The Effect of Organic Additives On a CUO Electroless Copper Bath

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An a-c impedance technique is employed to study the kinetic influence of various organic additives in a CuO electroless copper bath. It is shown that a trace amount of additive results in a remarkable increase of ohmic resistance and a slight decrease of capacitive reactance. The Gouy-Chapman-Stern model is proposed to interpret the experimental data. It is also demonstrated that an additive has a profound impact on crystallite morphology, but little effect on crystal orientation. Codeposition of additives occurs only at a very thin layer at the external deposit surface. The baths containing 2,2'-dipyridyl and 1,10phenanthroline show higher as-deposited ductility than those obtained from CuS0, systems. This can be attributed to synergism of the stabilizer, grain refiner, and surfactant, as well as more desirable anions.

he demand for surface-mounted devices has seen tremendous growth in the last 10 years. Future manufacturing trends of printed circuit boards are, therefore, progressively toward finer circuit traces, as well as smaller holes. A fairly sophisticated multilayer board (42 layers with 0.06 mm line width, 0.35 mm hole diameter and 20:1 aspect ratio) reported recently is a typical example.¹From a technological point of view, the conventional subtractive process has difficulty in producing dense. high-resolution circuitry because of serious undercut during chemical etching. The semi-additive process obtains better resolution, but still suffers from poor thickness distribution, unless special effort is made at the design stage.²The fully additive process is advantageous in resolving the etching and thickness distribution dilemma associated with the subtractive and semi-additive processes, It also eliminates complicated racking or thieving schemes during pattern plating.³ As far as plating rate, maintenance cost and ductility of deposit are concerned, however, high-build electroless copper for existing fully additive applications is far from perfect. Consequently, more intensive research in this area should be conducted.

Since the early 1970s, continuous advancements in formulating high-build electroless copper have been reported .⁴⁷Meanwhile, fundamental investigations were made of the kinetics, mechanisms and mechanical properties of electroless copper plating.⁸¹⁸Basically, the electroless copper bath contains a copper source, a completing agent, a reducing agent, a stabilizer and a pH adjuster. In order to accelerate the plating rate or to improve the mechanical properties of the deposit, trace amounts of additives are often added to the solution. Although separate research on the effects of various additives and complexing agents on reaction kinetics was well documented in the literature,¹⁹²⁵ little attempt **was** made to integrate both mechanistic and structural studies of a specific system. In the present study, an ac impedance technique was employed to investigate the kinetic impact of several organic additives in a CuO bath. At the same time, scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were applied to examine the surface structure of copper deposits.

Experimental Procedure

In order to accelerate deposition rate, solutions containing high copper concentration were formulated in the early stages.^{57 15} Recently, more stringent requirements were imposed on the quality of electroless copper to assure reliable performance. As a result, the mechanical properties of a copper deposit become the other critical constraint in addition to deposition rate. New formulations with low copper content and continuous replenishment of key components were developed to replace earlier ones. A number of dosing systems with appropriate control of chemical parameters have been recently released .²⁶⁻²⁸

In this study, CuO was used to replace CuSO₄as a copper source because accumulation of undesirable sulfate ions from copper sulfate might cause extraneous deposition on unexpected areas, causing the mechanical properties of the deposit to be degraded.^{29,30} Three commercially feasible additives—pyridine, 2,2'-dipyridyl and 1, 10-phenanthroline-were chosen for investigation. The formulations are shown in Table 1.

Although the a-c impedance technique finds wide application in examining electrochemical reactions,³¹ it is not until recently that this method has been applied to monitor electroless copper baths.³²³⁴ The experimental set-up in this investigation consists of a glass single-compartment cell and two platinum electrodes. The cell contained 500 mL of

Table 1Formulations of Additive Baths

Basic component	Cone., 1 L solution
CuO	0.016 M
EDTA .4 Na	0.25 M
Formalin, 37 %	16.5 g
Surfactant	5 ppm
NaCN	5 ppm
Bath	Plating rate
A: without additive	3.2 µm/hr
B: with 5 ppm, pyridine	3.0 µm/hr
C: with 5 ppm 2,2'-dipyridyl	2.8 µm/hr
D: with 5 ppm 1,10-phenanthrolin	e 2.5 μm/hr
Operating conditions:	pH 12.0-12.25
Temperature:	65-70°C



Fig. 1—Schematic diagram of an equivalent circuit, including Warburg impedance.

solution. Both working and counter electrodes were 1 x 1 cm. Prior to the experiments, these electrodes were polished by 1.0, 0.5 and 0.3 μ m alumina powder, successively, and further treated with cyclic voltage scanning in a 1 N sulfuric acid solution several times to obtain clean surfaces.

