Understanding the Effect of Additives in Electroless Copper Deposition: Correlating Deposition Rates with Absorption and Complexation

by Jun-Shang Chang, Show-Chin Kou and Aina Hung*

Electroless copper plating has potential in ultra-large scale integrated technology (ULSI) to provide a breakthrough for interconnect scaling, which is the performance limiting factor for further miniaturization of electronic devices. The effect of additives on electroless copper plating has been attributed to either complexation related to charge transfer resistance or adsorption related to double layer capacitance and charge transfer resistance. However, the relative contributions remain to be investigated. In this paper, we studied the effects of additives 2,2'-dipyridine, sodium thiosulfate and rhodanine by AC impedance spectroscopy. The double layer capacitance and charge transfer resistance were calculated from the AC impedance spectra. The electroless copper deposition rates were also measured. Based on these results and the stability constants of additive-Cu(I) complexes, there appear to be two effects of the addition of 2,2'dipyridine in electroless copper deposition: complexation and adsorption. The effect of sodium thiosulfate mainly arises from the strong complexation of thiosulfate with Cu(I). The effects of rhodanine are related to the strong adsorption of rhodanine onto the substrate surface. These results should be useful for predicting the operating mechanism for various additives in electroless copper plating.

Nuts & Bolts: What This Paper Means to You

As electronic circuitry gets smaller and smaller, greater demands are placed on the electroless copper processes used to manufacture the interconnects. This work looks into how additives work in an electroless copper plating bath. AC impedance spectroscopy is used as a tool to find out just how a particular additive works, and goes quite a ways in doing that. The authors looked at three different additives and found that they worked in different ways. This tool offers the potential of obtaining optimum deposits to meet the demands of ever smaller interconnects from the microcircuit to the "outside" world. Major developments in electronic device technology have focused on miniaturization. The performance-limiting factor for further miniaturization is the interconnect scaling. In order to decrease the parasitic capacitance of the interconnect, low-k dielectric and/or low resistivity metals are used. Therefore, copper has recently replaced aluminum metallization for interconnects in ultra large scale integrated (ULSI) technology because of low resistivity and stress-induced voiding.¹⁻⁶ The damascene process for the manufacture of sub-micron copper interconnects by copper deposition includes the: (1) deposition of the inner layer dielectric, (2) patterning by lithography and reactive ion etching, (3) deposition of the base metal, (4) copper deposition, (5) planarization of the surface by chemical mechanical polishing (CMP).^{2,6}

Copper can be deposited by plasma vapor deposition (PVD), laser-induced reflow, chemical vapor deposition (CVD), electroplating or electroless deposition. Electroless deposition is especially appealing because of its low cost, the high quality of electroless copper films deposited on very thin seed layers (<10nm) and good via filling capability. Very narrow copper lines down to a 100-nm width have been fabricated by selective electroless copper deposition.⁷

Electroless copper deposition involves a redox reaction at the surface of a catalytic substrate, which is immersed in an aqueous copper electroless plating solution. Continuous deposition of copper on the substrate is catalyzed by the copper deposit itself (autocatalysis).⁸ Electroless copper processes offer certain advantages over copper electroplating, such as the ability to plate on properly activated nonconductors and the independence of deposit distribution on part geometry, making it particularly suitable for processes such as plating through-holes (PTH) and addi-

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tive processes in the manufacture of printed circuit boards (PCB).9

Electroless copper deposition technology has been continuously improved over the last two decades. Stable electroless copper plating solutions containing various additives in small amounts can yield quality deposits.^{10,11} However, the nature of the kinetic mechanism and the effect of additives on the copper deposition reaction are still controversial and require further investigation.¹²⁻ ¹⁷ Furthermore, several critical technical challenges in electroless copper remain for ULSI manufacturing, including (1) a high deposition rate, (2) a stable solution pH, (3) a stable electroless copper plating solution that does not decompose randomly, (4) defect-free electroless copper filling of sub-half micron trenches/vias with high aspect ratios and (5) a low-resistivity electroless copper deposit.

