Effect of 2,2′-dipyridine on Borate-Buffered Electroless Copper Deposition

by Show-Chin Kou & Aina Hung*

Electroless copper plating is an important process in the fabrication of high density multilayer printed circuit boards (PCB). Recent developments in electroless copper plating have focused on increasing the deposition rate and decreasing the deposit electrical resistivity. We have previously reported a high deposition rate for an electroless copper plating solution containing a borate buffer.[1] However, the deposits from these solutions were rough, with large grains and high electrical resistivity. Herein, the use of a 2,2'-dipyridine additive was studied toward the goal of improving the quality of the deposit.

Electroless copper deposition technology has rapidly advanced in recent years including widespread application in areas such as through-hole plating in printed circuit boards, decorative plating of household utensils and in the automotive industry, electromagnetic interference shielding of electronic components, conductive traces in electronic interconnection devices and integrated circuit manufacturing.[2-4] The technique of plating into small high-aspect-ratio holes and the formation of reliable fine line circuit patterns are required in the manufacture of high density multilayer printed circuit boards. Fully additive electroless copper deposition is a feasible technology for meeting these needs. However, many challenges remain in the development of fully additive electroless copper deposition. The critical technical challenges are higher deposition rate, low resistance and fine grain structure of the copper deposit.

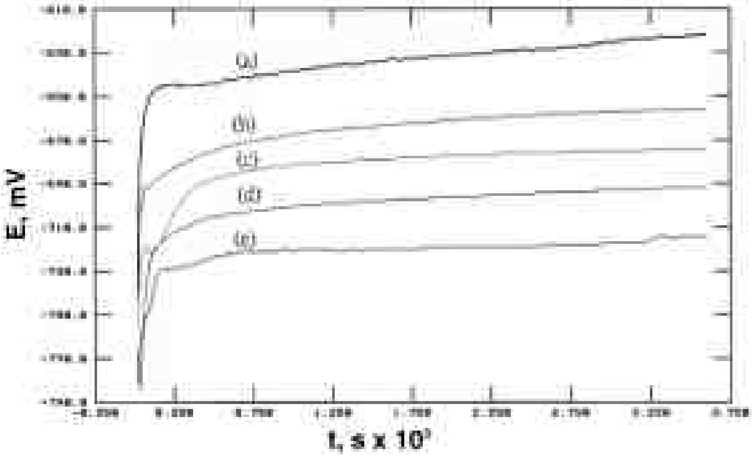

Figure 1—Mixed potential of electroless copper plating solution containing 2,2’-dipyridine: (a) 0 ppm, (b) 2 ppm, (c) 5 ppm, (d) 10 ppm, (e) 20 ppm.

Nuts & Bolts: What This Paper Means to You

In our February 2002 issue, these researchers reported on a high-rate borate-buffered electroless copper bath. It showed promise but fell short in matters of bath stability and deposit roughness. Those problems have been surmounted with the addition of an organic additive, 2,2′-dipyridine. This formulation now shows promise in providing a high electroless deposition rate from a stable bath *and* excellent surface finish to meet the requirements of today’s increasingly detailed and fine-line patterns on high density multilayer printed circuit boards.

The basic components of an electroless copper plating solution are a copper salt, a reducing agent, a copper (II) complexing agent and a pH adjusting compound. In addition, various proprietary additives have been incorporated in the plating solution.[5,6] Additives that stabilize the plating solution against undesirable spontaneous plate-out are called stabilizers.[7] Additives that increase the plating rate are called accelerators.[8] Additives that decrease the surface tension of the plating solution and eliminate hydrogen bubbles are called wetting agents.[9] Some functional additives can improve the adhesion of the copper film to nonmetal substrates or modify the grain size and surface morphology of the copper deposit. Regardless of their primary function, most additives have more than one effect on the electroless copper deposition.[10-12]

An electroless copper plating solution is thermodynamically unstable and prone to spontaneous decomposition. Stabilizing additives are necessary in practical operation. Such additives are usually incorporated at low concentrations to adsorb onto the active microseeds in the bulk solution and block the growth of the microseeds to prevent plate-out. However, at high concentrations, these additives may also adsorb onto the active surface and inhibit growth, decreasing the deposition rate. The adsorption of additives on the active surface nuclei may also modify the grain size and surface morphology of the deposit. Therefore, such additives have also been used as grain refiners. Among the organic additives that have been used as stabilizers or grain refiners are sulfur- or nitrogen-containing compounds.[13-17]

