Mechanistic insights into metal-mediated electroless copper plating employing hypophosphite as a reducing agent

by J. G. Gaudiello
G. L. Ballard

Electroless copper plating using systems containing a small amount of Ni^{2+} or Pd^{2+} as a mediator and hypophosphite as a reducing agent was investigated using several electrochemical techniques. Isothermal and component-dependent polarization, rate, E_{mix}, split-cell, and ac impedance data suggested that the systems obey mixed potential theory and function as follows: a) the mediator is initially deposited from solution to the surface of the workpiece via hypophosphite reduction, b) oxidation of the hypophosphite at mediator sites supplies charge for Cu reduction, and c) Cu plating occurs over the entire workpiece. XPS analysis and depth profiling of the resulting deposits suggested that they are homogeneous in nature and that the mediator is uniformly distributed throughout. The chemical composition determined by the XPS analysis agrees well with the results obtained by atomic emission spectroscopy. In addition, the analysis showed no evidence of Cu oxide formation.

Introduction

The electrochemical deposition of metals in the fabrication of electronic packages is accomplished by either electrolytic or electroless methodologies [1–4]. Electrolytic processes are typically used for the production of most circuit cards and boards, and utilize an external current source for metal-ion reduction. Electroless processes involve the use of a chemical reducing agent to drive the heterogeneous reduction of a metal ion or complex; the processes do not require a conductive substrate and lend themselves to more controlled and elaborate processing. For example, the fabrication of high-performance multilayer boards via plated through-hole interconnections is based on this methodology [1, 5]. However, since the deposition reaction is chemically driven, the composition and underlying reactivity of the plating system are critical to obtaining the desired results.

The electroless deposition of copper is one of the major process steps involved in the manufacture of electronic packages for the computer industry. Traditionally, Cu(EDTA)/formaldehyde-based systems have been used [1]. To ensure the desired stability and performance, these systems are typically operated at elevated temperatures (>60°C) and high pH levels (>11). Both the environmental concerns of formaldehyde and the requirement that materials withstand the pH-temperature-exposure time condition of these systems have driven work on alternative methods for electroless Cu deposition (see the accompanying paper by R. Jagannathan and M. Krishnan in this issue [6]). For example, formaldehyde-based baths cannot be used with most forms of polyimide or aqueous photoresists.

Recently, binary or composite-based electroless systems have been reported [7–11]. These systems include a small amount of an additional metal ion that greatly alters their underlying reactivity. As discussed below, the additional metal effectively "decouples" the redox chemistry of the reducing agent from the deposition reaction of the primary metal. This permits a reducing agent/metal ion combination that would normally not be autocatalytic to function as an effective electroless system. In addition, this decoupling allows a metal to be deposited under process conditions (pH level, temperature, substrate composition) that may not be obtainable using a conventional bath formulation.

In this paper we describe the basic reaction scheme involved for these types of electroless plating systems. A combination of conventional plating studies, electrochemical split-cell experiments, voltammetry, ac impedance techniques, and surface science characterizations is used to illustrate the mechanism and performance of electroless Cu plating systems using Ni or Pd.

Experimental procedures

Plating baths using Ni^{2+} as the mediator were prepared as described in the literature [7–11]. Typical composition was 24 mM (millimolar) $CuSO_4$, 52 mM sodium citrate, 2 mM $NiSO_4$, 100 mM sodium hypophosphite, and 150 mM boric acid; pH level was adjusted to 9.2 with NaOH, at a bath temperature of 65°C. Plating baths using Pd^{2+} were similarly prepared, except that palladium sulfate (tetramethylethylenediamine used as a complexing agent) was substituted for $NiSO_4$. Deposition rates were monitored by weight gain. The percentage of Ni or Pd deposited relative to the Cu deposited was determined by inductively coupled plasma (ICP) spectroscopy. Polarization, coulometric, and stripping experiments were carried out using a PAR Model 273 potentiostat/galvanostat (Princeton Applied Research, Princeton, NJ). Split-cell experiments were conducted using two independently addressable and controllable rotating electrodes (AFMSR high-speed rotator, Pine Instruments, Grove City, PA) and a Model 680 digital coulometer (Electrosynthesis, Buffalo, NY). The potential difference and charge passed between the two cells were determined using a voltmeter and the coulometer, respectively. The surfaces of the electrodes were modified with Cu, Ni, Pd, or a Cu/Ni alloy to accurately simulate the individual reactions of the entire plating bath (*vide infra*). Anodic stripping analysis was used to monitor the composition and mass (gain or loss) changes of the modified metal layer. The separate cells were joined via a 0.1 M Na_2SO_4 salt bridge. A PAR Model 273 potentiostat in conjunction with a PAR 5210 dual channel lock-in amplifier or a Solartron 1250 frequency response analyzer (Schlumberger Technologies, Burlington, MA) was used to perform ac impedance studies. A 5-mV sinusoidal waveform was used as the excitation source. To ensure reproducible plating rates, rotating electrodes (1000 rpm, 0.5 cm^2) and thermostatic solutions were employed.

