Modeling of Additive Effects on the Electroplating of a Through-Hole

A mathematical model of copper plating of a through-hole is developed which relates uniformity of deposition to bulk electrolyte composition, applied potential difference, aspect ratio, through-hole diameter, and deposition kinetics. The electrochemical transport equations governing plating in a through-hole are solved assuming that the fluid within the through-hole is stagnant. Conditions for uniform plating are determined both for Butler-Volmer kinetics considering the effects of dissociation of bisulfate ions in the electrolytic solution and for kinetics limited by complexation of cupric ions with an adsorbed neutral additive species.

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Introduction

Electroplated through-holes and blind holes provide the electrical connections between the many layers of a printed circuit board (PCB). Other applications include providing electrical connections to the surface of magnetic recording heads and to the inner sections of solar cells. The trend in the manufacture of multilayer PCB's is toward more layers with narrower diameter interconnection holes. At present, through-holes are about 500 μm in diameter with an aspect ratio, defined as the ratio of the board thickness to hole diameter of 5, but ratios of 20 are in the prototype stage (Peterson, 1984; Yung et al., 1989).

Generally, copper should be plated with a uniform thickness inside the through-hole, and the surface-to-hole copper thickness ratio should be close to unity. At a standard current density of approximately 20-40 mA/cm^2, the time required to plate a 25 μm (1 mil) thick deposit of copper is about 30-60 minutes (Yung et al., 1989). Hence, the electroplating step is still considered the bottleneck in PCB manufacturing. Although uniform plating of holes with an aspect ratio of 20 has been reported in 25 μm and 200 μm diameter holes (Yung et al., 1989), the need for improved uniformity of deposition in commercial processes with increasing aspect ratio through-holes and with an increasing plating rate still presents a challenge to the electroplating industry (Carano, 1986; Poskanzer, 1985a,b; Blurton and Nuzzi, 1987; Yung and Romankiw, 1989). An excellent review of the literature on the technology and modeling of plating of through-holes and blind holes has recently been written by Yung et al. (1989).

Acid copper sulfate solutions are widely used in through-hole plating processes. These plating baths have easily controlled solution chemistry and low toxicity, and are compatible with a variety of plating additives. A typical acid sulfate bath solution contains 0.42M $CuSO_4$, 1.4M H_2SO_4, 30 to 100 ppm Cl^-, and proprietary additives at the supplier's recommended strength (Poskanzer, 1985a). Practically all commercial plating baths contain one or more organic agents in concentrations from 10^{-6} to 10^{-1} M (Turner and Johnson, 1962). Additives in acid copper baths include dextrin, gelatin, and sulfur-containing compounds (Pletcher, 1982).

Plating additives can improve the metallurgical properties of the deposits and provide leveling, minimizing the wall roughness generated during hole drilling. Leveling is believed to occur as additives are adsorbed onto protrusions or sites of higher free energy, and more copper deposits into recesses (Kardos and Foulke, 1962). Plating rate also may be suppressed if the additives polarize the electrode; the ability to polarize depends on the additive concentration.

In spite of their extensive use, the development of plating additives has been mostly empirical and how they function is not well understood. It is not clear whether their effect is due to the additive itself or to decomposition products. Additives are capable of adsorbing on the cathode and in some cases are trapped in the deposits. The presence of an adsorbed organic molecule, in general, will cause a decrease in the rate of charge transfer. However, it has been postulated that an adsorbed ligand also may complex with the metallic ion, increasing the amount of metal ion adsorbed on the electrode and thus

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increasing the rate of reduction (Franklin, 1987). Experiments to investigate the effects of the addition of thiourea, 1(−) cystine, glycine, gelatine, and dextrin on acid copper electroplating showed that addition of glycine and dextrin had no effect on the polarization (i.e., current vs. voltage) curve from those without the additive, whereas the other additives did influence the polarization, but the behavior differed from one another (Turner and Johnson, 1962; Johnson and Turner, 1962). Kardos and Foulke (1962) noted that some additives do not appreciably influence the charge transfer kinetics or mass transfer processes in the acid copper system used.

