Studies on Formaldehyde-free Electroless Copper Deposition

By S. Karthikeyan, T. Vasudevan, K.N. Srinivasan & S. John

We have endeavored to develop a formaldehyde-free electroless copper deposition process. A suitable bath has been optimized with glyoxylic acid as a reducing agent. The bath parameters, such as temperature and the concentration of reducing and complexing agents, were studied. The influence of glyoxylic acid on the deposition of copper was studied by galvanostatic polarization measurements. SEM studies were also carried out to ascertain the structure of the copper deposits.

Electroless copper plating has been used primarily for plating on plastics and in the electronics industry. The main applications of electroless copper are in printed circuit boards (PCBs). Conventional PCB production is by subtractive technology. In this technology, about 60–90 percent of copper is wasted, and the recovery is also costly and troublesome. The subtractive method leads to pollution from the chromic acid etching solution. To avoid this, additive technology is being used in PCB processing.

The electroless copper plating solution generally available uses formaldehyde as the reducing agent. Formaldehyde is classified as a probable human carcinogen by the International Agency for Research on Cancer (IARC), and as a suspected human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH). Because acute exposure to formaldehyde causes considerable irritation to the eyes, throat and lungs, extreme care must be taken when handling the material. It is essential, therefore, to find an alternative to formaldehyde as a reducing agent. So far, many alternatives have been suggested, including the use of hypophosphite,[1-3] borohydrides,[4] hydroxene[5] and aminoboranes.[6] Darken[7] has developed an electroless copper plating bath based on glyoxylic acid as a reducing agent, but the rate of deposition was found to be low.

In the current investigation, glyoxylic acid was selected as an alternate to formaldehyde, and the work involves the following:

- Bath development,
- Effect of complexants on the rate and stability of the bath,
- Galvanostatic polarization studies, and
- Surface analysis by SEM studies.

Nuts & Bolts: What This Paper Means to You

Because of toxicity issues, it would be nice to eliminate formaldehyde from electroless copper solutions. Here, the authors search for a substitute, using glyoxylic acid as a reducing agent. Their results show potential.

Experimental Procedure

Various formulations available in the literature were selected and their rates of deposition at 30°C (87°F) were studied. Among them, a solution based on copper sulfate, sodium potassium tartrate, triethanolamine (TEA) and glyoxylic acid (reducing agent) was selected. The optimized bath composition is given as:

Copper sulfate	10 g/L
Sodium potassium tartrate	30 g/L
Triethanolamine (TEA)	30 mL/L
NaOH	15 g/L

To this bath, 20 mL/L of glyoxylic acid was added when ready to be used. The pH of the bath was adjusted to 12.0 using a 0.1N sodium hydroxide solution.

Deposition Rate

The rate of deposition was determined by a weight gain method. Activated mild steel panels were separately placed in a 250 mL beaker containing the above prepared bath with constant stirring. After 30 min, the panels were removed, washed, dried and weighed. The difference in weight was the weight of copper deposited. From the weight of copper deposited, the area of the panel and the density of copper, the deposition rate were calculated.

$$\text{Deposition rate, } \mu\text{m/hr} = \frac{\text{Wt of copper deposited, g}}{\text{Area of mild steel panel, cm}^2 \text{ x density, g/cm}^3}$$

Effect of Reducing Agent

Glyoxylic acid of various concentrations such as 20, 35, and 50 mL/L were tried at room temperature, as well as at 50°C (122°F). Based on deposition rate and stability, 20 mL/L was found to be the optimum concentration at both room temperature and at 50°C (122°F).

