Electroless Copper Deposition With Hypophosphite as Reducing Agent

By Aina Hung

A small amount of nickel ion promotes autocatalysis and continuous plating of hypophosphite-reduced electroless copper. A mechanism for this reaction is proposed, and the effects of various additives are discussed.

n 1950, a commercial electroless copper plating process was developed. By 1980, stable systems with automatic bath replenishment were commonplace in production facilities worldwide. The physical properties, structure, and composition of these coatings, ¹³as well as the kinetics and mechanism of their deposition, ⁴⁵ have been investigated. The effect of additives has also been the focus of research in recent years."""

Electroless copper has been used widely for plating nonconductors and in several functional areas, principally printed circuit boards. The common reducing agent for these baths is formaldehyde.

Recently, a non-formaldehyde bath was introduced and has been functioning in a production shop.⁸⁹ The system has wide operating parameters, a self-limiting deposit, long solution life, and generates no harmful formaldehyde vapors. Some predict it will become the electroless copper bath of the future.

The plating rate, deposit composition, and morphology of hypophosphite-reduced electroless copper in the presence of nickel ions are discussed here. The effect of additives on the coating is also examined.

Experimental Procedure

The electroless bath contained 0.024M copper sulfate, 0.052M sodium citrate, 0.27M sodium hypophosphite, 0.5M H_3BO_3 , and 0.002M nickel sulfate. The bath temperature was 65° C and the pH was maintained at 9.2. Fifty mL of solution was used for each gravimetric measurement of the plating rate. Prior to immersion in this solution, a sheet of copper with a surface area of 8 cm² was cleaned by immersion in 10 percent HNO₃ for 1 min. The copper was then weighed and activated in 0.1 percent PdCl₂ solution for 1 min. After 10 min of electroless copper plating, the sheet was removed from the bath, dried, and reweighed.

The surface composition of the copper plating was analyzed by scanning Auger micrograph/electron spectroscopy for chemical analysis (SAM/ESCA) using a spectrometer.* A scanning electron microscope** was used to study the morphology of the copper deposits.

Plating Rate

The catalytic activity of the metals for the anodic oxidation of hypophosphite reportedly decreases in the following order: Au>Ni>Pd>Co>Pt>Cu.¹⁰ Hence, the deposit thickness (usually <1 μ m) of the hypophosphite-reduced electroless finish is self-limiting because the reaction is not catalyzed by the deposited copper.

*Model PHI-590 AM, Perkin-Elmer, Norwalk, CT.

The introduction of nickel ions to the hypophosphitereduced solution promotes autocatalysis and continuous plating. It has been observed that the plating rate is essentially constant even after 60 min if a suitable amount of nickel ion is added. The effect of nickel on the plating rate, which was determined gravimetrically, is shown in Fig. 1. The deposition rate of copper on a suitably prepared ABS substrate" has also been studied and is identical to that on Pal-activated copper.

The plating rate decreased at low copper ion concentrations. However, there was still a lot of hydrogen gas evolution, which became more violent with an increase in the hypophosphite concentration. These phenomena

Additive	Conc.,*	Rate,
Nono	ing/ L	69
Saccharin	200	6.9
p-toluene sulfon- amide	200	6.9
Guanidine hydro-		
chloride	15	6.9
Thiourea	<0.2	6.7
	0.3	6.1
	>1	<1
	1**	6.3
2-MBT	<0.2	6.9
	0.6	4
	>1	<1
	0.9**	7.7

*Nickel ion concentration in bath was 0.002M except

where otherwise noted.





Fig.1—Effect of nickel ion on electroless copper plating rate.

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^{**}Model S-450, Hitachi, Tokyo, Japan.