X-ray photoelectron spectroscopy (XPS) was carried out with a Perkin-Elmer Model 5500 multiprobe spectrometer operating with a base pressure of 1.4×10^{-10} torr. X-rays ($K\alpha_{1,2}$) were produced by an aluminum anode and monochromatized using a series of quartz crystals. Survey spectra were collected in the range of 1100–0 eV in order to determine surface composition. High-resolution spectra were collected for the elements of interest (C, Pd, Cu, O). Typical spectral resolution at FWHM was 0.7 eV. Ion beam (Ar^+) profiling was combined with XPS spectral collection to obtain elemental distribution as a function of depth. The selected sputtering rate was 60 Å/min. During depth profiling the following photoemission lines were followed: C(1s), O(1s), Pd(3d 5/2, 3/2), and Cu(2p 3/2, 1/2). In addition, the Auger X-ray-generated transition for Cu, identified as $L_3M_{4,5}M_{4,5}$, was monitored to determine whether copper oxide was present.

Results and discussion

Most of the work on binary electroless baths has focused on the formulation of systems for Cu deposition. In the presence of small amounts of Co^{2+} or Ni^{2+}, hypophosphite acts as a reducing agent for Cu in a true autocatalytic sense [7–11]. These mediator/Cu^{2+}/hypophosphite systems have a number of properties that make them attractive. They operate at relatively low pH levels (6–10), and are therefore compatible with most substrates. They are composed of relatively innocuous components, making their handling and disposal easy. The low cost of hypophosphite per equivalent of charge delivered makes them economical for high-volume applications. As part of our efforts to explore new electroless Cu systems, we have undertaken a detailed study to understand how these systems operate. Although binary electroless Cu systems have been known for years, their mechanism of operation is still not clear [7–11]. It has been suggested that the reactions occurring in Ni^{2+}-based baths can be characterized by Equations (1)–(4); they include the oxidation of hypophosphite at plated nickel sites [Equations (2)–(3)] and a simple exchange reaction between the plated Ni and Cu^{2+} in solution [Equation (4)] [7–11]:

$$2H_2PO_2^- + Ni^{2+} + 2OH^- \rightleftharpoons Ni^0 + 2H_2PO_3^- + H_2, \qquad (1)$$

$$2H_2PO_2^- + 2OH^- \xrightarrow[\text{surface}]{\text{Ni or Pd}} 2e^- + 2H_2PO_3^- + H_2, \qquad (2)$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu^0, \qquad (3)$$

$$Ni^0 + Cu^{2+} \rightleftharpoons Ni^{2+} + Cu^0. \qquad (4)$$

As described below, on the basis of the characterization of the known Ni^{2+}/Cu^{2+}/hypophosphite system we have developed an improved binary bath employing Pd^{2+} as the additional metal.[1]

Shown in **Figure 1** are E_{mix} vs. Cu^{2+} concentration dependencies for systems[2] based on Ni^{2+} and Pd^{2+}. Initially, E_{mix} for each system shows a substantial shift to more negative potential as the amount of Cu^{2+} increases. After reaching a plateau, E_{mix} begins to shift toward more positive values and exhibits a steady increase as the Cu^{2+} concentration is raised. This shift continues until the concentration becomes so large that plating can no longer be maintained (*vide infra*). Similar behavior is observed for baths containing different amounts of mediator. The only difference is that the plateau occurs at different Cu^{2+} concentrations, shifting toward lower values as the mediator concentration is lowered. The associated compositions of the deposits are listed in **Table 1**.

