophosphite decreased with deposit thickness.

The catalytic activity of the copper surface for the oxidation of hypophosphite during copper plating was dependent on its chemical composition and microstructure. Figure 2 shows the morphology of the copper surface at different deposition times. The initial deposition of copper on the activated palladium surface was not uniform. After 5 min of plating, certain local areas were not yet plated with copper. Gradually, the surface became coated with copper, as shown

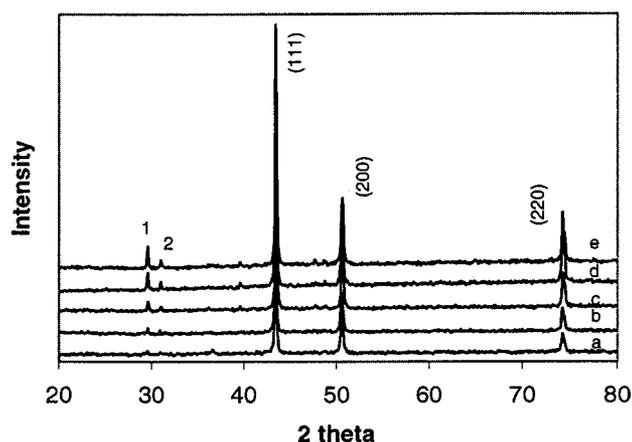


**Figure 2.** Surface morphology of the copper deposits at different deposition times (times 2500): (a) 5, (b) 15, (c) 30, (d) 60, and (e) 90 min.

in Fig. 2b (after 15 min plating). Finally, the copper deposit became compact and uniform, as shown in Fig. 2c (after 30 min plating) and Fig. 2d (after 60 min plating). The morphology of the copper deposit was completely changed after 90 min plating (Fig. 2e), at which point the average deposition rate had slowed to 4 µm/h. The physical appearance of the deposit is dark and small growth colonies are seen.

The surface composition of the copper deposits at different deposition times was investigated using XPS. The deposit surface mainly consisted of copper with no nickel or phosphorus detected (detection limit is 0.1 atom %). The XRD patterns of the copper deposits at different deposition times are shown in Fig. 3. All of the deposits exhibited the characteristic peaks of copper and strong (111) orientation. However, a pair of small peaks at about  $2\theta = 30^\circ$ , denoted as 1 and 2, appeared in the deposits at longer times. The relative intensity of each peak is listed in Table I. It can be seen that the intensity of peaks 1 and 2 increased with deposition time and deposit thickness, which may be due to the presence of copper oxide Cu<sub>4</sub>O<sub>3</sub><sup>14</sup> or other species.

Linear sweep voltammetry (LSV) was used to investigate the catalytic activity of the deposit for the oxidation of hypophosphite during plating. The LSV was recorded using the electrolessly deposited copper as the working electrode in the electrolyte in the absence of copper(II) and nickel ions. Figure 4 shows the LSV for hypophosphite oxidation [in the absence of Cu(II)] on electrolessly deposited



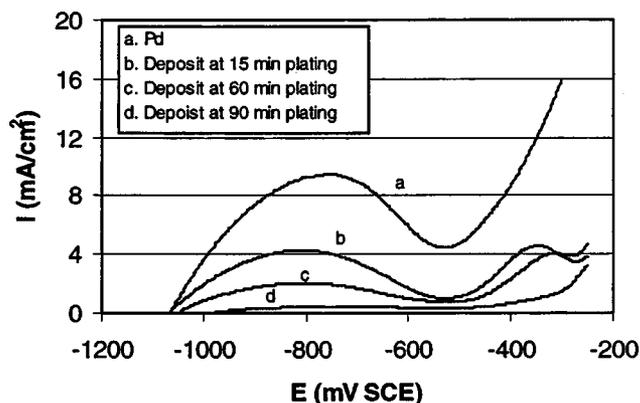
**Figure 3.** XRD patterns of the copper deposits at different deposition times: (a) 5, (b) 15, (c) 30, (d) 60, and (e) 90 min.