Fig. 2—Effect of thiourea and 2-MBT on microstructure of electroless copper deposits from baths containing (1) no addifives, (2) 4 mg/L guanidine hydrochloride, (3) 200 mg/L saccharin, (4) 200 mg/L p-toluene sulfonamide, (5) 0.2 mg/L thiourea, and (6) 0.3 mg/L 2-MBT.

indicate that a side reaction evolving hydrogen gas takes place:

 $H_2PO_2 + H_2O \rightarrow H_2PO_3 + H_2$ (1)

The electroless solution containing nickel ions is relatively unstable and often spontaneously decomposes (i.e., deposits all the copper) within 24 hr. A small amount (<0.2 mg/L) of thiourea or 2-mercaptobenzothiazole (2-MBT) can stabilize the solution for more than 10 days. However, a high concentration of thiourea or 2-MBT causes a decrease in the plating rate. The rate of electroless copper deposition following such additions is shown in Table 1.

The addition of saccharin, p-toluene sulfonamide or guanidine hydrochloride does not affect the rate of copper deposition, but about 0.3 mg/L thiourea or 0.6 mg/L guanidine hydrochloride can slow it down. With an excess (>1 mg/L) of thiourea or 2-MBT, copper deposition stops completely after 2 min. In such solutions, the addition of a



Fig. 3—Structure of (1) saccharin, (2) p-toluene sulfonamide, (3) guanidine hydrochloride, (4) 2-MBT, and (5) thiourea.



Fig. 4—ESCA spectra of copper deposits. Peak at 855 indicates relative amount of nickel deposited from baths containing (1) 0.002, (2) 0.003, (3) 0.006, and (4) 0.01 mol/L Ni²⁺ ions.

suitable amount of nickel ions promotes continuous plating.

Effects of Additives

Scanning electron microscopy showed that the surfaces of electroless copper deposits were fairly rough and porous, indicating a spherical crystalline structure. The grains became smaller when the nickel ion concentration in the bath was increased. Addition of saccharin, p-toluene sulfonamide or guanidine hydrochloride did not change the microstructure of copper deposits. However, adding only ~0.2 mg/L of thiourea or ~0.3 mg/L of 2-MBT produced needle-like, randomly oriented crystals (Fig. 2). It was also observed that the addition of thiourea or 2-MBT caused a longer incubation period. Thus, the plating rate decreased and the deposit became firmly anchored to the substrate. By adjusting the pH and the concentration of additives and other components, semi bright deposits could



Fig. 5—Auger spectra of electroless copper from baths containing (1) no additives, (2) 200 mg/L p-toluene sulfonamide, (3) 0.3 mg/L 2-MBT, (4) 0.2 mg/L thiourea, and (5) 4 mg/L guanidine hydrochloride.

be obtained from the electroless copper bath.

Differences in the effects of additives maybe correlated to the electronic structure of their molecules (Fig. 3). Molecules containing a thio group can strongly adsorb on the copper surface and thus introduce a new reaction pathway. Hence, thiourea and 2-MBT can stabilize the bath and change the deposit morphology. Although saccharin, p-toluene sulfonamide, and guanidine hydrochloride can be weakly adsorbed on the copper surface,⁶ the basic deposition pathway is similar to that in a solution without additives'. The plating rate and morphology of deposits from baths containing these compounds therefore remain unchanged.

It has been reported that when formaldehyde is used as a reducing agent, guanidine hydrochloride can increase the plating rate and change the microstructure of the copper deposit. However, with hypophosphite, guanidine hydrochloride had a negligible effect on plating rate and microstructure. This indicates the reaction mechanisms are different.

Although nickel ions play an important role in electroless copper deposition, there was no evidence of nickel in the ESCA spectrum of the deposit when the nickel ion concentration in the bath was low ($Ni^{2*}/Cu^{2*} = 0.002/0.024$). Even with a higher concentration ($Ni^{2*}/Cu^{2*} = 0.006/0.024$), only a trace amount of nickel was found (Fig. 4). The results imply that nickel can catalyze the oxidation of hypophosphite (Fig. 3) and can also react with copper ions in solution:

Ni +
$$Cu^{2*}$$
 - Ni^{2*} + CU (2)



Fig. 6—Auger spectra of electroless copper deposits at a depth of 500 angstroms from baths containing (1) no additives, (2) 0.3 mg/L 2-MBT, (3) 0.2 mg/L thiourea, and (4) 4 mg/L guanidine hydrochloride.