The electroless copper deposition reaction is a combination of the oxidation of a reducing agent, such as formaldehyde, and the reduction of a copper complex ion occurring simultaneously at active sites on the substrate. The open circuit potential of such reactions is called the mixed poten-

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tial, an important yardstick for determining the feasibility of deposition. The more positive the mixed potential, the more feasible the deposition and the less stable the plating solution. There are many factors that influence mixed potential, such as the concentration of the metal ion and reducing agent, the catalytic activity of the substrate surface, the temperature and pH of the plating solution, as well as the nature and amount of additives in the plating solution.[18]

In our previous study, a high deposition rate for an electroless copper plating solution with a borate buffer was reported.[1] However, the deposit from this solution was rough with a relatively large grain size and high electrical resistivity. In the present paper, 2,2’-dipyridine was used as an additive to improve the quality of the deposit. The effect of 2,2’-dipyridine on the mixed potential and deposition rate of electroless copper deposition was investigated. The influence of this additive on the composition, surface morphology, crystal structure and electrical resistivity of the copper deposits was also studied.

Experimental

The electroless copper plating solution used in this work contained 0.05 M copper sulfate, 0.1 M EDTA, 0.22 M formaldehyde, 0.3 M sodium tetraborate and amounts of 2,2'-dipyridine varying from 2.0 to 20 ppm. The pH of the plating solution was maintained at 12.5 at 25°C (77°F). The solution temperature was maintained at 60°C (140°F) during deposition.

The mixed potential was measured in situ with a potentiostat.[19*] The working electrode was a palladium-activated Cu/epoxy laminate, and the reference electrode was a saturated calomel electrode (SCE).

The substrate was a FR-4 epoxy plate. The samples were prepared by treating the substrate with a series of pretreatment steps before electroless copper deposition, including cleaning, swelling, microetching, neutralization, predip, activation and acceleration. After the required deposition time, the thickness of each sample was measured at least five times by the weight gain method. The rate of copper deposition was then calculated and the average value was obtained.

The surface morphology of each sample was examined by scanning electron microscopy (SEM).[**] The surface composition and depth profile of each sample were analyzed by scanning Auger micrography.[***] The crystal structure of each sample was determined by scanning from 40° to 140° at a scan rate of 4°/ min with an X-ray diffractometer.[****] The electrical resistance of each sample was measured by a four point probe.[*****]

Table 1

Effect of 2,2′-dipyridine on the Electroless Copper Deposition Rate

Amount of 2,2’-dipyridine in solution, ppm	0	2	5	10	20
Average deposition rate, μm/h	8.03	7.02	6.34	4.63	4.11

Table 2

Effect of 2,2′-dipyridine on the Crystal Structure of the Electroless Copper Deposit

2,2’-dipyridine Content	**Crystal Structure of Electroless Copper Deposit**	
	Reflection Plane	**Texture Coefficient**
0 ppm	(111)	1.35
	(200)	0.68
	(220)	0.97
2 ppm	(111)	1.24
	(200)	0.85
	(220)	0.91
5 ppm	(111)	1.23
	(200)	0.87
	(220)	0.90
10 ppm	(111)	1.24
	(200)	0.89
	(220)	0.87
20 ppm	(111)	1.22
	(200)	0.91
	(220)	0.87

Table 3

Effect of 2,2′-dipyridine on the Resistivity of the Electroless Copper Deposit

Amount of 2,2’-dipyridine in solution, ppm	0	2	5	10	20
Average resistivity, μÝ-cm	4.43	2.87	3.10	3.00	3.30

Results & Discussion

Steady State Mixed Potential

The mixed potentials were monitored with time *in situ* for the plating solutions containing 2,2’-dipyridine (Fig. 1). The mixed potentials were all more negative at the beginning of the deposition. As the deposition reaction proceeded, the mixed potentials became more positive. After 15 min the mixed potential reached the steady state mixed potential. The steady state mixed potential was about -0.63V_{SCE} for deposition without the additive in solution. As the amount of 2,2’-dipyridine was increased from 2 to 20 ppm, the steady state mixed potential changed from -0.63 V_{SCE} to -0.72 V_{SCE}.