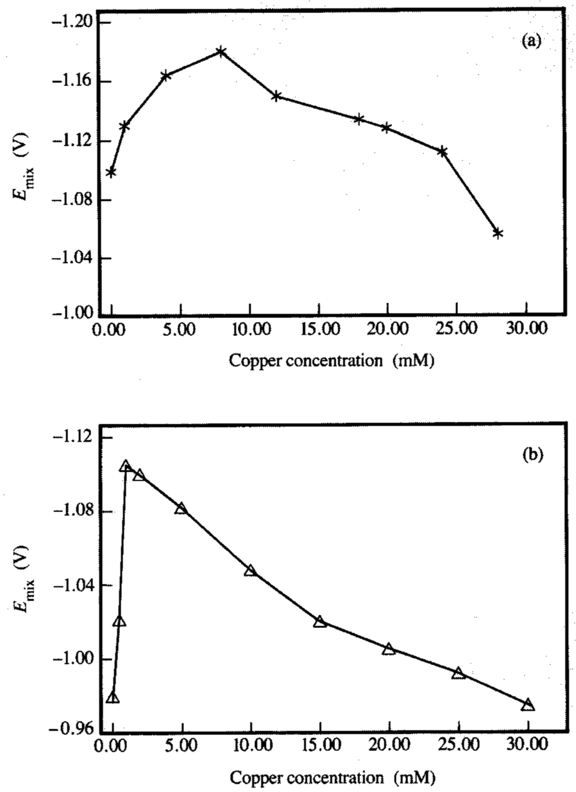

Figure 1

Variations in E_{mix} as a function of Cu^{2+} concentration for the following conditions: hypophosphite concentration = 100 mM, boric acid concentration = 150 mM (pH 9.2), bath temperature = 65°C. (a) Nickel-based system; Ni^{2+} concentration = 2 mM. (b) Palladium-based system; Pd^{2+} concentration = 12.5 μM.

Shown in **Figure 2** are the corresponding plating rates for the E_{mix} data discussed above. As can be seen, the rates for both systems are initially governed by the concentration of Cu^{2+} in solution. The rates change nearly linearly for Cu^{2+} concentrations of ≤ 10 mM. At concentrations of ≥ 17 mM, both systems begin reaching a limiting behavior. Increases in concentration have little effect on both plating rate and deposit composition. Increasing the concentration of hypophosphite also has little effect on the rate. For example, doubling the hypophosphite concentration increases the rates by only ~11%. This behavior is unlike that observed for conventional electroless systems and gives the appearance upon first inspection of not conforming to mix potential theory (*vide infra*) [12–15].

To clarify the unusual E_{mix} and plating-rate dependencies on Cu^{2+} concentration, a study of the polarization characteristics of the bath components was undertaken.[3] In addition, the polarization behavior as a function of electrode composition was also examined. Shown in

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[1] J. Gaudiello and G. Ballard, unpublished work.

[2] For an electroless system at equilibrium, the partial currents associated with the anodic and cathodic reactions are equal in magnitude but opposite in sign. The potential associated with this equilibrium condition is referred to as the mixed potential (E_{mix}).

[3] Boric acid was included in these solutions. Hypophosphite was also included for the cathodic data. Both have been shown to influence the performance of the bath (see [7]).

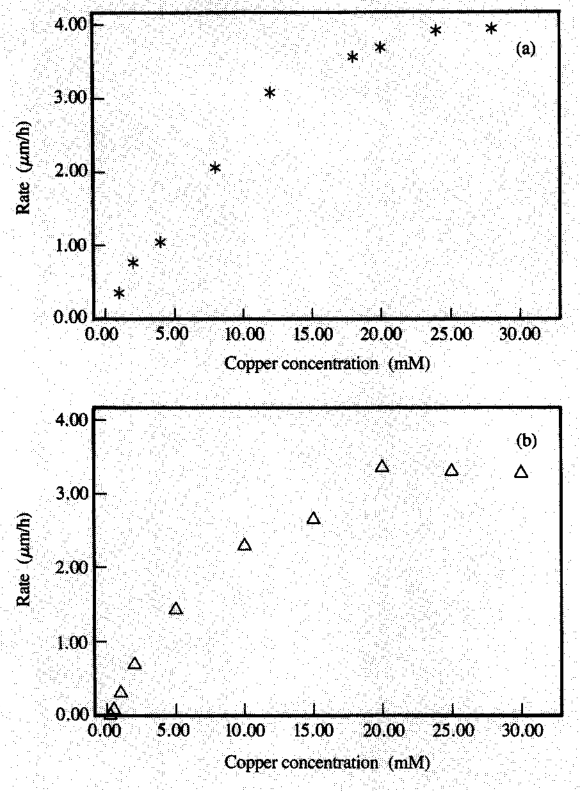

Figure 2

Variations in plating rate as a function of Cu^{2+} concentration for the following conditions: hypophosphite concentration = 100 mM, boric acid concentration = 150 mM (pH 9.2), bath temperature = 65°C. (a) Nickel-based system; Ni^{2+} concentration = 2 mM. (b) Palladium-based system; Pd^{2+} concentration = 12.5 μM.