The **a-c** impedance system used **for** automatic measurements, data storage and plotting comprised a commercial electrochemical interface, ^a coupled with a dynamic signal analyzer ^b and a desktop computer. ^cThe composition of the electroless copper baths was the same as shown in Table 1, except that the temperature was maintained at 25 °C and the pH was set at 11.0, so that copper deposition did not actual I y occur on the electrodes and the effect of additives was not conufused with other factors.³³ The substrates chosen for morphology studies were 1 x 2-in. copper-clad laminates. Since electroless copper was directly deposited on copper substrate, mismatch between substrate and deposit was minimized.

Results and Discussion

The basic concept of impedance measurements is to treat an electrochemical interface as a combination of passive electrical circuit elements. The equivalent circuit proposed by Randles can be expressed by the following equation :³⁶

*Electrochemical Interface 1286, Solartron Transducers, Houston, TX *Model 3562A, Hewlett-Packard, Palo Alto, CA *Model 9153B, Hewlett-Packard, Portland, OR



Fig. 3—Bode amplitude plots for the electroless copper baths in Table 1.





$$Z(j\omega) = R_{\Omega} + \frac{R_{ct}}{1 + j\omega C_{a}R_{ct}}$$

where Z is the total impedance of the equivalent circuit, ω is angular frequency, j represents $\sqrt{-1}$, R_{α} is ohmic resistance, R_{d} is charge transfer resistance and C_{d} is double layer capacitance.

In practice, the diffusion effect often plays an important role in electrochemical systems. It is necessary to include an additional circuit element W, in series with R_a , as shown in Fig. 1. This element, Warburg impedance, describes the impedance of the diffusion-related process. The response of this equivalent circuit can be expressed in terms of a Nyquist plot in the complex plane, as shown **in Fig. 2.** The diffusion-control region distorts the low-frequency end of the semicircle, and is represented by a straight line at 45° extrapolated to the real axis. Therefore, Fig. 2 combines the features of two limiting cases—kinetic and mass transport control regions.

The Bode diagram based on Table 1 is plotted in Fig. 3. Some scattered data points at the low-frequency end may



g. 4-Complex impedance diagrams for the electroless copper baths in Table 1.



Fig. 5-(a) SEM micrograph of deposit obtained from the additive-free bath; (b) SEM micrograph of deposit obtained from the bath containing pyridine.

account for **mass** transport in the cell.³⁵The Nyquist diagram corresponding to Fig. 3 is illustrated in Fig. 4. The near semicircular impedance plots in the high- and medium-frequency ranges indicate that a capacitive electrode/solution interface is formed and the reaction is under kinetic control. The charge transfer resistance R_{α} of each bath can be determined by the diameter of the semicircle. The double layer capacitance C_{α} is calculated in terms of the following equation,

$$\omega_{\rm max} = \frac{1}{R_{\rm ct}C_{\rm di}}$$

where ω_{max} is the angular frequency when the imaginary impedance reaches its maximum value. It was obtained experimentally.

The calculated R_{α} and C_{α} for baths A to D in Table 1 are shown in Table 2. It is noted that a trace amount of organic additive causes a remarkable increase in R_{α} . It implies that the electrode reaction is inhibited; thus the plating rate is reduced. Since the three additives have a similar functional group, the extent of inhibition generally increases with molecular weight, except for pyridine, for which minor discrepancies between plating rate and impedance measurements were noted.

The variations of C_{a} can be interpreted by using the Gouy-Chapman-Stern model (i.e., the double layer capacitance is composed of two capacitors in series). One is the capacitance of the outer Helmholtz plane (OHP) and the other is the

capacitance of the truly diffuse layer. This theory takes into account both the structure of the dielectric in the OHP and the chemical adsorption of the electrode surface.³⁸When specific adsorption occurs, there is a strong interaction between the adsorbate and the electrode material, so that a laver can be formed on the electrode surface. The locus of the center of those adsorbed species is called the inner Helmholtz plane (IHP). Since the exact location of the IHP is difficult to obtain, it is often replaced by OHP. If a cation is adsorbed on the electrode, it will cause the potential at the OHP to become more positive and C₄ to increase. On the other hand, specific adsorption of an ion sometimes blocks the electrode surface. The reaction rate is, therefore, inhibited. In our study, the addition of pyridine, 2,2'-dipyridyl and 1,10-phenanthroline all have negative effects on C_{at}, meaning that although specific adsorption occurs, the effect of blocking the active electrode surface and inhibiting electrode reaction predominates.

 Table 2

 Calculated Parameters for Baths A to D

A 1,100 20.18	45.04
в 3,200 7.12	43.88
c 3,050 9.14	35.88
D 3,400 6.70	43.88



Fig. 6—(a) SEM micrograph of deposit obtained from the bath containing 2,2'-dipyridyl; (b) SEM micrograph of deposit obtained from the bath containing 1, 10-phenanthroline.