Since electroless copper deposition is based on mixed potential theory and a combination of two simultaneous electrochemical redox reactions, the polarization curves for formaldehyde oxidation and copper complex ion reduction may be added to predict the mixed potential. Adding 2,2’-dipyridine to the plating solution should influence the both polarization curves. Because 2,2’-dipyridine is less polar than water, it tends to preferentially accumulate within the double layer region of the substrate surface by its hydrophobic interaction with water. According to the literature, the adsorption of 2,2’-dipyridine occurs on the active sites in the bulk or on the substrate surface.[15] The active sites are usually those having higher surface energy, i.e., the dislocations of the microscopic convex point of the surface and the newly formed copper nuclei. The adsorbate layer of 2,2’-dipyridine on the active site will cause a substantial decrease in the catalytic activity of the substrate surface and the deposition reaction must therefore be catalyzed over a greater distance. Thus, with

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[*] *EG&G Model 273A, Princeton Applied Research, Princeton, NJ.*

[**] *Cambridge Instruments Model 360 Steroscan, Cambridge Instruments, Cambridge, UK.*

[***] *Perkin-Elmer. Model PHI-590 AM, Perkin Elmer Corp., Wellesley, MA.*

[****] *Schimadzu Model XD-5, Schimadzu Corp., Kyoto, Japan.*

[*****] *CDE model ResMap273, Creative Design Engineering, Inc., Cupertino, CA.*

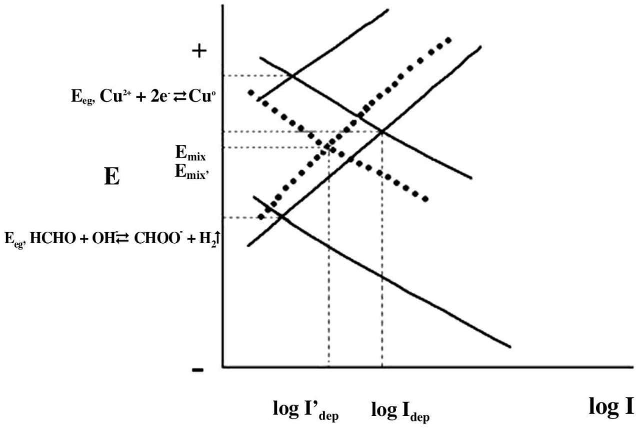

Figure 2—Schematic diagram of the effect of 2,2'-dipyridine on copper ion reduction and formaldehyde oxidation polarization curves:
▬ *Polarization curves without 2,2'-dipyridine in the plating solution*
•••• *Polarization curves with 2,2'-dipyridine in the plating solution.*

