### **Technical Article**

### Effect of Buffer On Electroless Copper Deposition

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Fully additive electroless copper plating technology has recently been employed to satisfy the need of increasing wire density in more advanced multilayer printed circuit boards (PCBs). Because the pH of the plating solution affects the rate of deposition and the properties of the deposit, maintaining a steady pH during plating is important. In the present study, borate or phosphate was added to the electroless copper plating solution to stabilize the pH of the solution. Studies of these buffered solutions dealt with the mixed potential, plating rate, composition and some physical deposit properties. The pH of both the borate- and phosphate-buffered electroless copper plating solutions was more stable than without buffering. Furthermore, the deposition rate for the borate-buffered plating solution was much faster (13.74 µm/h), and no codeposition of borate was observed by the scanning Auger micrography. Additionally, the crystal structure and the resistivity of the deposit from the borate-buffered electroless copper plating solution were similar to those without buffering. Although the deposit from the borate-buffered solution was rougher and the grain size was larger, the quality of the deposit could be improved with the addition of small amounts of additive. The use of borate buffer in electroless copper plating solutions should be useful for the future fabrication of advanced multilayer PCBs.



Fig. 1—EPR spectra of plating solutions (A: no buffer; B: acetate buffer; C: phosphate buffer; D: borate buffer).

Electroless copper is important for many commercial applications including decorative plating-on-plastics, electromagnetic interference shielding, plating through-holes and vias, as well as full build electroless copper in the additive processes for printed circuit boards (PCBs) and some interconnecting devices. Increasing the wire density of printed circuit boards is the current trend as electronic products use highly integrated semiconductor devices. Thus, plating techniques that yield higher throwing power are required for the plating of small high-aspect-ratio holes and formation of reliable fine line circuit patterns. Fully additive electroless copper plating, with plate distribution independent of electric current fields, has been found to be a viable technology for such requirements. However, because of the relatively poor physical properties of electroless copper, fully additive electroless plating has been mostly limited to the manufacture of simple PCBs. With refinements in technique, fully additive electroless copper plating technology has been recently employed for the fabrication of more advanced multilayer PCBs.

Electroless copper deposition in alkaline media using formaldehyde as the reducing agent was first reported in 1957 by Cahill.<sup>1,2</sup> Over the last 30 years, various reducing agents, such as sodium hypophosphite, borohydride or dimethylamine borane; and chelating agents, such as glycerine, quadrol or triethanolamine, have been reported for use in electroless copper plating solutions.<sup>3,8</sup> Electroless

copper deposits and the stability of the plating solutions have been improved by introducing additives in the solutions.<sup>9-13</sup> The kinetics and mechanism of electroless copper deposition have also been investigated in detail.<sup>14-19</sup> The electroless copper deposition reaction is an oxidation-reduction reaction where the two reactions occur simultaneously at the catalytic substrate, and the result of these reactions is the establishment of a steady-state with a compromised potential called steady-state mixed potential.<sup>14</sup> This potential has been used as a diagnostic criterion for the feasibility of deposition.

The desirable characteristics for full-build electroless copper deposition include high plating rate, high ductility, high tensile strength, low resistance and a uniform fine grain structure with over a thickness range of  $18-25 \mu m$ . Furthermore, appropriate bath control is crucial in maintaining a steady high rate and a reliable deposit for long periods of plating. Since the thermodynamic driving force for copper deposition becomes greater

as the pH increases, electroless plating is usually performed at high pH. However, the pH of the solution changes after long periods of plating, thereby affecting the rate of deposition and the properties of the deposit. Hence, maintaining a steady pH of the plating solution during plating is important for the successful application of full-build electroless copper for manufacturing PCBs. Including buffers in the plating solution may maintain a steady pH and result in deposits with the desired properties. To test this hypothesis, we investigated plating solutions in the presence of acetate, borate or phosphate buffers, and the results are presented in this paper.

Phosphoric and boric acids are weak oxyacids, each with three dissociable protons. The pKa values of the third dissociation constant are 12.3 and 12.8 for phosphoric and boric acid, respectively. A solution containing phosphoric or boric acid in the alkaline region would be buffered, which can protect the solution against large fluxes of hydroxide ions or protons. Acetic acid is a weak acid, and the buffering range is around 4.74. There is no buffering action with the addition of acetate in the alkaline region.