copper surfaces after 15, 60, and 90 min of deposition. The scan rate was 10 mV/s toward positive potentials from the OCP to  $-0.250$  V at  $72.5^\circ\text{C}$ . A copper foil (99.9% purity) was immersed in the dilute acidic  $\text{PdCl}_2$  solution for 2 min, and a layer of Pd was formed on the copper surface by a displacement reaction. For comparison in Fig. 4, the catalytic oxidation of hypophosphite on the Pd is shown in Fig. 4a. The OCP of the Pd in the electrolyte was  $-1.064$  V, and the anodic peak for the oxidation of hypophosphite on the Pd surface occurred at  $-0.760$  V. The copper deposit after 15 min of plating (Fig. 4b) had an OCP of  $-1.064$  V and two anodic peaks were observed. The first peak was at  $-0.786$  V and attributed to the oxidation of hypophosphite on the active palladium surface still exposed to the electrolyte. The peak current was significantly less than that on the Pd surface in Fig. 4a. The second peak occurred at  $-0.336$  V and was most likely due to the oxidation of hypophosphite on the copper surface. The immediate OCP for the copper surface deposited for 60 min in the hypophosphite electrolyte was  $-0.532$  V. The OCP gradually shifted to more negative values and stabilized at  $-1.046$  V. The anodic peak current density (Fig. 4c) was significantly smaller than that on the copper surface after 15 min of plating. It took a longer time for the 90 min plated copper surface to reach its steady OCP of  $-0.981$  V from an initial value of  $-0.528$  V. The anodic current density for the oxidation of hypophosphite was very small showing that the catalytic activity of the 90 min plated copper surface for the oxidation of hypophosphite had nearly disappeared. The shift in the OCP of the deposited copper surface in the electrolyte indicates that the activated palladium catalyst on the epoxy substrate played an important role for the initial catalytic oxidation of hypophosphite in the electroless plating process.

The standard redox potential of  $\text{Cu}/\text{Cu}^{2+}$  ( $0.34$  V vs. NHE) is more positive than that of  $\text{Ni}/\text{Ni}^{2+}$  ( $-0.25$  V vs. NHE). The complexing agent in the electroless copper solution shifts the redox potentials of  $\text{Cu}/\text{Cu}^{2+}$  and  $\text{Ni}/\text{Ni}^{2+}$  toward more negative values as given by the Nernst equation<sup>15</sup>

**Table I.** Relative intensity of the characteristic peaks of the copper deposits at different deposition times.

Copper deposits (min)	$I(111)$	$I(200)$	$I(220)$	$I_{\text{peak1}}$	$I_{\text{peak2}}$
5	100	20.9	7.0	3.4	...
15	100	21.5	6.7	5.5	...
30	100	31.8	10.4	7.5	3.2
60	100	22.2	8.4	8.9	3.8
90	100	37.3	12.3	20.7	6.9



**Figure 4.** Current-potential curves for the oxidation of hypophosphite on the palladium surface and copper deposits at different deposition times: (a) palladium; (b) 15, (c) 60, and (d) 90 min. The electrolyte contains 0.17 M sodium hypophosphite, 0.051 M sodium citrate, 0.015 M HEDTA, 0.485 M boric acid, 200 ppm polyethylene glycol, and 0.5 ppm Pd. The pH was 9.3 and the temperature was held at  $72.5^\circ\text{C}$ .

$$E_{\text{Cu}/\text{Cu}^{2+}} = E_{\text{Cu}/\text{Cu}^{2+}}^0 - \frac{0.059}{2} \log \beta_{\text{Cu}^{2+}} \quad [1]$$

$$E_{\text{Ni}/\text{Ni}^{2+}} = E_{\text{Ni}/\text{Ni}^{2+}}^0 - \frac{0.059}{2} \log \beta_{\text{Ni}^{2+}} \quad [2]$$