Previous mathematical models of plating in through-holes have helped understand the effects of critical plating operating parameters, particularly under the specific regimes of control of charge transfer kinetics, mass transport, or ohmic resistance (Alkire and Mirarefi, 1973; Kessler and Alkire, 1976a,b; Engelmaier and Kessler, 1978; Ben-Poret et al., 1983; Sullivan and Middleman, 1985; Lanzi and Landau, 1988; Lanzi et al., 1989; Pesco and Cheh, 1989). While examining the transient problem, Sullivan and Middleman (1985) determined that the steady-state solution is a good approximation of the solution of the transient equations for through-hole plating processes. This finding laid an important foundation for modeling of through-hole plating using steady-state equations. Various agitation schemes have been employed to enhance plating rates (Poskanzer, 1985c) and analyzed including: air sparging (Haak et al., 1981), mechanical board movement (Galasco et al., 1987), and forced flow (Middleman, 1986; Alkire and Ju, 1987).

The influence of plating additives has been modeled in some of these analyses as a variation of the current density of the equilibrium exchange, which is proportional to the standard charge transfer rate constant, or as a change in the dimensionless ratio of ohmic resistance to charge transfer resistance (Alkire and Mirarefi, 1973; Engelmaier and Kessler, 1978, Alkire and Ju, 1987). Alkire and Ju (1987), in their investigation of mass transport inside through-holes under an impinging jet, showed that plating additives only affected the plating distribution at low plating rates. Yung and Romankiw (1989) have solved the two-dimensional current distribution to understand the interaction of through-holes and surface pads during plating. The effect of additives was investigated by decreasing the exchange current density by a factor of 10. They determined that at low plating rates, deposition is controlled by change transfer kinetics and additives improve uniformity. When charge transfer kinetics and ohmic resistance both control the plating, their model results showed that plating additives improve uniformity, although the effectiveness diminishes with increasing plating speed. When ohmic resistance dominates, additives no longer were shown effective in enhancing uniformity.

Although the effects of plating additives on electrodeposits have been widely acknowledged, their influence on through-hole plating uniformity has been controversial. The mechanism through which additives influence electroplating still needs elucidation. Mechanistic knowledge would help formulate and select plating agents, particularly in accommodating high-speed plating.

In this paper, we are concerned with the plating of an individual through-hole rather than the entire panel surface or the hole wall topography, as in leveling. Often more copper is deposited near the mouth of the hole than in the center; it is commonly referred to as "dogboning." The detrimental effects of this nonuniform plating distribution are a decrease in current-carrying ability, higher probability of mechanical failure, and difficulty of wire insertion.

The purpose of this investigation is to develop a mathematical model for electroplating inside a through-hole with an acid copper sulfate bath in which the effects of plating additives on uniformity can be evaluated. This model is developed in such a general way that a specific mode of control for electrodeposition is not selected at the outset. However, as a simplification, it is assumed that convection into the through-hole is negligible. This operating condition is prevalent in a number of industrial plating processes (Peterson, 1984; Poskanzer, 1985a; Carano, 1986). With this approach, we can compare the uniformity of plating inside a through-hole from additive and additive-free baths, and understand the effects of major operating parameters. In order to investigate the effects of additives, a simple adsorption mechanism for an additive is proposed and is incorporated within this general model.

Model Development

The configuration to be considered is a cylindrical through-hole of diameter, D, and length, L, positioned in a plating solution equidistant between two parallel counter electrodes. Therefore, the through-hole aspect ratio, a, is defined as L/D. The surrounding plating bath on both sides of the circuit board is assumed to be a well-agitated solution of a metallic compound and a supporting electrolyte. This plating configuration is illustrated in Figure 1, in which only half of the through-hole is shown due to the geometrical symmetry. Only the region in the through-hole is considered accessible to plating. Since the fluid within the through-hole is assumed to be quiescent, convection is assumed not to contribute to the transport of any dissolved species into the through-hole. It is also assumed that the plating bath is operated at steady state and the physical properties are constant.

To simplify the mathematics, the radial variations of concentration and potential difference within the through-hole are assumed negligible compared to axial variations. This assumption has been shown to be valid for a through-hole with an aspect ratio of five or greater from results of a two-dimensional model

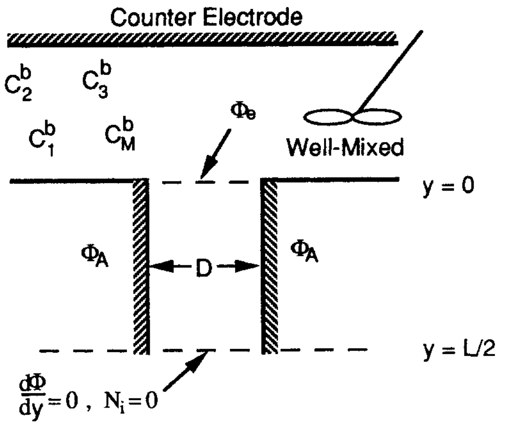

Figure 1. Definition of a through-hole for the mathematical model.