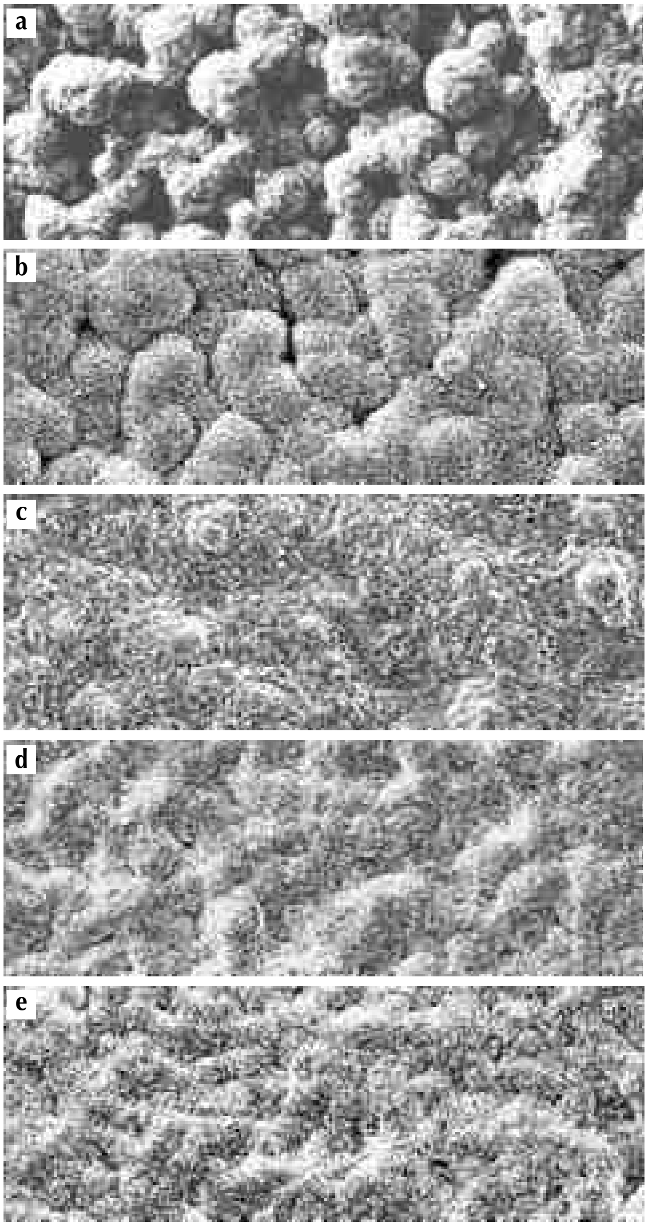

Figure 3—Surface morphology of copper deposit from the electroless copper plating solution containing 2,2'-dipyridine: (a) 0 ppm, (b) 2 ppm, (c) 5 ppm, (d) 10 ppm, (e) 20 ppm.

the addition of 2,2'-dipyridine, the oxidation polarization curve of formaldehyde was shifted more positive, the reduction polarization curve of copper complex ion was shifted more negative, and the result was a shift of mixed potential to more negative values (Fig. 2).

Deposition Rate

The effect of 2,2'-dipyridine on the deposition rate of electroless copper was determined by the weight gain method (Table 1). As the amount of 2,2'-dipyridine in the plating solution was increased from 2 to 20 ppm, the deposition rate decreased from 8.03 to 4.11 μm/h. The rate of decrease of the deposition rate decreased as the amount of 2,2'-dipyridine in the plating solution increased. The deposition rate reached a steady value of 4 μm/h at 2,2'-dipyridine concentrations above 20 ppm .

According to the schematic diagram of Fig. 2, adding 2,2'-dipydidine shifted the mixed potential to a more negative value and simultaneously decreased the deposition current . As the amount of 2,2'-dipyridine increased, the mixed potential was further shifted more negative and the deposition rate decreased.

As with the shift of the mixed potential, the inhibition of the electroless copper deposition rate by 2,2'-dipyridine can be explained by the adsorption of 2,2'-dipyridine on the active sites of the substrate surface.[15] Because of the steric hindrance of the 3,3' hydrogen of the 2,2'-dipyridine molecule, the adsorption of 2,2'-dipyridine on the substrate surface was very possibly at the 1,1' positions of the 2,2'-dipyridine's nitrogen with the 2,2'-dipyridine molecule aligned perpendicular to the substrate surface.[20] Therefore, in the presence of 2,2'-dipyridine adsorbate only a certain fraction of the substrate surface is available to catalyze the deposition reaction and the deposition rate is thus reduced.

Our results showed that, at 2,2'-dipyridine levels above 20 ppm, the deposition rate reached a steady deposition rate of 4 μm/h. Therefore, the adsorption of 2,2'-dipyridine was expected to followed the Langmuir adsorption isotherm. In the limit, when the concentration of 2,2'-dipyridine was above 20 ppm, the substrate surface was saturated with 2,2'-dipyridine and the system reached a steady deposition rate.

Surface Morphology

The surface morphology of the copper deposits was studied by scanning electron microscopy (Fig. 3). The surface of the copper deposit from the plating solution without 2,2'-dipyridine was rough, and exhibited loose grains of polycrystalline copper having an average grain size of 8 μm. The copper deposit from plating solutions containing 2,2'-dipyridine was more compact, and the average grain size was smaller. At 2,2'-dipyridine concentrations above 5 ppm, the grains of polycrystalline copper overlapped each other. The surface became smoother with increasing amounts of 2,2'-dipyridine.