where  $E_{\text{Cu}/\text{Cu}^{2+}}^0$  and  $E_{\text{Ni}/\text{Ni}^{2+}}^0$  are the standard redox potentials of  $\text{Cu}/\text{Cu}^{2+}$  and  $\text{Ni}/\text{Ni}^{2+}$  and  $\beta_{\text{Cu}^{2+}}$  and  $\beta_{\text{Ni}^{2+}}$  are the formation constants of copper(II) and nickel(II) complexes, respectively. Table II lists the formation constants of copper(II) and nickel ions with sodium citrate and HEDTA.<sup>16</sup> Although the formation constants of copper(II) complexes are higher than that of nickel(II) complexes, the redox potential of  $\text{Cu}/\text{CuL}(\text{II})$  is more positive than that of  $\text{Ni}/\text{NiL}(\text{II})$  in solution. Furthermore, the concentration of copper(II) ions in the solution is higher than that of nickel ions ( $\text{Cu}^{2+}/\text{Ni}^{2+}$  mole ratio is 42), further favoring the deposition of copper over nickel. Therefore, when the Pd-activated epoxy substrate is immersed into the electroless solution, copper(II) ions are preferentially reduced with respect to nickel ions. In addition, the concentration of deposited nickel is constrained by the displacement reaction with copper(II)

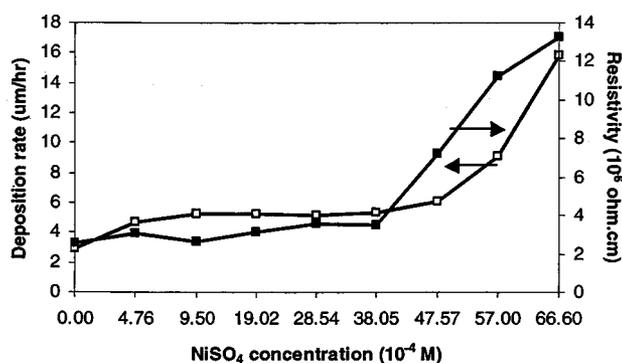


Therefore, the concentration of codeposited nickel in the deposit is low. Once the palladium catalyst is coating with copper, the copper deposition rate is lowered by the weak catalytic activity of copper for hypophosphite oxidation. Eventually, the deposition rate becomes quite low because the palladium is no longer exposed and fractional coverage of nickel in the deposit decreases due to displacement reaction.

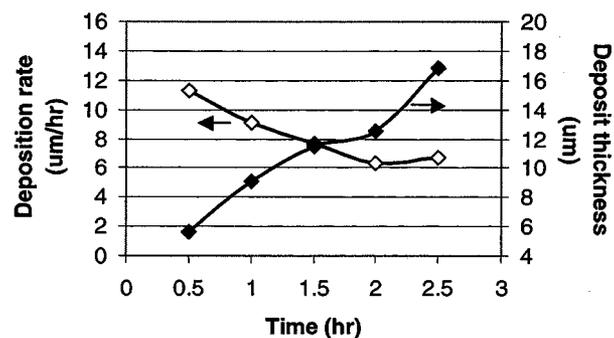
Nickel ions were required in the solution to maintain the deposition rates because nickel has catalytic activity for the oxidation of

**Table II.** Complex formation equilibrium constants and redox potentials of copper(II) and nickel(II) complexes (room temperature).

Complexing agent	Complex formation	Formation constant ( $\log \beta$ )	Redox potential (V vs. NHE)
$\text{Cu}^{2+}$ -sodium citrate	$\text{CuL}$	18.0	$-0.191$
$\text{Ni}^{2+}$ -sodium citrate	$\text{NiL}$	14.3	$-0.672$
$\text{Cu}^{2+}$ -HEDTA	$\text{CuL}$	17.4	$-0.173$
$\text{Ni}^{2+}$ -HEDTA	$\text{NiL}$	17.0	$-0.752$



(a)



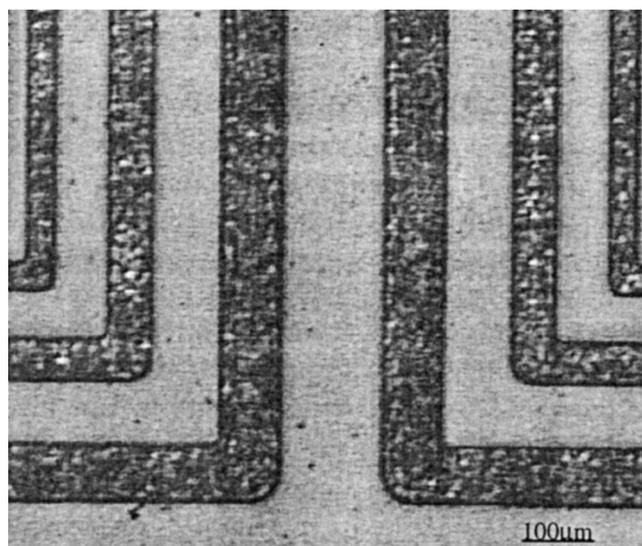
(b)