Figure 3 is a schematic representation of the general trends observed experimentally in the polarization behavior for either the Ni^{2+}- or the Pd^{2+}-mediated system. The cathodic response is represented by the solid lines (1–5). Curve 1 depicts the polarization characteristics of the mediator (Ni^{2+} or Pd^{2+}), while curves 2–5 depict the combined response for a constant amount of mediator and increasing amounts of Cu^{2+}. The small wave for the mediator occurring at less negative potentials is observed regardless of the magnitude of the Cu^{2+} wave. At all potentials sufficient for Cu citrate reduction, the mediator is reduced at a mass-transport-limited rate. The magnitude and position of these curves are independent of the initial composition of the electrode.[4]

The anodic polarization curves are represented by the dashed lines in Figure 3. Although hypophosphite is not electroactive on pure Cu, it can easily be oxidized on Ni or Pd at potentials ~250 mV less positive than those required to reduce Cu citrate. Curve 6 depicts the oxidation of hypophosphite at a pure mediator electrode; its position and magnitude are essentially invariant with concentration. Curves 7–10 depict the oxidation at electrodes with decreasing amounts of incorporated mediator. These electrodes (curves 7–10) were fabricated from electroless baths with relative mediator/Cu^{2+} concentrations similar to those used to obtain cathodic curves 2–5, respectively. The oxidation of hypophosphite occurs at less positive potentials as the amount of incorporated mediator decreases. This shift and the observed increase in current suggest that the oxidation of

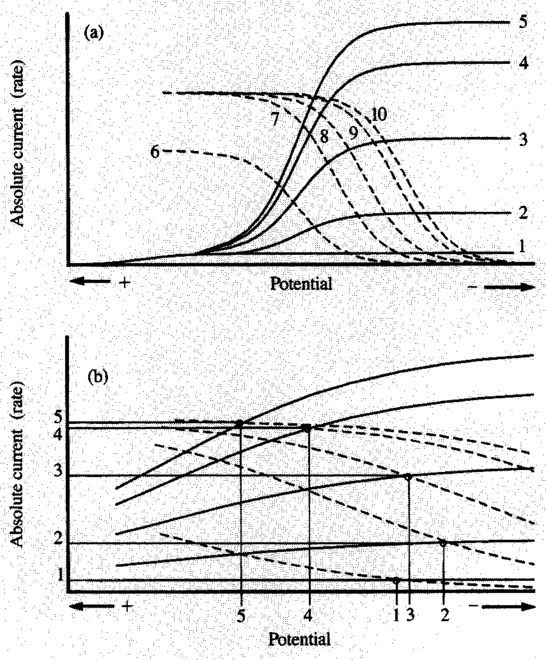

Figure 3

(a) Schematic representation of observed polarization curves for the electroless plating systems mediated by Ni^{2+} or Pd^{2+}. The solid lines depict the deposition of the metals, and the dashed lines the oxidation of the hypophosphite. Curve 1 depicts the polarization behavior of the mediator. Curves 2–5 depict the combined response for a constant amount of the mediator and increasing amounts of Cu^{2+}. Curve 6 depicts the oxidation of hypophosphite at a pure mediator electrode, curves 7–10 the oxidation at electrodes with decreasing amounts of incorporated mediator. The hypophosphite concentration was the same for each case examined. (b) Expanded view of the points of intersection. The values for the potential and current for each crossing correspond to the relative E_{mix} and current (rate), respectively.

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[4] Electrodes of varying composition were fabricated by electroless deposition from solutions of known composition (see Table 1). It is recognized that the surface composition may change during the polarization experiments, but we believe these changes to be minor because of the short duration of the experiments and the relative concentrations of the components.

Table 1 Typical compositions of deposits obtained from mediator/Cu^{2+}/hypophosphite-based baths.*

Mediator	*Mediator conc. in solution* (mM)	*Cu^{2+} conc. in solution* (mM)	*Cu^{2+}/mediator in solution*	*Cu in deposit* (at. %)	*Mediator in deposit* (at. %)
Ni^{2+}	2.0	0.0	—	—	100
Ni^{2+}	2.0	1.0	1:2	51.89	48.10
Ni^{2+}	2.0	4.0	2:1	81.20	18.79
Ni^{2+}	2.0	8.0	4:1	90.74	9.24
Ni^{2+}	2.0	12.0	6:1	95.50	4.47
Ni^{2+}	2.0	18.0	9:1	96.04	3.93
Ni^{2+}	2.0	28.0	14:1	96.36	3.63
Pd^{2+}	0.0125	0.0	—	—	100
Pd^{2+}	0.0125	0.5	40:1	83.15	16.84
Pd^{2+}	0.0125	1.0	80:1	92.20	7.78
Pd^{2+}	0.0125	2.0	160:1	97.74	2.26
Pd^{2+}	0.0125	5.0	400:1	99.02	0.98
Pd^{2+}	0.0125	10.0	800:1	99.40	0.57
Pd^{2+}	0.0125	20.0	1600:1	99.76	0.25
Pd^{2+}	0.0125	30.0	2400:1	99.77	0.22

*Elemental composition was determined by atomic emission spectroscopy (ICP).

hypophosphite is becoming progressively more facile despite a decrease in mediator concentration. It is this enhanced catalytic activity that accounts for the observed E_{mix} and rate behavior. According to mixed potential theory [12–15], the intersection of cathodic and anodic polarization curves should represent the E_{mix} (potential) and rate (current) of the plating reaction. The theory states that an electroless system can be modeled as the superposition of the partial cathodic and anodic reactions (curves 1–5 and 6–10, respectively). As discussed below in detail, E_{mix}, rate, split-cell, and ac impedance data suggest that these binary systems act as if they are governed solely by mixed potential theory.