(Hazlebeck, 1989). Therefore, the model equations become one-dimensional with respect to the distance into the through-hole, y. Since transport by convection is considered negligible, the flux of each species, i, is due only to diffusion and electrical migration. Applying dilute solution theory, the flux of any ionic species can be written as:

$$N_i = -z_i C_i D_i \frac{F}{RT}\frac{d\Phi}{dy} - D_i \frac{dC_i}{dy} \tag{1}$$

Electroplating is performed potentiostatically at a constant voltage Φ_A and applied between the through-hole and the counterelectrodes. The potential difference at the entrance of the through-hole, Φ_e, can be determined from the current density at the hole entrance. The required applied potential difference, Φ_A, to maintain the total current density to plate a through-hole can be obtained by solving Laplace's equation (Newman, 1973). Laplace's equation applies since there are no concentration gradients in the well-mixed bulk solution.

It is assumed that the only ions that can be generated or consumed by reaction are the ions of the metal being deposited. The depositing metallic ions may react either heterogeneously or homogeneously. The electrodeposition of the metal is assumed to proceed with nearly 100% cathodic current efficiency: other charge transfer reactions, such as hydrogen evolution, are negligible. Additives may complex with metallic ions in solution and on the electrode surface. Heterogeneous kinetics enters the continuity equation as a pseudo-homogeneous reaction term for this one-dimensional analysis. The continuity equation for deposition metal ions is:

$$\frac{dN_M}{dy} = \frac{-4\mathcal{R}_s}{D} - \mathcal{R}_b \tag{2}$$

and for the other species, j, are:

$$\frac{dN_j}{dy} = 0 \tag{3}$$

These equations may be nondimensionalized by defining a dimensionless distance, concentration, and potential as follows:

$$X = \frac{2y}{L}, \quad \pi_i = \frac{C_i}{C_M^b}, \quad \phi = \frac{F(\Phi - \Phi_e)}{RT} \tag{4}$$

Substituting Eq. 1 into Eqs. 2 and 3 and nondimensionalizing yields:

$$\frac{d}{dX}\left\{z_M \pi_M \frac{d\phi}{dX} + \frac{d\pi_m}{dX}\right\} = \frac{D\mathcal{R}_s}{D_M C_M^b} a^2 + \frac{\mathcal{R}_b L^2}{4 D_M C_M^b} \tag{5}$$

$$\frac{d}{dX}\left\{z_j \pi_j \frac{d\phi}{dX} + \frac{d\pi_j}{dX}\right\} = 0 \tag{6}$$

The plating solution also is assumed to be electrically-neutral. For a solution of metallic ions and a supporting electrolyte, the electroneutrality equation may be written as:

$$z_M \pi_M + \sum_{j \neq M} z_j \pi_j = 0 \tag{7}$$

The electroneutrality equation can be used to eliminate a concentration variable, π_i, from the differential continuity equation. Boundary conditions are needed for the concentrations of each of the nonreactive species and the potential difference.

The boundary conditions of Figure 1 are such that at the entrance of the through-hole the ionic concentrations are equal to those of the bulk solution and the dimensionless potential difference is zero.

At $X = 0$:

$$\pi_i = \pi_i^b, \quad \phi = 0 \tag{8}$$

Due to symmetry of the counterelectrodes position outside of the through-hole, the potential difference gradient, $d\phi/dy$, vanishes at the center of the through-hole. Additionally, there is no flux of ions, N_i, at the center of the through-hole as the concentrations at both ends of the through-hole are equal.