Effect of Temperature

Activated mild steel panels were placed in electroless copper solutions at 30° and 50°C (87° and 122°F) for 30 min. The panels were then removed, washed with water and dried. As before, the rate of deposition was calculated

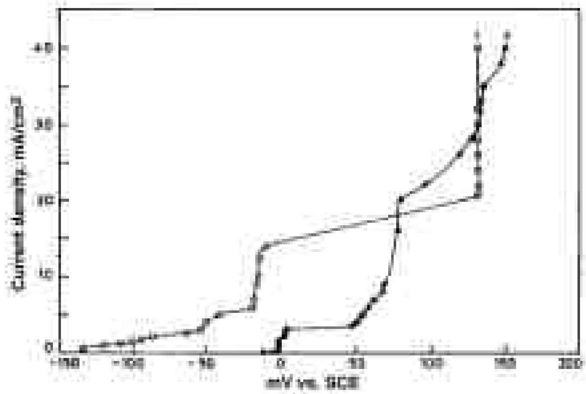

Fig. 1—Cathodic polarization behavior of electroless copper deposits (1) with reducing agent and (2) without reducing agent.

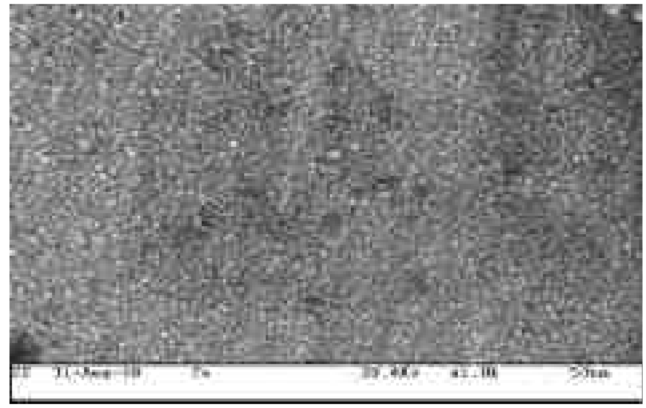

Fig. 2—SEM photograph of the electroless copper deposit (1000X).

Table 1—Effect of Complexing Agents on Deposition Rate & Bath Stability

Complexing agent	Deposition rate, µm/hr	Stability	Nature of deposit
Triethanolamine (TEA) (30 mL/L)	4.54	Decomposes after 30 min	Dull
Sodium potassium tartrate (30 g/L) with Triethanolamine (30 mL/L)	4.84	Very stable	Bright
EDTA (30 g/L) with Triethanolamine (30 mL/L)	2.46	Very stable	Semi bright
Lactic acid (25 mL/L) with Triethanolamine (30 mL/L)	2.16	Very stable	Semi bright

Table 2—Effect of Reducing Agent Concentration & Deposition Rate at Various Temperatures

Sample No.	Reducing agent conc.	Temperature	Deposition rate, µm/hr
1	20 mL/L	30°C (87°F)	4.84
2	20 mL/L	50°C (122°F)	4.97
3	35 mL/L	30°C (87°F)	5.30
4	35 mL/L	50°C (122°F)	5.38

from the weight of the deposit. The choice of this concentration is based on the stability of the bath without much sacrifice in the rate of deposition.

Polarization Studies

Polarization measurements were carried out galvanostatically by exposing a 1.0 cm^2 area of the plated specimens. A platinum foil of large surface area was used as an auxiliary electrode, and a saturated calomel electrode was used as the reference electrode. Current was varied from 0 to 40 mA, and the corresponding change in the potential was recorded. The specimens were cathodically polarized in the absence and presence of the reducing agent.

Surface Analysis

Surface analysis on the specimens was made by scanning electron microscopy (SEM) at 1000X and 2000X.

Results & Discussion

Effect of Complexing Agents

The main constituents of the electroless copper bath used in the current study were copper sulfate, sodium potassium tartrate with triethanolamine, sodium hydroxide, and glyoxylic acid. Table 1 shows the effect of complexing agents on the rate of deposition and stability of the bath. From the table, it can be seen that complexing agents—such as sodium potassium tartrate with triethanolamine, ethylenediamine tetraacetic acid (EDTA) with triethanolamine and lactic acid with triethanolamine—produced bright copper deposits with a very stable bath life.

The rate of deposition was very low in the case of EDTA with triethanolamine and lactic acid with triethanolamine. Stronger chelation of the copper ions accounted for this lower rate. The bath with the complexing agent sodium potassium tartrate with triethanolamine produced a bright deposit with high stability. Therefore, this bath was used for further studies.