As shown in Figure 3(b), the value of E_{mix} is not constant with changes in Cu^{2+} concentration, but initially moves toward more negative values as the Cu^{2+} concentration increases. This shift is driven mainly by the movement of the hypophosphite polarization curve. The large increase in the Cu^{2+} curve relative to the hypophosphite response causes E_{mix} to shift to more positive values, even though the hypophosphite wave is still moving negatively. Eventually the hypophosphite wave has shifted so much negatively that the Cu^{2+} response crosses only near the limiting value, resulting in a monotonic positive shift in E_{mix} (curves 4–5).

The above description results in E_{mix} and rate changes with increasing Cu^{2+} concentration that are similar to those observed experimentally (Figures 1 and 2). In addition, we see no evidence for the exchange reaction represented by Equation (4). Immersion of a freshly plated Ni or Pd surface in a copper citrate/boric acid solution results in no displacement. [This is not surprising considering the relative potentials for the reduction of the mediators and copper citrate outlined in Figure 3(a).] These results suggest the following mechanism for the operation of these binary baths:

$$H_2PO_2^- + Ni^{2+}(Pd^{2+}) + 2OH^- \rightleftharpoons Ni^0(Pd^0) + 2H_2PO_3^- + H_2, \qquad (5)$$

$$2H_2PO_2^- + 2OH^- \xrightarrow[\text{surface}]{\text{Ni or Pd}} 2e^- + 2H_2PO_3^- + H_2, \qquad (6)$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu^0. \qquad (7)$$

Plating is initiated by the hypophosphite-catalyzed deposition of the mediator [Equation (5)]. The resulting islands then serve as the catalytic sites for the oxidation of hypophosphite [Equation (6)]. This reaction poises the potential of the workpiece sufficiently negative and supplies the charge for Cu^{2+} reduction [Equation (7)]. Copper is plated over the entire workpiece, requiring fresh deposition of the mediator to maintain the reaction. Thus, the deposit will always be a homogeneous mixture of mediator and Cu; pure deposits cannot be obtained. As described below, XPS depth-profiling studies support these conclusions. The amount of mediator co-deposited is believed to be dictated by the ratio of mediator to Cu^{2+} in solution, the activity of the mediator for hypophosphite oxidation, and the plating rate (Table 1). There must be a minimal amount of mediator in solution to maintain plating, the amount depending on the concentration of Cu^{2+} present. For example, for a 24 mM Cu^{2+} solution the minimal concentrations of Ni^{2+} and Pd^{2+} required are ~2 and ~0.008 mM, respectively. Once this threshold is reached, the performance of the system is dictated by the polarization behavior shown in Figure 3. The difference in the threshold values between the two mediators is believed

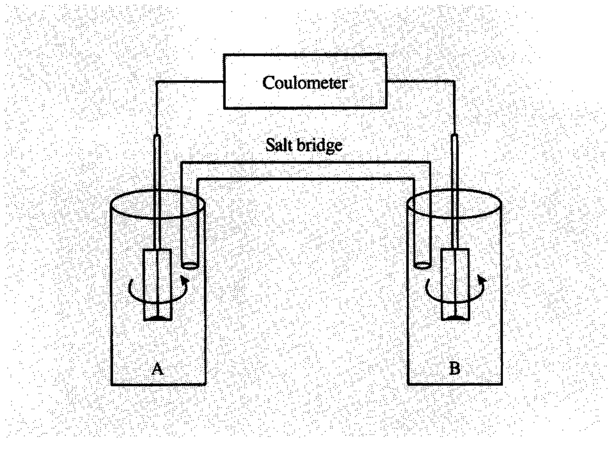

Figure 4

Schematic representation of split-cell apparatus. Cell A depicts the mediator reaction, cell B the deposition reaction. Experimental conditions and typical results are presented in Table 2.

to be due to their relative catalytic ability for hypophosphite oxidation [16]. Palladium exhibits a larger exchange current for the oxidation of hypophosphite than does Ni. If the ratio of Cu^{2+} to mediator becomes too large or the plating rate too high, not enough mediator sites can be created relative to their coverage with Cu to sustain autocatalytic behavior. We believe this interplay among the number of sites, mediator activity, solution concentration, and plating rate causes the abrupt initiation and termination and governs the overall plating process.