In our previous work, a borate-buffered electroless copper plating solution was found to be a pH stable process.¹⁸ The addition of small amounts of 2,2'bipyridine to the plating solution produced low resistivity copper deposits.¹⁹ These results showed that small amounts of organic additives in electroless plating solutions had a significant effect on the kinetics and deposition mechanism. The effect of additives has been thought to be either (1) absorption of the additive onto the substrate surface and thus inhibiting the copper deposition reaction on the substrate,²⁰ or (2) formation of a strong complex with the Cu(I) ion near the substrate surface,²⁰ resulting in an increase of deposition potential and retardation of the copper deposition reaction. In this paper, we consider the relative contributions of these mechanisms for various additives using AC impedance spectroscopy.

The AC impedance technique is a well-known electrochemical method for studying interfacial phenomena and mechanisms.^{21,22} In an electrochemical cell, slow electrochemical reactions, slow mass transport and double layer capacitance can impede electron flow. These factors are analogous to the resistors, capacitors, and inductors that impede the flow of electrons in AC circuits. Therefore, an electrochemical system is analogous to an electronic circuit consisting of a specific combination of resistors and capacitors. Hence, one can correlate a given electrochemical system with one or more equivalent circuits, and use this information to verify a mechanistic model for the system. In order to determine which equivalent circuit best describes the behavior of an electrochemical system, both the in-phase and out-of-phase impedance components have to be measured over a wide range of frequencies. These data can then be analyzed by various plot formats, including the Nyquist plot, the Bode plot, or the Randles plot. The Nyquist plot, also known as the impedance spectrum, is a popular format which plots the imaginary impedance component (Z") against the real impedance component (Z') at each excitation frequency. The Bode plot examines the absolute impedance, |Z|, versus the phase shift (θ) of the impedance, at each excitation frequency. The Randles plot format plots the real impedance component (Z'), versus the frequency (ω). Each plot format offers specific advantages for revealing certain characteristics of a given electrochemical system. One can discover the true behavior of a real electrochemical system simply by examining at all of the available plotting formats.

In the present work, the effects of various additives on electroless copper deposition were studied by the AC impedance technique. The results were analyzed by Nyquist plots to qualify the relative contributions of different additives on the double layer capacitance and polarization resistance of the electroless copper deposition.

Experimental

The electroless copper plating solution used contained 0.05M copper sulfate, 0.1M EDTA, 0.22M formaldehyde, 0.3M sodium borate and 1 to 20 ppm of various additives. The additives used

were a nitrogen-containing additive, 2,2' dipyridine, a sulfur-containing additive, sodium thiosulfate and an organic ring structure containing both sulfur and nitrogen, rhodanine. The effect of borate content was studied by comparison with a plating solution formulated like the one above, but without borate. For the study of the independent cathodic process, the catholyte was 0.05M copper sulfate and 0.10M EDTA. The pH of the solutions was adjusted with sodium hydroxide to pH 12.5 at 25°C (77°F). Electroless copper deposition is usually carried out around 60°C (140°F). However, at that temperature, the rapid evolution of hydrogen gas interfered with the AC impedance measurement system, making it impractical to perform the experiment. Therefore, in the impedance experiments, the solution temperature was kept at 25°C (77°F) using a thermostat. It should be kept in mind that the impedance data thus obtained were based on molecules that could overcome the reaction activation energy at 25°C (77°F), although the number of molecules that could overcome the reaction activation energy is less at 25°C (77°F) than at 60°C (140°F).

The substrate used was a 6×6 cm (2.4 × 2.4 in) FR-4 epoxy plate. The electroless copper samples were prepared by first pretreating the substrate by the sequence of cleaning, predip, activation and acceleration. The electroless copper solution temperature was thermostatically maintained at 60°C (140°F) during deposition. After the desired 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 from the average of the sample weighings.

Electrochemical impedance spectra were recorded in the frequency range of from 10 kHz to 5 mHz with a 5 mV peak-to-peak amplitude sine wave generated by a frequency response analyzer coupled to a 273A potentiostat^{**} from EG&G controlled by a personal computer. The working electrode was copper, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum.