The smaller polycrystalline grain size and improved leveling obtained from plating solutions containing 2,2'-dipyridine may also be related to the adsorption of 2,2'-dipyridine on the active sites of the substrate surface. The reduction in grain size is related to the preferential adsorption of 2,2'-dipyridine on the higher surface energy dislocations. As the copper grain size is reduced, the deposit becomes more compact. The adsorbate on microscopic convex points of the substrate surface may inhibit copper deposition on those particular sites, and cause a leveling effect. Therefore, addition of 2,2'-dipyridine results in smaller polycrystalline grain size and smoother deposits.

Composition

The composition of the copper deposit was studied by scanning Auger micrography. On the surface of the copper deposits obtained from solutions containing 2,2'-dipyridine, oxygen and carbon signals were observed because of exposure to the air and adsorption of 2,2'-dipyridine on the substrate surface. However, neither carbon nor nitrogen were observed with depth profiling down to 100 nm, indicating there was no codeposition of 2,2'-dipyridine in the copper deposit.

Crystal Structure

The texture coefficient of the three reflection planes of each copper deposit is shown in Table 2. For the copper deposited from the plating solution without 2,2'-dipyridine, the texture coefficient for the reflection planes followed the trend: (111) plane = 1.35 > (220) plane = 0.97 > (200) plane = 0.68. This indicates that the copper deposit is a textured deposit with preferred orientation in the (111) plane and not in the (200) plane. Adding 2,2'-dipyridine lowered the texture coefficients of the (111) and (220) reflection planes, and raised the texture coefficient of the (200) reflection plane. When the concentration of 2,2'-dipyridine reached 20 ppm, the copper deposit was still a textured deposit with slight (111) preferred orientation. Although the texture of the copper deposit was modified by the addition of 2,2'-dipyridine, the preferred orientation remained the (111) reflection plane. The reduction of the texture coefficient for the (111) and (220) reflection planes resulted led to the adsorption of 2,2'-dipyridine on these reflection planes, increasing the (200) texture coefficient.

Resistivity

The resistivities of copper deposits are shown in Table 3. Because the surface of the copper deposit from plating solutions containing 2,2'-dipyridine was smoother, the average grain size of the polycrystals was smaller, and thus the structure of copper deposit was more compact. Furthermore, there was no 2,2'-dipyridine codeposited with copper. Therefore, the resistivity was lower (~3 μÝ-cm).

Conclusions

Recent technical challenges require electroless copper processes with higher deposition rates, low resistivity and fine deposit grain structure. High copper deposition rates (8.03 μm/h) have been achieved with borate as a buffer in the plating solution. However, the deposit was rough and the grain size was large. Therefore, 2,2'-dipyridine was investigated as an additive to improve these deposit properties.

With 2,2'-dipyridine in the plating solution, the steady state mixed potential of electroless copper deposition was shifted to a more negative value with decreased deposition current. When the amount exceeded 20 ppm, the deposition reaction reached a steady deposition rate of 4 μm/h.

The resistivity of the copper deposit (~3μÝ-cm) was lower with 2,2'-dipyridine in the plating solution. Also, the polycrystalline grain size was reduced, yielding a more compact deposit structure and smoother deposit surface. There was no codeposited 2,2'-dipyridine in the copper deposit. Although the texture of copper deposit was modified by the addition of 2,2'-dipyridine, the preferred orientation remained in the (111) reflection plane.

According to the molecular structure of 2,2'-dipyridine, the effects of 2,2'-dipyridine can be attributed to the adsorption at the 1,1' nitrogen of 2,2'-dipyridine on the copper surface with the 2,2'-dipyridine molecule aligned perpendicular to the substrate surface. Furthermore, the adsorption of 2,2'-dipyridine followed the Langmuir adsorption isotherm.

These results reinforce the value of a borate-buffered electroless copper plating solution for fully additive electroless copper deposition for the fabrication of high density multilayer printed circuit boards.

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