To gain additional insight into the individual reactions comprising the overall plating process, experiments were carried out using both split-cell and ac impedance techniques. The split-cell experiments consisted of two individual cells connected both electrically and ionically, as depicted in **Figure 4**. Rotating electrodes and thermostatic solutions were used to ensure reproducible performance. The experiments essentially separated the chemical components of the plating bath into two separate half-cell reactions. One half of the cell was configured to mimic the Ni- or Pd-mediated oxidation of hypophosphite, the other the deposition of Cu. Cell A depicts the mediator reactions [Equations (5)–(6)], and consisted of a Ni or Pd electroless plated electrode (Pt) and a solution containing a constant amount of hypophosphite and varying amounts of mediator ion. Cell B depicts the Cu plating reaction [Equation (7)], and consisted of an electrolytically plated Cu electrode (Pt) and a Cu^{2+} solution containing hypophosphite. The inclusion of hypophosphite was necessary, since it was found to lower the overpotential for Cu deposition even though it does not catalyze the deposition of Cu directly [Figure 3(a)]. **Table 2** lists typical results obtained for the Ni^{2+} systems. (The Pd^{2+}/Cu^{2+} system gave identical results.)

It is possible to calculate the efficiency of the overall plating process, even when Ni deposition is occurring, by measuring the number of coulombs transferred between the two cells (coulombs passed) and the amount of charge passed when the individual electrodes are stripped (ΔCu, ΔPd). Clearly, the mediator reaction can thermodynamically drive the reduction of Cu^{2+}. Also, the amount of mediator reduction occurring with the Cu deposition appears to have little effect on the overall performance of the system. The current efficiencies remain constant, and near 100%, regardless of how much Ni^{2+} is present and being plated. The number of coulombs passed is nearly the same for a nickel cell containing a 2.0 mM Ni^{2+}/100 mM hypophosphite solution as for one with a solution containing only 100 mM of hypophosphite. These results also suggest that the active mediator surface does not become poisoned during plating, and that new sites are only required to replace those covered, and thus lost, by Cu deposition. Furthermore, plating can still be maintained at the efficiency observed for a pure Ni electrode, even when an electrode with an electroless Cu deposit surface obtained from a "standard" Cu/Ni bath (24 mM Cu^{2+}/2 mM Ni^{2+}, ~3% Ni in the deposit) is used for the Ni cell.

Table 2 Typical split-cell results for variable Ni^{2+}/24 mM Cu^{2+} bath.[*]

Ni^{2+} conc. (mM)	E_{mix} (V)	*Couls passed per hour*[†]	*Δ Cu couls per hour (stripped)*	*Δ Ni couls per hour (stripped)*	*Efficiency*[‡] (%)
2.0	−1.10	14.5 + 0.09	14.1 + 0.08	1.61 + 0.15	97 + 1
0.2	−1.10	16.3 + 0.08	17.3 + 0.10	0.19 + 0.04	106 + 1
0.0	−1.10	15.9 + 0.09	14.2 + 0.09	~0	97 + 1
0.0[§]	−1.10	5.80 + 0.08	6.03 + 0.07	—	104 + 2

[*] Each cell contained hypophosphite at a concentration of 100 mM and boric acid at a concentration of 150 mM (pH 9.2), and was held at a temperature of 65°C. The electrodes had an area of 0.5 cm^2 and were rotated at 1000 rpm.

[†] Corrected for any background processes.

[‡] Percent efficiency was calculated by relating the number of coulombs passed between the cells to the number obtained from Cu stripping (Δ Cu couls).

[§] Electrode had a Cu-plated surface obtained from a "standard" Ni^{2+}-based binary bath (2 mM Ni^{2+}/24 mM Cu^{2+}).

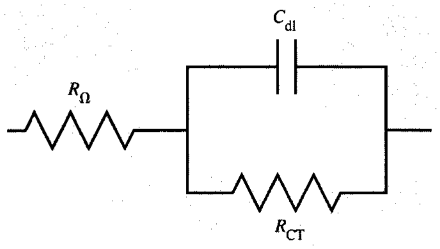

Figure 5

Equivalent circuit for a simple electroless plating system. R_{Ω} represents the solution resistance, C_{dl} the capacitance of the double layer, and R_{CT} the charge-transfer resistance.

These results are consistent with the mechanism outlined by Equations (5)–(7).