In the present report, the phosphate or borate was added individually to the electroless copper plating solution to stabilize the pH of the solution, while acetate was added as a

control. The mixed potential, plating rate, composition and some physical properties of deposits obtained from the buffered solution were determined and compared with those obtained from solution with either the addition of acetate or without buffer.

#### **Experimental Procedure**

The electroless copper plating solution used in this experiment contained 0.05M copper sulfate, 0.1M EDTA, and 0.22M formaldehyde. The concentration of phosphate, borate or acetate was 0.3M. The pH of the plating solution was adjusted to 12.5 at  $25^{\circ}$ C ( $77^{\circ}$ F). The solution temperature was kept at  $60^{\circ}$ C ( $140^{\circ}$ F) during deposition. The four different electroless copper plating solutions studied in the present experiment are shown in Table 1.

The mixed potential was measured in situ with a potentiostat.<sup>20</sup> The working electrode was a palladium-activated copper/epoxy laminate, and the reference electrode was a saturated calomel electrode (SCE).

The substrates used for this study were FR-4 epoxy plates. The electroless copper samples were prepared by treating the substrate with a series of pretreatment processes before electroless copper deposition. The pretreatment processes included cleaning, swelling, microetching, neutralization, predip, activation and acceleration. After the desired deposition time, the thickness of each sample was measured at least five times by an X-ray fluorescence coating thickness measurement instrument. The deposition rate was then calculated for all of the measurements, and the average value was reported.

The surface morphology of each sample was examined by scanning electron microscopy. The surface composition and the depth profile of each sample were analyzed by scanning Auger micrography. The crystal structure of each sample was studied by X-ray diffractometry, scanning from 40° to 140° at a scan rate of 4°/min. The electrical resistance of each sample was measured by a four-point probe.

#### Results & Discussion Electroless Copper Plating Solution pH

In the highly alkaline electroless copper plating solution, the addition of phosphate and borate should stabilize the pH of the solu-

# Table 1Composition of the Electroless Copper Solution& Steady-state Mixed Potential of Deposition

Bath	Composition of plating solution	Steady-state mixed potential
Α	Copper sulfate + EDTA	-0.68 V
В	Copper sulfate + EDTA + acetate	-0.68 V
С	Copper sulfate + EDTA + phosphate	e -0.80 V
D	Copper sulfate + EDTA + borate	-0.70 V

## Table 2Average Deposition Rate

Bath	Α	В	С	D
Deposition rate	22.2 µm/h	21.9 µm/h	7.5 µm/h	22.2 µm/h
during first 10 min				
Deposition rate	9.84 µm/h	9.82 µm/h	5.44 µm/h	13.74 µm/h
over full plating time				

A: no buffer; B: acetate buffer; C: phosphate buffer; D: borate buffer

tion, because the buffer ranges of the phosphate or borate solutions are in the alkaline region (vide supra). Furthermore, there should be no buffering action of acetate in the alkaline plating solution because the buffer range of acetate is in the acidic region.

Indeed, the electroless copper plating solution was stabilized by both phosphate- and borate-buffers, and there was no buffering action of acetate in the plating solution. The initial pH values of all the copper plating solutions were 12.5 at 25°C (77°F). After depositing the same 3.2-µm thickness on epoxy substrates of equal size, the pH of the plating solution with no buffer and with acetate were both around 12.0, while the pH of the phosphate- and boratebuffered plating solutions were around 12.3. This demonstrated the utility of phosphate-and borate-buffers in stabilizing the pH of the plating solution.

#### **Deposition Mixed Potential**

The mixed potential of electroless deposition has been used as a diagnostic criterion for the feasibility of deposition. A mixed potential more negative than the reduction potential of the copper complex ion would be required but not sufficient for deposition. However, if the mixed potential is less negative than the reduction potential of the copper complex ion, deposition will not occur.

The steady-state mixed potentials were measured by the in situ measurement method (Table 1).<sup>20</sup> They were all more negative at the beginning of deposition (approximately -0.85V vs. SCE) most likely because of the high catalytic activity of the initial palladium catalytic surface. As the deposition reaction proceeded, the mixed potentials became more positive because of the coverage of the palladium catalytic surface by the copper deposit. After approximately 15 minutes of deposition, the mixed potentials reached a steady-state value for all solutions.