At $X = 1$:

$$\frac{d\pi_i}{dX} = 0, \quad \frac{d\phi}{dX} = 0 \tag{9}$$

The concentrations of the nonreactive species are a function of the dimensionless potential difference when Eq. 6 subject to the boundary conditions, Eqs. 8 and 9, is solved. The resulting equation is:

$$\pi_j = \pi_j^b e^{-z_j \phi} \tag{10}$$

The depositing metal ion concentration now may be expressed as a function of the dimensionless potential difference by substituting the equation for the concentrations of nonreactive species, Eq. 10, into electroneutrality, Eq. 7. Thus, the concentration of the depositing metallic ion is:

$$\pi_M = \frac{-1}{z_M} \sum_{j \neq M} z_j \pi_j^b e^{-z_j \phi} \tag{11}$$

By substituting Eq. 11 into Eq. 5, the following differential equation results:

$$\frac{d}{dX}\left\{\frac{d\phi}{dX} \sum_{j \neq M} \left(\frac{z_j^2}{z_M} - z_j\right) \pi_j^b e^{-z_j \phi}\right\} = \frac{D\mathcal{R}_s}{D_M C_M^b} a^2 + \frac{\mathcal{R}_b L^2}{4 D_M C_M^b} \tag{12}$$

A kinetic function, Ψ, can be defined as:

$$\Psi = \frac{D\mathcal{R}_s}{D_M C_M^b} a^2 + \frac{\mathcal{R}_b L^2}{4 D_M C_M^b} \tag{13}$$

and the dimensionless microscopic ionic strength, $\xi(\phi)$, is:

$$\xi(\phi) = \sum_{j \neq M} \left(\frac{z_j^2}{z_M} - z_j\right) \pi_j^b e^{-z_j \phi} = \frac{2I}{z_M C_M^b} \tag{14}$$

The microscopic ionic strength, I, is defined as (Newman, 1973):

$$I = \frac{1}{2} \sum_i z_i^2 C_i \tag{15}$$

The solution of Eq. 12 (Hazlebeck, 1989) gives the dimensionless distance into the through-hole as an integral function of the dimensionless potential difference:

$$X = \int_0^{\phi} \frac{-\xi(\Phi')\, d\Phi'}{\left[2 \int_{\phi_c}^{\Phi'} \Psi(\Phi)\xi(\Phi) d\Phi\right]^{1/2}} \tag{16}$$

We wish to relate the degree of electroplating uniformity to the model parameters of interest, such as the dimensions of the through-hole, bulk solution concentrations, and deposition kinetics. Therefore, the uniformity of deposition, f, is defined as the rate of deposition at the center of the through-hole divided by the rate of deposition at the entrance to the through-hole:

$$f = \frac{\mathcal{R}_c}{\mathcal{R}_e} \tag{17}$$

Note that the uniformity as defined by Eq. 17 is essentially an effectiveness factor. It is assumed that the surface of the through-hole remains smooth during the course of electrodeposition and that the thickness is smaller than the through-hole diameter. Hence, a deposition is completely uniform when f equals unity. The solutions for the concentration and dimensionless potential difference at the center of the through-hole are used to evaluate the rate of deposition at the center of the through-hole. At the entrance of the through-hole, the rate of deposition is evaluated considering the bulk solution concentration and a dimensionless potential difference of zero.

For specific reaction kinetics and electrolyte composition, the functions ψ and ξ can be specified from Eq. 13 and Eq. 14, respectively. The computational procedure was initiated by specifying a deposition uniformity, f. By assuming f, the dimensionless potential difference at the center of the through-hole was determined from Eq. 17. Then by numerical integration of Eq. 16, the dimensionless potential difference was calculated as a function of the distance into the through-hole. Subsequently, the ionic concentrations as a function of distance into the through-hole were determined from Eqs. 10 and 11.

The model developed thus far is generally applicable to the electrodeposition of a metal in a through-hole, considering the main assumptions of a quiescent fluid and negligible radial variations of concentration and potential difference within the hole. Accordingly, we shall apply this general model to compare the effects of plating from solutions with and without additives. Therefore, we consider the acid copper sulfate plating bath commonly used in electroplating of PCB's. Generally, sulfuric acid is added in high concentrations as the supporting electrolyte to give the bath maximum conductivity and control the solution pH to limit undesired reactions, such as metal hydroxide formation and hydrogen evolution. Specific reaction kinetics to be considered must be incorporated into the general model and the results compared to study the effects of additives on the deposition. Therefore, to investigate the electrodeposition of copper from $CuSO_4 - H_2SO_4$ solutions without an additive, an empirical kinetics relationship of Cabán and Chapman (1977) is used. The effect of additives is studied by modeling the kinetics of a simple adsorption mechanism. Lastly, since the general model includes the effects of diffusion and electrical migration, the limiting conditions of deposition under mass transfer control or ohmic control in a through-hole can be compared to the results of the cases considered.