By using a personal computer, the Nyquist and Bode plots were obtained from the data taken at each measured frequency. The double layer capacitance ($C_{dl} = 1/_{wmax^*2^*}R_{cl}$) and the charge transfer resistance ($R_{cl} = R_{low frequency} - R_{uncompensated}$) of the electroless copper deposition system were then calculated.^{21,22}

Results and discussion

Copper deposition rate

The deposition rates of copper on FR-4 epoxy for various electrolytes were determined with no external voltage applied and are given in Table 1. In the absence of a certain external voltage, the catholyte should not deposit copper on the substrate. However, copper was deposited on the substrate with no external voltage because of the presence of the reducing agent formaldehyde in the electroless plating solution. The copper deposition rate was significantly reduced with the addition of very small amounts of various additives in the electroless copper plating solution. The addition of only 5 ppm of 2,2'dipyridine, sodium thiosulfate or rhodanine reduced the copper deposition rate from 14.78 μ m/hr to 7.8, 9.89 and 4.56 μ m/hr (582 μ -in/hr to 307, 389 and 180 μ -in/hr), respectively.

The effect of additives on electroless copper deposition has been considered to be either related to (1) the absorption of the additive onto the substrate surface, thereby inhibiting the copper deposition reaction on the substrate, or (2) a strong complexation with Cu(I) ions in solution and near the substrate surface, resulting

^{**} Model 5210 Frequency Response Analyzer and a Model 273A Potentiostat, AMETEK Princeton Applied Research, Oak Ridge, TN.

Table 1Copper deposition rates, double layer capacitances (Cdl)and charge transfer resistances (Rcl) of various electrolesscopper deposition systems

Electrolytes (pH=12.5)	Deposition rate (µm/hr)	$\mathbf{C}_{\mathbf{dl}}(\mu \mathbf{F})$	$\mathbf{R}_{\mathrm{ct}}(\Omega)$
0.05M CuSO ₄ + $0.10M$ EDTA	0	2045	638.26
0.05M CuSO ₄ + 0.1M EDTA + 0.22M HCHO	14.74	305.0	13.68
0.05M CuSO ₄ + 0.1M EDTA + 0.22M HCHO + 0.3M Na ₃ BO ₃	14.78	318.6	14.05
$\begin{array}{c} 0.05M \operatorname{CuSO}_4 + 0.1M \operatorname{EDTA} \\ + 0.22M \operatorname{HCHO} + 0.3M \operatorname{Na_3BO_3} \\ + 5 \operatorname{ppm} 2,2' \operatorname{diyridine} \end{array}$	7.8	443.4	45.97
0.05M CuSO ₄ + 0.1M EDTA + 0.22M HCHO + 0.3M Na ₃ BO ₃ + 5 ppm sodium thiosulfate	9.89	314.3	20.65
$0.05M \text{ CuSO}_4 + 0.1M \text{ EDTA} + 0.22M \text{ HCHO} + 0.3M \text{ Na}_3\text{BO}_3 + 5 ppm rhodanine}$	4.56	368.3	54.05



Figure 1(a)—Nyquist plot of Cu electrode in the following electrolytes: (\blacktriangle) CuSO₄ + EDTA; (\ast) CuSO₄ + EDTA + HCHO; (\blacklozenge) CuSO₄ + EDTA + HCHO + Borate.



Figure 1(b)—Nyquist plot of Cu electrode in the following electrolytes (scale up): (\blacktriangle) CuSO₄ + EDTA; (\ast) CuSO₄ + EDTA + HCHO; (\blacklozenge) CuSO₄ + EDTA + HCHO + Borate.

in an increase of deposition potential and retardation the deposition reaction. Again, which effect was dominant was the primary goal of this study.

Effect of formaldehyde on copper ion reduction

The impedance spectra (Nyquist plot) for the various electrolytes are shown in Fig. 1. Figure 1(a) shows the complete spectrum, while Fig. 1(b) is an enlargement of the lower impedance range. The Nyquist plot of the catholyte (\blacktriangle) showed a somewhat depressed charge transfer single semicircle capacitive feature. The absence of the Warburg component indicated that the copper ion reduction was charge transfer controlled with negligible contribution from diffusion.