Fig. 7-(a) XRD spectra of deposit obtained from the additive- free bath; (b) XRD spectra of deposit obtained from the bath containing pyridine.

SEM micrographs obtained from various baths are shown Figs. 5 and 6. Figure 5a illustrates the surface morphology of the additive-free bath. Significant amounts of nodules are randomly distributed. When pyridine is added, smaller crystallite are formed and the number of nodules is reduced, as shown in Fig. 5b. Figures 6a and 6b demonstrate surface morphology of copper deposits obtained from baths C and D listed in Table 1. It is evident that both 2,2'-dipyridyl and 1,10phenanthroline greatly retard nodule formation. Smaller and more compact crystallite are then obtained. In order to understand further how these additives affect crystal orientation, XRD is applied on those samples prepared from baths A to D. Their spectra are shown in Figs. 7 and 8. Four major reflection planes (1 11), (100), (1 10) and (31 1) are observed. Although individual peak height of each plane varies slightly with different additives, there is no dramatic change of

Table 3Results of Tests of DuctilityAnd Tensile Strength

Bath	Ductility, %	Tensile strength, Kgf/mm ²
Α	6.9	34.2
В	8.5	36.8
С	12.3	34.3
D	10.2	35.2

Note: Gage length = 22.0 mm. Results are obtained from the avg. of 3 measurements.

surface orientation. The diffraction pattern does not deviate too far from random orientation.³⁷ Recently, it was reported that in the absence of a surfactant, (111)-oriented crystals dominated and thus formed a columnar structure.³⁸ Because a surfactant was used in all cases of our study, substantial intensity of both (100) and (1 10) planes was detected, even for the additive-free bath. Other additive-containing baths (Figs. 7a, 8a, 8b) show a similar trend. It implies that once a surfactant is present, the columnar (1 11)-textured structure **no** longer prevails. More fine-grained structure can be achieved if an additive is properly selected.

Examination for inclusion of impurities was performed by XPS. The typical spectra for a deposit with 2,2'-dipyridyl are shown in Fig. 9. It illustrates that small amounts of impurities, such as Na, O, N, C, S, and Cl, are included in the original deposit. These impurities can be completely removed, however, by ion sputtering for about five min. The approximate penetration depth of impurities is around 100 to 200 Å. It means that although surface adsorption of foreign atoms occurs, codeposition of an additive happens only in a very thin layer in the outermost external surface. This observation is in good agreement with that reported in the literature.³⁹

The ductility and tensile strength for deposits obtained from baths A to D were measured.^dThe coupons prepared for testing were electroless-plated copper on carbon steel substrates. These samples were immersed in dilute hydrochloric acid for about 24 hours to peel off the copper foils.

^dModel Autograph AG-5000A, Shimadzu, Japan



Fig. 8—(a) XRD spectra of deposit obtained from the bath containing 2,2'-dipyridyl; (b) XRD spectra of deposit obtained from the bath containing 1,10-phenanthroline.





Thickness of the deposits was about two roils. Test results are given in Table 3. The as-deposited ductility is superior to that obtained from a copper sulfate bath.¹⁴ Higher ductility can be achieved if the deposit is annealed. Since ductility has direct correlation with cyclic fatigue damages, the benefit of ductility enhancement obtained from 2,2'-dipyridyl and 1,10-phenanthroline baths is quite promising for future commercial applications.

Smoother and more compact morphology is likely to yield better ductility, which can be attributed to the synergistic effect of NaCN, surfactants, and grain refiners as well as more desirable anions, such that the possibility of forming nodules, microvoids and diffusible molecular hydrogen is minimized.⁴¹⁻⁴³

Conclusions

A-c impedance measurements show that addition of pyridine, 2,2'-dipyridyl and 1,10 phenanthroline in a CuO bath results in a significant increase of $R_{\rm et}$ and a slight decrease of $C_{\rm d}$. The Gouy-Chapman-Stern model is applied to interpret the experimental data. It is shown that although specific adsorption occurs, the effect of blocking the active electrode surface by organic additives predominates.

SEM micrographs reveal that the baths containing 2,2'dipyridyl and 1,10-phenanthroline greatly retard nodule formation and yield more compact crystallite. Four major reflection planes (111), (100), (110) and (311) are observed in XRD spectra. The patterns do not deviate too far from random orientation and additives have little influence on crystal orientation. XPS spectra show several impurities, such as Na, O, N, C, S and CI present in the deposit. However, codeposition happens only in a very thin layer, 100 to 200 Å from the external surface.

The as-deposited ductility found is generally higher than that obtained from CuSO₄systems. Deposits based on 2,2'-dipyridyl and 1,10-phenanthroline baths show good agreement between surface morphology and ductility measurements, which can be attributed to the synergistic effect of NaCN, surfactants, and grain refiners, as well as more desirable desirable anions, such that nodules, microvoids and molecular hydrogen are minimized.

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