Electrolyte Composition

The model developed will be applied to electroplating of copper in a through-hole. Therefore, the electrolyte considered will be a $CuSO_4 - H_2SO_4$ solution. Aqueous solutions of sulfuric acid strongly dissociate to protons and bisulfate ions. Bisulfate ions, however, generally do not completely dissociate in a sulfuric acid solution, and the equilibrium between sulfate and bisulfate ions must be considered:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-} \tag{18}$$

Therefore, the ionic species to be considered for a plating solution of copper sulfate and sulfuric acid are Cu^{2+}, H^+, SO_4^{2-}, and HSO_4^-. Thus, the dimensionless ionic strength defined by Eq. 14 becomes:

$$\xi(\phi) = 4\pi_{SO_4}^b e^{2\phi} + 3/2\, \pi_{HSO_4}^b e^{\phi} - 1/2\, \pi_H^b e^{-\phi} \tag{19}$$

Since the bulk concentrations of copper sulfate and sulfuric acid in a plating bath are usually known, the dimensionless bulk concentrations of the ionic species in Eq. 19 should be related to these values. The second dissociation constant of sulfuric acid, K_d (in moles/liter), of Eq. 18 has been correlated with the microscopic ionic strength from experimental data for H_2SO_4 concentrations up to 2.95 M as follows (Newman, 1973):

$$K_d = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 0.0104 \exp\left(\frac{5.29\sqrt{I}}{1 + 0.56\sqrt{I}}\right) \tag{20}$$

To simplify matters, it is often assumed that bisulfate ions have either completely dissociated or have not dissociated at all. However, the degree of dissociation of bisulfate ions can dramatically effect ionic migration (Newman, 1973). Therefore, the dimensionless bulk ionic concentrations shall be expressed in terms of the ratio of sulfuric acid to copper sulfate in the bulk solution, s, and the extent of dissociation. The extent of bisulfate dissociation, χ, is defined as:

$$\chi = \frac{[SO_4^{2-}]}{[HSO_4^-] + [SO_4^{2-}]} \tag{21}$$

Complete dissociation of bisulfate ions corresponds to $\chi = 1$, and no dissociation corresponds to $\chi = 0$. Hence, the dimensionless bulk ionic concentrations can be expressed as follows:

$$\pi_{SO_4}^b = \chi(s + 1), \quad \pi_{HSO_4}^b = (1 - \chi)(s + 1),$$
$$\pi_H^b = s - 1 + \chi(s + 1) \tag{22}$$

where s is defined as the ratio of the concentrations of sulfuric acid to copper sulfate in the bulk solution. Therefore, for the limiting cases, the dimensionless bulk concentrations for complete bisulfate dissociation are:

$$\pi^b_{SO_4} = s + 1, \quad \pi^b_{HSO_4} = 0, \quad \text{and } \pi^b_H = 2s \tag{23}$$

and for no bisulfate dissociation are:

$$\pi^b_{SO_4} = 0, \ \pi^b_{HSO_4} = s + 1, \quad \text{and } \pi^b_H = s - 1 \tag{24}$$

The ionic strength of the bulk solution can be written as:

$$I^b = \{s + 2 + 2\chi(s + 1)\}C^b_{Cu} \tag{25}$$

By substituting both Eq. 22 and Eq. 25 into the equilibrium expression, Eq. 20, the extent of dissociation can be determined for various bulk sulfuric acid to copper sulfate ratios, s, and copper sulfate concentrations. Once s and χ are known, the dimensionless bulk concentrations can be calculated from Eq. 22.

Reaction Kinetics

In this paper, it is assumed that only heterogeneous reactions occur during the electroplating of copper in a through-hole. Therefore, the homogeneous reaction rate, $\mathcal{R}_b$, in the general model can be neglected. However, expressions for the heterogeneous reaction rate for copper deposition from additive and additive-free plating baths must be determined. To investigate the electrodeposition of copper from $CuSO_4 - H_2SO_4$ solutions without an additive, an empirical relationship for the kinetics is used (Cabán and Chapman, 1977). The effect of additives is studied by modeling the kinetics of a simple adsorption mechanism.