As seen in the scaled enlargement in Fig. 1(b), the Nyquist plots of the electroless copper plating solution exhibited two separate capacitive features (*; •). On adding formaldehyde, a significant change in the copper ion reduction kinetics was observed. In addition to the high frequency charge transfer capacitive loop related to the double layer relaxation, a second capacitive feature related to quasirelaxation processes appeared in the low frequency range. The high frequency semicircle with semicircle width on the real impedance axis is expected to be the rate-determining step of overall reaction. Therefore, the high frequency capacitive feature may be related to the relaxation of methylene glycolate [H₂C(OH)O⁻], the deprotonated species of the hydrated form of formaldehyde. The low frequency capacitive feature most likely originated from the epitaxial growth of copper. In the present system, the lower frequency capacitive feature may be related to the relaxation of the complex ion of Cu(II).

On adding formaldehyde to the plating solution, the dominant high frequency semicircle shifted to the lower frequency and the charge transfer resistance was reduced from 638.26 to 13.68 Ω , which is consistent with the enhancement of the deposition rate (Table 1). Also, the double layer capacitance decreased from 2045 to 305.0 μ F upon adding formaldehyde. This decrease in double layer capacitance may be due to the adsorption of methylene glycolate [H₂C(OH)O⁻] on the substrate surface.

Effect of borate on copper ion reduction

The addition of borate as a buffer to the plating solution had minimal effect on the reduction kinetics and the corresponding Nyquist plot [Fig. 1(b): $*; \bullet$]. Also, the

charge transfer resistance and double layer capacitance did not change significantly on adding borate (Table 1). Therefore, the effect of borate was simply a buffering effect.

Effect of additives on electroless copper deposition

The electroless deposition process is in effect a competition between nucleation and crystal growth. Additives can increase the number of nucleation sites and hamper crystal growth. The corresponding copper deposits would have smaller crystal sizes according to this mechanism. In SEM surface morphology and Xray studies we observed differences in the copper deposits with and without additives in the plating solution. Smaller grain sizes were observed when the additive was present (Fig. 2).



Figure 2–Effect of additives on the surface morphology of electroless copper deposits: (a) substrate, (b) no additive, (c) 5 ppm 2,2'dipyridine, (d) 5 ppm sodium thiosulfate, (e) 5 ppm rhodanine.

The Nyquist plots for the electroless copper plating solutions containing additives exhibit a high frequency capacitive feature, corresponding to one time constant. This is due to the inhibition by the additive on the electrode reaction by complexation of the additive with Cu(I) ion and/or adsorption of the additive onto the electrode surface (Figs. 3 thru 5, for each of the three additives, respectively).

Adsorption of the additive on the cathode lowered the discharge process rate and increased the double layer capacitance, which may increase the charge transfer resistance. Also, the adsorption and desorption processes of intermediates at the cathode surface have different time constants in the presence of different additives.

Complexation of additives with Cu(I) ion generated in the copper electroless plating solution near the substrate surface would result in the increase of deposition potential, *i.e.*, an increase of charge transfer resistance, and retard the copper deposition reac-

tion. Cu(I) ions do not have partly filled "d" shells, and therefore complex formation is mainly due to ionic interaction. Further, the size of the ligand plays an important role in the structure of the complex. Among the additives employed in the present study, 2,2'dipyridine is a nitrogen bidentate ligand with π conjugation, and may form a stable five-member chelate ring with the metal ions. For 2,2'-dipyridine, its complexing ability with Cu(I) ions is much stronger than with Cu(II) ions. Sodium thiosulfate contains a negatively charged softer sulfur and may also have a strong ability to complex with Cu(I), but it should not complex with Cu(II). The stability constant of 2,2'dipyridine and thiosulfate with Cu(I) are stronger than the stability constant of EDTA with Cu(I). Rhodanine is a heterocyclic compound containing both nitrogen and sulfur, and may form a stronger complex with Cu(II) than with Cu(I).²³

A cathode film caused by the adsorption of the additive onto the cathode increases in ohmic resistance. This increase will introduce another reaction overvoltage, which may inhibit the deposition reaction.