AC impedance methods based upon mixed potential theories have also been utilized to study electroless plating systems [17]. Both the instantaneous plating rate and mechanistic information can be obtained using these methods. For a system under "mixed potential control," the current for the anodic (i_a) and cathodic (i_c) reactions must be equal to the instantaneous plating current i_{pl}. If an external source polarizes the workpiece, the resulting current i is the difference in current between these two sets of reactions. When the polarization curves are Tafel-like in character and the magnitude of the excitation wave is small ($\Delta\eta \ll RT/\alpha nF \cong 29$ mV @ 65°C), the plating current (or rate) is inversely proportional to the charge-transfer resistance of the system,

$$\left[\frac{\Delta i}{\Delta \eta}\right]_{E=E_{mix}} = \frac{1}{R_{CT}} = \frac{i_{pl}}{K}, \qquad (8)$$

where R_{CT} is the net charge-transfer resistance of the electroless plating reaction and $K = RT/\alpha nF$. Thus, the determination of R_{CT} as a function of bath composition permits a relative estimate of the plating rate for a variety of conditions [17]. The interfacial impedance can be represented by the $R_{\Omega}(C_{dl}R_{CT})$ network shown in **Figure 5**, where R_{Ω} is the solution resistance and C_{dl} the capacitance of the double layer. The total impedance of the circuit shown is given by the complex function

$$Z(j\omega) = R_{\Omega} + \frac{R_{CT}}{1 + j\omega C_{dl} R_{CT}}, \qquad (9)$$

where ω is the angular frequency ($\omega = 2\pi f$). R_{CT} can easily be obtained from the diameter of the circle formed when the frequency-dependent results are plotted in a complex plane [18].

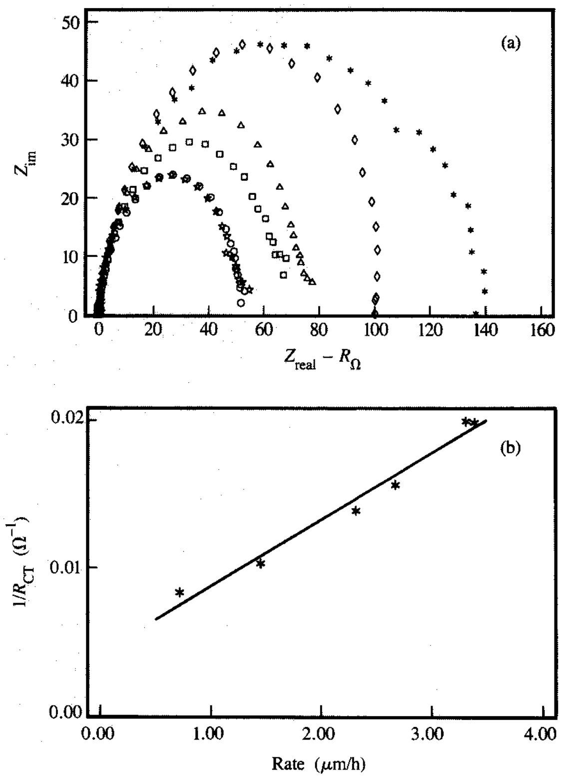

Figure 6

(a) Complex impedance plots and (b) $1/R_{CT}$ vs. rate dependence for Pd^{2+}/Cu^{2+}/hypophosphite electroless baths. Frequency range = 10^4–0.5 Hz, boric acid concentration = 150 mM (pH 9.2), hypophosphite concentration = 100 mM, temperature = 65°C, Pd^{2+} = 12.5 μM. Cu^{2+} concentrations: ☆ = 25 mM, ○ = 20 mM, □ = 15 mM, △ = 10 mM, ◇ = 5 mM, and * = 2 mM.

Shown in **Figure 6(a)** are a series of impedance plots for a binary Pd^{2+}/Cu^{2+}/hypophosphite bath. The formulations used were identical to those used to generate the E_{mix} and rate data shown in Figures 1(b) and 2(b); the Pd^{2+} concentration was maintained at 12.5 μM and the Cu^{2+} concentration was varied. The expected semicircle behavior was observed, with R_{CT} becoming progressively smaller as the Cu^{2+} concentration increased. The results obtained suggested that the impedance observed for these baths could be represented by the equivalent circuit of Figure 5, and provided independent proof that the system follows mixed potential theory at all Cu^{2+} concentrations. As illustrated by **Figure 6(b)**, a plot of $1/R_{CT}$ vs. rate exhibits the predicted linear behavior. In addition, the impedance response becomes essentially invariant at the same Cu^{2+} concentration as does the rate [Figure 2(b)], again supporting the assumption that the polarization behavior of Figure 3 accurately represents the systems.