The steady-state mixed potentials of plating solutions with no buffer or with acetate were -0.68 V vs SCE, indicating no obvious effect of acetate on the mixed potential of the solution. By contrast, the steady-state mixed potential for the deposition of the electroless copper plating solution with phosphate and borate buffers was -0.80 V and -0.70 V vs. SCE, respectively. The steady-state mixed potentials for all four plating solutions were far more negative than the reduction potential of copper complex ion (-0.25 V vs SCE), consistent with the observed electroless deposition.



Fig. 2—Surface morphology examined by SEM: (a) epoxy substrate; electroless copper deposit of (b) A, (c) B, (d) C, (e) D. (A: no buffer; B: acetate buffer; C: phosphate buffer; D: borate buffer).

#### **Deposition Rate**

When the palladium catalyzed substrate was immersed in any of the electroless copper plating solutions, hydrogen gas evolved after an induction period. The induction period of deposition was very short (< 2 s) for all plating solutions except the phosphate-buffered solution, which exhibited an induction period of four min. This may be because of complexation between copper ions and phosphate, since the ligand type and concentration that complexes the copper ion determine the duration of this induction period.<sup>21</sup>

After the induction period, the rates of deposition were relatively fast for the first ten minutes for all plating solutions (Table 2). The rates of copper deposition were higher at the beginning of the deposition for all four solutions, consistent with the extremely negative initial mixed potentials mentioned earlier. Furthermore, the rates of deposition decreased as the mixed potentials became more positive. This can be attributed to the high catalytic activity of the initial palladium catalytic surface, which was eventually covered by the copper deposit.

The deposition rates for the plating solutions with acetate and without buffer were approximately the same (~9.82  $\mu$ m/h), indicating that there was no obvious effect of acetate on deposition rate. Strikingly, the rate of deposition was the lowest for the plating solution containing phosphate buffer (5.44  $\mu$ m/h), and was the highest for the plating solution with the borate buffer (13.74  $\mu$ m/h).

There is an unpaired electron in the Cu(II) complex ion. This complex ion can be detected by electron paramagnetic resonance spectroscopy (EPR). From the position of the line, one may calculate the "g" value, which is characteristic of the paramagnetic species, and may be used as a fingerprint. According to the solution EPR spectroscopy, the signal of the copper hydroxide complex ion (g = 2.0930) appeared only when the pH of copper EDTA ion solution was higher than 11.

Interestingly, the relative signal intensity of the copper hydroxide complex ion to the other copper complex ions was the smallest for the phosphate-buffered plating solution (Fig. 1). This suggests that the deposition rate may correlate with the concentration of copper hydroxide complex ion, which would explain the low deposition rate for the phosphate-buffered plating solution. However, the concentration of copper hydroxide complex ion alone does not account for the high deposition rate for the borate-buffered plating solutions. Further studies are necessary to reveal the other factors that determine the deposition rate.

#### Deposit Surface Morphology

The surface morphology of the epoxy substrate after microetching and the copper deposits from four electroless copper plating solution were studied by scanning electron microscopy (Fig. 2). After microetching, the surface morphology of the epoxy substrate showed concave porous structures, which were susceptible to adsorption of palladium colloid. The diameters of the concave structures and their associated pores were 10  $\mu$ m and 2  $\mu$ m, respectively. The deposit surfaces from the solutions with acetate and without buffer were expected to be similar, because deposition rates in these two plating solutions were similar. Indeed, the surfaces of the copper deposits from both solutions were rough, and showed loose grains of polycrystalline copper with an average grain size of 5  $\mu$ m.

In contrast, the copper deposit from phosphate-buffered plating solution was more compact, and the average grain size of the polycrystalline copper was smaller (~3 µm), and the concave substrate underneath was apparent. The small polycrystalline grain size for the copper deposit from the phosphate-buffered plating solution may be related to the low deposition rate. The copper deposit from borate-buffered solution was rougher, with a larger average polycrystalline grain size of ~8 µm, and was most likely related to the high deposition rate. Nevertheless, we did find that the quality of the deposit can be improved with addition of small amounts of additives.<sup>22</sup>

#### **Deposit Composition**

The compositions of all four samples were studied by energy dispersion analysis by X-ray (EDAX) and scanning Auger micrography. Only the copper signal was observed on the EDAX spectra for all four samples. However, at the surface of all four samples, in addition to the copper signal, there was an oxygen signal observed by scanning Auger micrography from the exposure of the sample to the air. At a depth of 5000 nm, however, no oxygen signal was observed. Only the copper signal was present, indicating that there was no codeposition of phosphate, borate, or acetate.