Cabán and Chapman (1977) measured the kinetics of copper electrodeposition from copper sulfate-sulfuric acid solutions. Their empirical Butler-Volmer kinetic expression (Bockris and Reddy, 1970) relates the rate (i.e., current density) of deposition and dissolution of copper to the concentrations of cupric ion and sulfuric acid (in M):

$$i(\text{mA/cm}^2) = 15.6C^{0.67}_{Cu}e^{-0.37C_{H_2SO_4}} \cdot \{e^{1.08\eta F/(RT)} - e^{-0.39\eta F/(RT)}\} \tag{26}$$

where η is the surface overpotential. The surface overpotential is related to the applied potential difference, equilibrium potential difference and concentration overpotential by:

$$\eta = \Phi_A - \Phi_b - \Phi - \eta^* \tag{27}$$

where Φ_b is the equilibrium potential difference for the conditions in the bulk of the solution, and η^* is the concentration overpotential given in an approximate form as:

$$\eta^* = \frac{RT}{2F}\ln\frac{C_{Cu}}{C^b_{Cu}} \tag{28}$$

The dependence of the reaction rate on sulfuric acid concentration in Eq. 26 was included by Cabán and Chapman (1977) as a first-order approximation for the strong variation of the copper sulfate activity coefficient with the concentration of sulfuric acid.

By only considering the deposition of copper, the anodic term in Eq. 26 can be neglected and the rate expression can be written in terms of dimensionless potential difference and concentration as:

$$\mathcal{R}_s = \mathcal{R}_e\pi^{0.87}_{Cu}e^{0.39\phi}e^{-0.37(C_{H_2SO_4} - C^b_{H_2SO_4})} \tag{29}$$

where the heterogeneous of reaction rate at the entrance to the through-hole, $\mathcal{R}_e$, is defined by:

$$\mathcal{R}_e = -15.6C^{b^{0.67}}_{Cu}e^{-0.37C^b_{H_2SO_4}}e^{-0.39F(\Phi_A - \Phi_e - \Phi_b)/(RT)}. \tag{30}$$

The kinetic expression for copper deposition from an additive-free bath, Eq. 29, can now be incorporated into the model of through-hole electroplating by substituting for Eq. 13. The following kinetic function is obtained:

$$\Psi(\phi) = (\gamma a)^2\pi^{0.87}_{Cu}e^{0.39\phi}e^{-0.37(C_{H_2SO_4} - C^b_{H_2SO_4})} \tag{31}$$

where γ is the Thiele modulus defined as:

$$\gamma^2 = \frac{\mathcal{R}_e D}{D_{Cu}C^b_{Cu}} \tag{32}$$

The square of the Thiele modulus, which is a measure of the ratio of the heterogeneous reaction rate to the rate of diffusion in the through-hole, is a convenient dimensionless parameter for our model of through-hole plating. The dimensionless cupric ion concentration can be expressed by:

$$\pi_{Cu} = \pi^b_{SO_4}e^{2\phi} + 1/2\,\pi^b_{HSO_4}e^{\phi} - 1/2\,\pi^b_H e^{-\phi} \tag{33}$$

The difference in sulfuric acid concentration between the bulk solution and the through-hole surface in Eq. 31 is:

$$C_{H_2SO_4} - C^b_{H_2SO_4} = 1/2\,C^b_{Cu}\{\pi^b_{HSO_4}(e^{\phi} - 1) + \pi^b_H(e^{-\phi} - 1)\} \tag{34}$$

where the dimensionless bulk concentrations, π^b_i, are determined from Eq. 22.

Although the effects of various additives used in acid copper electroplating have been studied (Turner and Johnson, 1962; Johnson and Turner, 1962), a kinetic expression for dependence of copper electrodeposition on cupric ion concentration with an additive in the plating bath is not readily available in the literature. Therefore, to consider the effect of additives a simple adsorption reaction mechanism is proposed:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_{ad} \tag{35}$$

$$Cu^{2+} + A_{ad} \xrightarrow{k_3} Cu^{2+}A_{ad} \tag{36}$$

It is assumed that a neutral additive species adsorbs on the through-hole surface, and copper electrodeposition is limited by cupric ion complexing with the adsorbed additive species. Therefore, Langmuir-Hinshelwood-Hougen-Watson adsorption kinetics is used for the heterogeneous reaction term:

$$\mathcal{R}_s = \frac{K_{ad}C_{\mathrm{Cu}}}{K_o + C_{\mathrm{Cu}}} \tag{37}$$

where K_{ad} is the adsorption rate constant and K_o is the inverse of the kinetic adsorption coefficient. By substituting Eq. 37 and Eq. 11 into Eq. 13, the following kinetic function for adsorption kinetics is obtained.:

$$\Psi_{ad}(\phi) = (\gamma a)^2 \frac{(\pi^b_{\mathrm{SO_4}}e^{2\phi} + {}^1\!/_2\pi^b_{\mathrm{HSO_4}}e^{\phi} - {}^1\!/_2\pi^b_{\mathrm{H}}e^{-\phi})(1 + \pi_o)}{\pi_o + (\pi^b_{\mathrm{SO_4}}e^{2\phi} + {}^1\!/_2\pi^b_{\mathrm{HSO_4}}e^{\phi} - {}^1\!/_2\pi^b_{\mathrm{H}}e^{-\phi})} \tag{38}$$

where:

$$\pi_o = \frac{K_o}{C^b_{\mathrm{Cu}}} \tag{39}$$

and $\mathcal{R}_e = K_{ad}/(1 + \pi_o)$ in the Thiele modulus. The kinetic functions necessary for the solution of the general model are thus defined by Eqs. 33 and 38.

Limiting Cases

The relative contributions of the electrical migration and the diffusion terms to the flux of cupric ions can be determined by substituting Eq. 7 into Eq. 1:

$$N_{\mathrm{Cu}} = \left(\frac{1}{2}z^2_{\mathrm{Cu}}C_{\mathrm{Cu}} + \frac{1}{2}\sum_{j\neq \mathrm{Cu}} z^2_j C_j\right) D_{\mathrm{Cu}}\frac{d\phi}{dy} \tag{40}$$

The first term in parentheses is the contribution to the flux of migration and the second term is the contribution of diffusion. The total of the two terms is the microscopic ionic strength, as defined in Eq. 15. Therefore, the fractional contribution of the migration term to the total cupric ion flux is the ratio of the copper ion contribution to the total ionic strength:

$$\frac{N_{\mathrm{migr}}}{N_{\mathrm{Cu}}} = \frac{4C_{\mathrm{Cu}}}{I} = \frac{4}{\xi(\Phi)} \tag{41}$$

Conversely, the contribution of the diffusion term is the ratio of the contribution of all ions except cupric to the total ionic strength. Thus, the contribution of the migration term is 50% of the flux for a binary electrolyte and negligible for high supporting electrolyte ratios. Due to cupric ion depletion in the interior of the through-hole, the contribution of the migration term will be greatest at the entrance to the through-hole.

In plating baths with high relative ionic strengths (high supporting electrolyte ratios), migration within the through-hole will be negligible. Under these conditions, which is the diffusion-limited case, the first term in Eq. 1 may be neglected. By substituting Eq. 1 into Eq. 2 and nondimensionalizing, the following differential equation for diffusion-limited plating results:

$$\frac{d^2\pi_{\mathrm{Cu}}}{dX^2} = \Psi \tag{42}$$

The kinetic function, Ψ, is defined by Eq. 13. The boundary conditions are no flux at the center of the through-hole, Eq. 9, and the bulk concentration prevails at the entrance of the through-hole, Eq. 8. Assuming no homogeneous reactions and that the heterogeneous kinetics are defined by Eq. 29, the kinetic function given in Eq. 31 may be used. The factors containing the dimensionless potential difference and the bulk sulfuric acid concentration in Eq. 31 can be neglected for the diffusion-limited case. Thus, the kinetic function will take the form:

$$\Psi = (\gamma a)^2 \pi^{\beta}_{\mathrm{Cu}} \tag{43}$$

where β, the order of the reaction, is 0.87 for the experimental kinetics measured by Cabân and Chapman (1977). Noting that the uniformity of deposition, f, is:

$$f = \pi^{\beta}_{\mathrm{Cu}}|_{X=1} \tag{44}$$

Equation 42 can be integrated to yield:

$$\gamma a X = \sqrt{\frac{1+\beta}{2}} \int_{\pi_{\mathrm{Cu}}}^{1} \frac{d\pi}{\sqrt{\pi^{\beta+1} - f^{(1+1/\beta)}}} \tag{45}$$

which can be evaluated numerically by first assuming a value for f.

If the reaction order is one, than Eq. 45 can be integrated analytically. The result is:

$$\pi_{\mathrm{Cu}} = \frac{\cosh[\gamma a(1 - X)]}{\cosh(\gamma a)} \tag{46}$$

Thus, the uniformity of deposition is:

$$f = \frac{1}{\cosh(\gamma a)} \tag{47}$$

Hence, the dependence of the uniformity of deposition on the plating variables for the one-dimensional, diffusion-limited model is determined either by Eq. 47 if the reaction rate order is one or by Eq. 45 if the reaction rate order is not equal to one.