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Auger spectrometry showed that additives introduced only small amounts of impurities to the deposits (Fig. 5). Coatings from baths containing either thiourea or 2-MBT exhibited very small amounts of N and S. The results suggest that adsorption of additives on the copper surface may be fairly strong, but at a depth of 500 angstroms, impurities could not be detected (Fig. 6). This implies that the additive does not codeposit with copper.

The oxygen content was relatively high at the surface because the deposit was exposed to the air. At 500 angstroms, the oxygen level decreased and even the deposits from baths containing additives were pure (Fig. 6). Because there is a close relationship between the reaction mechanism and the morphology and composition of the deposit, the experimental results indicate that, except for hydrogen evolution, no non-productive side reactions take place in the bath.

Plating Mechanism

The principle redox reactions in the bath are the reduction of copper ion to copper metal and the oxidation of hypophosphite ion to phosphite ion. Because the reactions can only take place at the catalytic surface, dehydrogenation of the reductant¹² is proposed as the first step of the reaction mechanism:

$$H_2PO_2^{-} \frac{\text{catalytic}}{\text{surface}} HPO_2^{-} + H$$
(3)

The HPO₂ formed can react with hydroxide ion as follows

$$HPO_2^- + OH^- \rightarrow H_2PO_3^- + e^-$$
(4)

The electron can transfer the charge to the copper or nickel ion to produce a copper or nickel deposit:

$$Cu^{2+} + 2e^{-} \rightarrow Cu \tag{5}$$

$$Ni^{2+} + 2e^{-} \rightarrow Ni \tag{6}$$

The nickel can further react with copper ions (Eq. 2). In solution, water molecules can compete with copper and nickel ions for electrons:

$$H_2O + e^- \rightarrow OH^- + H_2 \tag{7}$$

The hydrogen atoms formed in Eq. 3 or 7 can combine to form hydrogen gas:

$$H + H \rightarrow H_2$$
 (8)

The main overall reaction can thus be represented by

$$2H_2PO_2^{-} + Cu^{2+} + 2OH^{-} \rightarrow Cu + 2H_2PO_3^{-} + H_2$$
(9)

The combination of Eq. 3, 4 and 7 is the side reaction observed when the copper ion concentration is low or the hypophosphite level is high.

$$H_2PO_2^- + H_2O \to H_2PO_3^- + H_2$$
 (10)

Conclusions

An electroless bath prepared with hypophosphite as the reducing agent is not catalyzed by the plated deposit.

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Therefore, the reaction stops after the Pal-activated surface is completely covered by the copper. However, a small amount of nickel ion (Ni²⁺/Cu²⁺>0.0015/0.024) promotes autocatalysis and continuous plating. The bath can be stabilized by adding a small amount of thiourea or 2MBT.

Hypophosphite-reduced electroless copper baths with other completing agents, lower pH values, and different activation methods have also been studied.¹³The results indicate that the composition and microstructure of the coating depend on the method of activation, type of completing and reducing agents, concentration of each bath component, pH, temperature, additives, and plating time. The proper combination will produce quality deposits to meet specific requirements.

The rate of deposition and stability of the bath can be controlled at desired levels. However, maintaining a stable bath, a fast deposition rate, and acceptable coverage can be difficult. Because hypophosphite provides so many benefits as a reducing agent,' a more quantitative description of the physical and chemical aspects of the system is needed.

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About the Author

Aina Hung is an associate professor at Ming-Hsin Engineering College, Dept. of Chemical Engineering, Hsin-Feng, Hsin-Chu, Taiwan 30404, Republic of China. Her research centers on electroless plating. Ms. Hung holds a BS degree from National Taiwan University and an MS In chemistry from Washington University.