**Figure 5.** Effect of the addition of nickel ions in the electroless copper plating solution on the deposition process: (a) dependence of the deposition rate (60 min plating) and resistivity on the concentration of nickel ions; (b) dependence of the deposition rate and deposit thickness on plating times when the concentration of nickel ions is 0.0057 M.

hypophosphite. If the overall rate of the deposition reaction was limited by the half reaction for the oxidation of hypophosphite on the exposed nickel region, then one would expect the deposition rate to be controlled by the surface content of nickel. Figure 5 shows the effect of nickel ion concentration in the solution on the overall electroless copper deposition rate (60 min plating). As shown in Fig. 5a, in the absence of nickel ions, a deposition rate of 2.91  $\mu\text{m/h}$  was obtained in the solution with 0.5 ppm fd. In this case, hypophosphite was oxidized on copper or exposed palladium. The deposition rate of the electroless plating increased with the initial addition of nickel ions in the solution and was constant with nickel ion concentrations from 0.00095 to 0.0029 M. When the concentration of nickel ions increased further, the deposition rate increased dramatically. At 0.0057 M nickel(II), the deposition rate stabilized at 6.28  $\mu\text{m/h}$  after 2 h plating resulting in a linear increase in thickness with time (Fig. 5b). Table III lists the atomic concentration of nickel in the deposits obtained at different  $\text{Cu}^{2+}/\text{Ni}^{2+}$  mole ratio in the solutions, as measured by XPS. The codeposited nickel increased with solution con-

**Table III.** The effect of the  $\text{Cu}^{2+}/\text{Ni}^{2+}$  mole ratio in the solution on the nickel content in the deposit.

Ni(II) concentration in the solution ( $10^{-4}$ M)	$\text{Cu}^{2+}/\text{Ni}^{2+}$ mole ratio in the solution	Nickel content in the deposit (atom %)
9.50	42.00	0
38.04	10.51	0
47.57	8.41	2.3
57.06	7.01	6.2
66.57	6.01	8.1



**Figure 6.** Surface morphology of the copper deposited on the activated high density lines.

centration. The codeposited nickel in the deposits during plating accelerated the overall rate by most likely increasing the rate of the hypophosphite oxidation. The resistivity of the corresponding deposits increased with the nickel ion concentration (Fig. 5a).

At 0.0038 M nickel(II), the deposition rate of the electroless plating was 5.23  $\mu\text{m/h}$ . The plating rate was relatively linear with time, and the deposit had a resistivity of  $3.49 \times 10^{-6}$   $\Omega$  cm, prior to annealing. Figure 6 shows the surface morphology of the electroless copper deposit on the patterned epoxy substrate using the solution containing 0.0038 M nickel(II).

The lack of electroless copper acceleration with thiourea in a citrate complexing agent is contrary to the effect seen with the HEDTA complexing agent. Also, it was observed to accelerate the electroless process using either citrate or HEDTA complexing agents. Since thiourea could be oxidized to fd in HEDTA, one can postulate that the lack of acceleration of thiourea with citrate complexing agent may be due to the lack of oxidation to fd. This point will be investigated and may be the subject of future reports.

## Conclusions

Formamidine disulfide increased the deposition rate of the electroless copper plating where sodium citrate was used as the complexing agent and sodium hypophosphite was used as the reducing agent. Nickel ions were added to improve the catalytic activity of the deposit for hypophosphite oxidation. At a  $\text{Cu}^{2+}/\text{Ni}^{2+}$  mole ratio of 42, the deposition rate of the electroless plating decreased with time and nearly terminated after 90 min of plating due to the decreased surface catalytic activity for the oxidation of hypophosphite. The resistivity of deposited copper was 2.72  $\mu\Omega$  cm at an average deposition rate of 7.15  $\mu\text{m/h}$  (30 min of plating). Higher nickel ion concentration improved the deposition rate, but increased the deposit resistivity. An optimized electroless copper plating process with a nearly constant deposition rate with time and low deposit resistivity was developed.

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