#### Deposit Crystal Structure

The preferred orientation of the deposit can be expressed in terms of a texture coefficient, TC,<sup>23</sup> defined as follows:

$$TC' = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{n} \Sigma \left[\frac{I(hkl)}{I_0(hkl)}\right]}$$

where I(hkl) is the relative intensity of the (hkl) reflections measured for various electroless copper deposits, I0(hkl) is the standard intensity for randomly-oriented copper powder and n is the number of reflection planes. In this experiment, three reflection planes were used to calculate TC: (111), (200) and (220). When the TC value of all reflection planes is equal to unity, the crystal is randomly-oriented. When the TC value of any plane is greater than unity, a preferred orientation exists. The larger the value of TC, the greater is the degree of the preferred orientation.

The texture coefficients for all deposits were determined and are given in Table 3. There was a minor preferred orientation in the (111) plane for all deposits. Furthermore, the deposit from boratebuffered plating solution also showed a minor preferred orientation in the (220) plane. However, the texture coefficient of all deposits and all the reflection planes studied were close to unity, indicating that all deposits were nearly randomly-oriented.

The mean crystallite diameters were calculated from the half line width by the Scherrer equation<sup>24</sup> (Table 3). The mean crystallite diameters were similar for all samples, indicating that there was no obvious effect on crystal structure by adding acetate, phosphate or borate to the plating solution.

#### Deposit Resistivity

Many factors can influence the resistivity of the deposit such as purity, crystal structure and surface morphology of the deposit. In general, less contaminated, less porous and smoother surfaces would result in a lower resistivity. The composition and crystal structure of all four deposits were similar as discussed earlier. Although the surface of the deposit from the phosphate-buffered plating solution was more compact, and the surface of the deposit from the borate-buffered plating solution was rougher, these were minor differences. Therefore, the resistivity would be expected to be similar for all four deposits.

The resistivities of the four different deposits were measured and are given in Table 4. The resistivity of the deposit from the plating solution with acetate was slightly higher than the others, and the resistivity the deposit from the plating solution with phosphate was slightly lower than the others. However, the four deposits should be considered the same in terms of resistivity, because the values were all of the same order of magnitude and the variations were well within experimental error.

#### Conclusions

The pH of the electroless copper plating solution was stabilized with the addition of phosphate or borate in the plating solution, and there was no obvious effect of acetate on the pH of the plating solution. As expected, the deposition rates were similar for plating solutions with no buffer and with acetate (~9.82  $\mu$ m/h), while the deposition rate in the borate-buffered plating solution was much higher (13.74  $\mu$ m/h). However, the deposition rate in the phosphate-buffered plating solution was the lowest (5.44  $\mu$ m/h), which may be related to complexation between copper ions and phosphate. Regardless, no codeposition of acetate, phosphate or

### Table 3Deposit Crystal Structure

Bath	Reflection plane	Texture coefficient	Mean crystallite diameter
А	(111)	1.11	3.44Å
	(200)	0.91	
	(220)	0.98	
В	(111)	1.06	3.41Å
	(200)	0.90	
	(220)	1.04	
С	(111)	1.08	3.34Å
	(200)	0.89	
	(220)	1.03	
D	(111)	1.06	3.22Å
	(200)	0.83	
	(220)	1.11	

A: no buffer; B: acetate buffer; C: phosphate buffer; D: borate buffer

#### Table 4 Average Deposit Electrical Resistivity, $\mu$ Ω-cm

Bath	Α	В	С	D
Resistivity	4.60	6.29	3.80	4.49

A: no buffer; B: acetate buffer; C: phosphate buffer; D: borate buffer

borate was observed. Furthermore, the crystal structure and the resistivity of all four deposits were similar. While the deposit from the plating solution with phosphate buffer was more compact and the grain size was smaller than with no buffer or with acetate, the deposit from the borate-buffered solution was rougher and the grain size was greater than the others. Nevertheless, the quality of the deposit from the borate-buffered solution can be improved with addition of small amounts of additive. This demonstrates the potential of the borate-buffered electroless copper plating solution in fully additive electroless copper deposition technology for the fabrication of advanced multilayer PCBs.

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