The charge transfer resistance and double layer capacitance for different plating solutions were calculated from the impedance spectra (Table 1) and indicate that the adsorbed additive can interfere with the electron transfer and increase the charge transfer resistance at the solution-cathode interface where the discharge processes occur. The total double layer capacitance is made up of that ascribed to the inner adsorption layer and outer diffusion layer connected in series. In the present study, the electrolyte was rather concentrated, and therefore the double layer capacitance was essentially that due to the compact Helmholtz layer. The double layer capacitance was drastically increased with the adsorption of additive onto the cathode (Table 1).

Effect of 2,2' dipyridine. The Nyquist plots for the electroless copper plating solution with varying amounts of 2,2' dipyridine are shown in Fig. 3. With the addition of 2,2' dipyridine, a capacitive feature related to one kinetic step was resolved from the impedance data, and the semicircle shifted to successively lower frequencies with the amount of 2,2' dipyridine added. The electroless copper deposition rates were measured and the charge transfer resistance and double layer capacitance were calculated from the Nyquist plots (Table 2). The stability constant of the 2,2'dipyridine-Cu(I) complex was 12.95, which was much higher than that for the Cu(II) complex (6.33). It was also higher than the stability constant of EDTA-Cu(I) complex, indicating that the increase in charge transfer resistance may have resulted from the strong complexation of Cu(I) with 2,2'dipyridine. The double layer capacitance increased from 318.6 to 614.8 μ F with the addition of 2,2'dipyridine (Table 3). This increase may be because of the adsorption of 2,2'dipyridine onto the surface of the cathode, which may also enhance the charge transfer resistance and further retard the deposition rate. Therefore, there were two effects related to 2,2'dipyridine in the electroless copper process, complexation and adsorption.

Effect of sodium thiosulfate. The Nyquist plots for the electroless copper plating solution with varying amounts of sodium thiosulfate are shown in Fig. 4. As a result of adding sodium thiosulfate, a high frequency semicircle capacitive feature related to one kinetic step was easily resolved from the Warburg impedance which appeared at very low frequencies. The semicircle shifted slightly to successively lower frequencies with increasing sodium thiosulfate. The electroless copper deposition rates were measured and the charge transfer resistance and double layer capacitance were calculated from the Nyquist plots (Table 3). The stability constant of sodium thiosulfate with Cu(I) was 10.35, which was much stronger than that with the Cu(II) complex, as well as stronger than the stability constant of the EDTA-Cu(I) complex, indicating that the increase



Figure 3—Nyquist plot of Cu electrode in the electroless plating solution containing various amounts of 2-2'bipyridine: (\bullet) 0 ppm, (*) 5 ppm, (\blacktriangle) 10 ppm, (\square) 20 ppm.



Figure 4—Nyquist plot of Cu electrode in the electroless plating solution containing various amounts of sodium thiosulfate: (\bullet) 0 ppm, (\star) 5 ppm, (\star) 10 ppm, (\square) 20 ppm.

of the charge transfer resistance may have been due to the strong complexation of Cu(I) with thiosulfate. The double layer capacitance was changed only slightly when sodium thiosulfate was added to the solution (Table 3). This slight change may have been related to the weak absorption of thiosulfate on the surface of the cathode. Therefore, the effects of sodium thiosulfate on electroless copper deposition were primarily because of the strong complexation of thiosulfate with Cu(I).

Effect of rhodanine. The Nyquist plots for the electroless copper plating solution with varying amounts of rhodanine are shown in Fig. 5. Figure 5(a) shows the complete spectrum, while Fig. 5(b) is an enlargement of the lower impedance range. When the amount of rhodanine was less than 5 ppm two capacitive features were resolved from the impedance data. When the amount of rhodanine was above 10 ppm, only one capacitive feature was resolved. All the semicircles shifted to successively lower frequencies with an increasing amount of rhodanine. The electroless copper deposition rates were measured and charge transfer resistance and double layer capacitance were calculated from the Nyquist plots (Table 4). The complexing ability of rhodanine with Cu(I) was very weak and not determined. The double layer capacitance increased significantly from 318.6 to 1540.1 μ F with successive additions of rhodanine to the plating solution (Table 4). This significant increase may have been related to the strong adsorption of rhodanine onto the surface of the cathode. Therefore, the effect of rhodanine in the electroless copper deposition process was due to the strong adsorption of rhodanine onto the substrate surface.