Effect of Reducing Agent Concentration & Temperature on Deposition Rate

Table 2 shows the effect of reducing agent concentration on the rate of deposition at various temperatures. Glyoxylic acid at various concentrations, 20, 35 and 50 mL/L were studied at room temperature, as well as at 50°C (122°F). Of these, 20 mL/L was found to be the optimum concentration at room temperature. At 50°C (122°F), vigorous gas evolution was noted on the panel and the bath decomposed. This was attributed to the presence of more free cupric ions and reducing agents on the reaction sites and an enhanced rate of oxidation of glyoxylic acid. Any further studies were carried out at room temperature, therefore.

Mechanism of Electroless Copper Deposition with Glyoxylic Acid as Reducing Agent

In an alkaline solution, glyoxylic acid is present in the form of the glyoxalate ion, $CHOCOO^-$, which has a reducing potential very similar to that of formaldehyde (*i.e.*, +1.01 V). It also undergoes a Cannizaro reaction producing glycolate and oxalate:

$$CHOCOO^- + OH^- \rightarrow C_2O_4^{-2} + CH_2OHCOO^-$$

$$RCHO^- + 3OH^- \rightarrow RCOO^- + 2H_2O + 2e^-$$
where $R = COO^-$

The copper reduction, therefore, takes place in two steps:

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

$$2Cu^+ + 2e^- \rightarrow 2\ Cu$$

The reduction from the cupric to cuprous state is the rate-determining step. Additionally, because the glyoxalate exists in solution as an ion, it is totally nonvolatile in contrast to the fumes generated by formaldehyde.[7,8]

Polarization Studies

Figure 1 shows the polarization diagram for electroless copper with and without the reducing agent. It was found that the anodic process, namely the oxidation of glyoxylic acid, was the limiting reaction and was very vital to improving the plating rate.[9-10] The figure shows that in the presence of the reducing agent, the polarization curves were shifted to more negative potentials, from -15 to -140 mV (vs. SCE), indicative of an enhanced plating rate.

SEM Surface Analysis

Figure 2 shows the SEM photomicrograph of electroless copper at a magnification of 1000X. The small nodular structure of the deposited copper is visible.

Conclusion

Replacement of formaldehyde by glyoxylic acid as a reducing agent in electroless copper plating bath produces deposit at a high deposition rate. There is no pollution to the environment and the bath is free of carcinogenic material. The following is the optimum bath composition for obtaining bright copper deposits:

Copper sulfate	10 g/L
Sodium potassium tartrate	30 g/L
Triethanolamine	30 mL/L
Glyoxylic acid	20 mL/L
pH	12 – 12.5
Deposition rate	4.84 µm/hr
Temperature	30°C (87°F)

References

1. J. Flis & D.J. Duquette, *J. Electrochem. Soc.*, **131**, 34 (1984).
2. A. Hung, *Plating & Surface Finishing*, **75**, 62 (January 1988).
3. A. Hung, *Plating & Surface Finishing*, **75**, 74 (April 1998).
4. H. Narcus, *Plating*, **54**, 380 (1967).
5. J.P. Randin & H.E. Hintermann, *J. Electrochem. Soc.*, **117**, 160 (1970).
6. C. Baroberger & R. Schweitzer, *Chemikerzeitung*, **51**, 212 (1947).
7. J. Darken, *Trans. IMF*, **69**, 66 (February 1991).
8. O.E. Roberto, *Proc. AESF 76th Ann. Tech. Conf., Session I*, AESF Orlando, FL, 1989.
9. S.J. Harris, A.J. Gouid & P.J. Boden, *Trans. IMF*, 64, 24 (1986).
10. K.N. Srinivasan, S. John & S. Karthikeyan, *Proc. International Conf. on Adv. in Surface Science & Eng.* (2001), p. 21.

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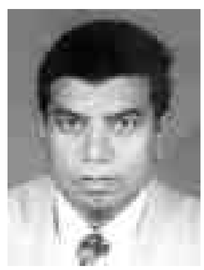

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