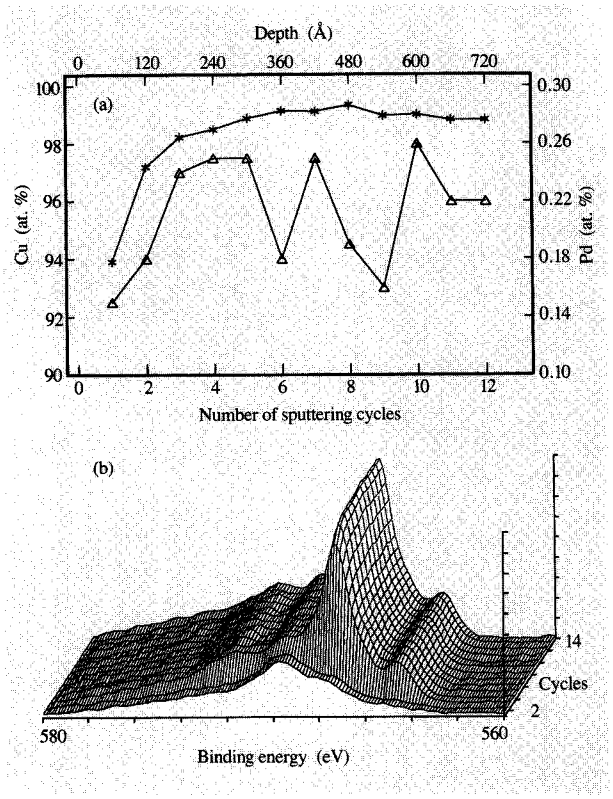

Figure 7

(a) Elemental composition (determined by XPS) as a function of depth of a deposit obtained using a 12.5 μM Pd^{2+}/30 mM Cu^{2+}/ 100 mM hypophosphite bath. * = Cu, △ = Pd. (b) Auger spectra after varying degrees of sputtering.

The mechanism outlined above should result in deposits that are a homogeneous mixture of Cu and mediator. XPS depth profiling studies were undertaken to determine the nature and spatial composition of the deposits. Shown in **Figure 7(a)** is a plot of composition in atomic percent for the elements Pd, Cu, and O vs. sputtering time for a deposit generated from a 12.5 μM Pd^{2+}/30 mM Cu^{2+}/100 mM hypophosphite bath. Each sputter cycle corresponds to a depth of approximately 60 Å. Once the surface oxide layer was removed by the first sputter cycle, the composition appeared to be homogeneous and contained ~0.26% Pd. This agreed well with the value of 0.22% obtained by bulk analysis using atomic emission spectroscopy (Table 1). To ascertain the nature of the deposited Cu, the X-ray-generated Auger transition ($L_3M_{4,5}M_{4,5}$) was also followed. This transition has been shown to be extremely sensitive to oxidation state [19]. Shown in **Figure 7(b)** are the Auger spectra obtained after varying degrees of sputtering. Initially two bands centered around 569.5 and 568.4 eV were found to be present, characteristic of Cu_2O [20, 21] and CuO [20, 21], respectively. After the first sputtering cycle, these signals disappeared and a new transition at 567.6 eV was seen, corresponding to the presence of metallic Cu. It was the only transition present in subsequent cycles. The deposition appeared to be homogeneous and involved the complete reduction of Cu, with little or no oxide being formed. Similar results were obtained regardless of the amount or type of mediator present.

Conclusions

The behavior of the electroless Cu plating systems mediated by Ni^{2+} and Pd^{2+} that were examined in this study was in accord with mixed potential theory, leading to the inclusion of the mediator in the resulting Cu. This limits the electrical and metallurgical properties of the Cu deposits and their usefulness for most applications. They may, however, be useful as additive strike layers, for which requirements are less stringent. The investigation of the use of other mediators is underway and will be described elsewhere.

Acknowledgments

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John G. Gaudiello *IBM Technology Products, 1701 North St., Endicott, New York 13760 (GAUDIELL at ENDVMTKL, gaudiell@endvmtkl.vnet.ibm.com).* Dr. Gaudiello is an Advisory Engineer in the Materials Science Department at the IBM Endicott Technology Laboratory. He joined IBM in 1989 and has worked in the area of electroless and electrolytic deposition of metals and the development of chemical processes for microelectronics applications. Dr. Gaudiello received a B.S. in chemistry from Towson State University in 1975 and a Ph.D. in chemistry from the University of Texas at Austin in 1984. He is a member of the American Chemical Society, The Electrochemical Society, Sigma Xi, and the Society of Plastics Engineers.

Gerald L. Ballard *IBM Technology Products, 1701 North St., Endicott, New York 13760 (GBALLARD at ENDVMTKL).* Mr. Ballard is a Technical Laboratory Specialist at the IBM Endicott Technology Laboratory. He joined IBM in 1969 and has worked on the development of acid copper, immersion and electroless plating, thermal compression bonding, and photosensitive dielectric coating.