Conclusions

There are two potential effects of additives on the behavior of electroless copper deposition. One is the absorption of the additive onto the substrate surface, inhibiting the copper deposition reaction on the substrate. This results in increased double layer capacitance and charge transfer resistance. The other effect is strong complexation with Cu(I) ion generated in the copper electroless plating process near the substrate surface, resulting in increased deposition potential and retardation of the copper deposition reaction.

Based on the stability constant data of additives 2,2' dipyridine, sodium thiosulfate and rhodanine with Cu(I), the electroless copper deposition rates, and calculated charge transfer resistance and double layer capacitance, the following conclusions can be made:

- 1. The effect of borate is simply a buffer effect.
- 2. There are two effects resulting from 2,2'dipyridine, complexation and adsorption.
- 3. The effect of sodium thiosulfate is mainly related to the strong complexation of thiosulfate with Cu(I).
- The effect of rhodanine in the electroless copper deposition is mainly related to the strong adsorption of rhodanine onto the substrate surface.

Table 2Effect of 2-2'bipyridine on the deposition rate,double layer capacitance (C_{dl}) and the charge transfer resistance(R_{cl}) of electroless copper deposition system

Amount of 2,2'dipyridine (ppm)	Deposition rate (µm/hr)	$C_{dl}(\mu F)$	$\mathbf{R}_{ct}(\Omega)$
0	14.74	318.6	14.05
5	7.8	443.4	45.97
10	6.61	544.8	75.44
20	5.86	614.8	121.47

These studies demonstrate that AC impedance spectroscopy is a very helpful electrochemical technique for determining the effects of additive on the characteristics of electroless copper deposition. The results can be useful in predicting the operating mechanisms for various additives in electroless copper plating.

Acknowledgments

This study was supported by the National Science Council of Taiwan, Project No. NSC 92-2214-E-233-002. The authors wish to thank Professor Richard P. Cheng, Department of Chemistry at the University at Buffalo, for help in the preparation of this manuscript.

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Figure 5(a)—Nyquist plot of Cu electrode in the electroless plating solution containing various amounts of rhodanine: (•) 0 ppm (*) 1 ppm (\triangle) 3 ppm (\ominus) 5 ppm (\ominus) 10 ppm (\square) 20 ppm.



Figure 5(b)—Nyquist plot of Cu electrode in the electroless plating solution containing various amounts of rhodanine (scale up): (\bullet) 0 ppm (*) 1 ppm (\blacktriangle) 3 ppm (P) 5 ppm (\oiint) 10 ppm (\square) 20 ppm.

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Table 3Effect of thiosulfate on the deposition rate,double layer capacitance (C_{dl}) and the chargetransfer resistance (R_{cl}) of electrolesscopper deposition system

$\begin{array}{c} \textbf{Amount of} \\ \textbf{Na}_2\textbf{S}_2\textbf{O}_3 \\ \textbf{(ppm)} \end{array}$	Deposition rate (µm/hr)	$C_{dl}(\mu F)$	$\mathbf{R}_{ct}(\Omega)$
0	14.74	318.6	14.05
5	9.89	314.3	20.65
10	7.21	343.1	36.25
20	4.18	423.5	49.95

Table 4

Effect of rhodanine on the deposition rate, double layer capacitance (C_{dl}) and the charge transfer resistance (R_{cl}) of electroless copper deposition system

Amount of rhodanine (ppm)	Deposition rate (µm/hr)	$C_{dl}(\mu F)$	$\mathbf{R}_{ct}(\Omega)$
0	14.74	318.6	14.05
3	5.83	333.1	27.31
5	4.56	368.3	54.05
10	2.91	1109.3	602
20	NA	1540.1	1342

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