Results and Discussion

The nondimensional potential difference as a function of distance into the through-hole was calculated from Eq. 16 with the appropriate kinetic function, $\Psi(\Phi)$, and dimensionless microscopic ionic strength, $\xi(\Phi)$. A Gaussian-Legendre quadrature method (Carnahan et al., 1969) was used to numerically evaluate the integrals in Eq. 16. The dimensionless bulk concentrations from Eq. 22, 23 or 24 were substituted into Eq. 25 to obtain the function for the dimensionless ionic strength for the cases of partial dissociation, complete dissociation, and no dissociation of bisulfate ions, respectively. The dimensionless microscopic ionic strength was determined by substituting the bulk concentrations into Eq. 19. For Butler-Volmer kinetics, the kinetic function was obtained by substituting Eqs. 33 and 34 into Eq. 31. For adsorption kinetics, the kinetic function was obtained from Eq. 38. Once the dimensionless potential difference profile was known, the ionic concentrations as a function of distance into the through-hole were determined from the relationships in Eqs. 10 and 11.

Typical profiles of dimensionless potential difference and cupric ion concentration in the through-hole are illustrated in Figure 2 for $CuSO_4$ binary electrolyte ($s = 0$) and three cases of bisulfate dissociation with $s = 1$. The values of the dimensionless ionic strength of the bulk solution are 3, 4, 5.4, and 7 for the cases of no dissociation ($\chi = 0$), binary electrolyte, partial dissociation ($\chi = 0.6$), and complete dissociation ($\chi = 1$), respectively. The potential gradient decreases and the cupric ion concentration gradient increases as the dimensionless ionic strength of the bulk solution increases. This is expected because the analysis of the contributions of migration and diffusion showed that the contribution of migration is inversely proportional to the dimensionless ionic strength. Therefore, both the potential and concentration gradients contribute to the cupric ion flux for low dimensionless ionic strength solutions, but only the concentration gradient contributes to the flux for dimensionless high ionic strength solutions.

The effect of bulk cupric ion concentration, cupric ion diffusivity, through-hole dimensions, applied potential difference, and current density on deposition uniformity can be correlated by the Thiele modulus parameter, $(\gamma a)^2$. The Thiele modulus parameter contains the product of the through-hole diameter and the aspect ratio squared. Therefore, the important geometrical parameter is L^2/D rather than simply the aspect ratio, which has been verified in experimental studies (Yung et al., 1989). A plot of the uniformity of deposition, f, vs. the Thiele modulus parameter, for the four cases discussed previously is shown in Figure 3. As expected, the uniformity of deposition decreases with increasing Thiele modulus parameter. This indicates that smaller diameter through-holes, lower aspect ratios, higher cupric ion diffusivities, higher cupric ion concentrations, and lower current densities will improve the uniformity of plating. The plating also is more uniform for the low bulk ionic strength solutions. This indicates that more uniform plating is obtained from a flux created by both migration and diffusion, than from a flux due to diffusion alone.

The dependence of uniformity, f, on the bulk sulfuric acid to copper sulfate concentration ratio, s, for constant $(\gamma a)^2$ and $C^b_{Cu} = 0.3$ M is illustrated in Figure 4 for the three cases of bisulfate dissociation. The results indicate that low-conductivity solutions will provide higher uniformity for plating without convection, in which case both diffusion and migration are important. For s greater than ten, the uniformity is nearly independent of s and the degree of dissociation. Hence, for a highly conductive electrolyte, diffusion of the cupric ions is the dominant mode of transport. For s less than ten, the uniformity increases as the bisulfate ion dissociation or s decreases. The case of no dissociation is limited to electrolyte compositions of s greater than one. Additives may alter the bisulfate dissociation through complexation of sulfate or bisulfate ions. Therefore, optimum uniformity would be achieved with s equal to unity and an additive in the plating bath that would shift the dissociation equilibrium toward the predominance of bisulfate ions. Without this type of additive effect, the optimum uniformity is achieved with a binary electrolyte.

A plot of the uniformity of deposition vs. the microscopic ionic strength of the bulk solution is shown in Figure 5. The graph includes the results from three different electrolytes: no dissociation containing ions of charge +2, +1, and −1; complete

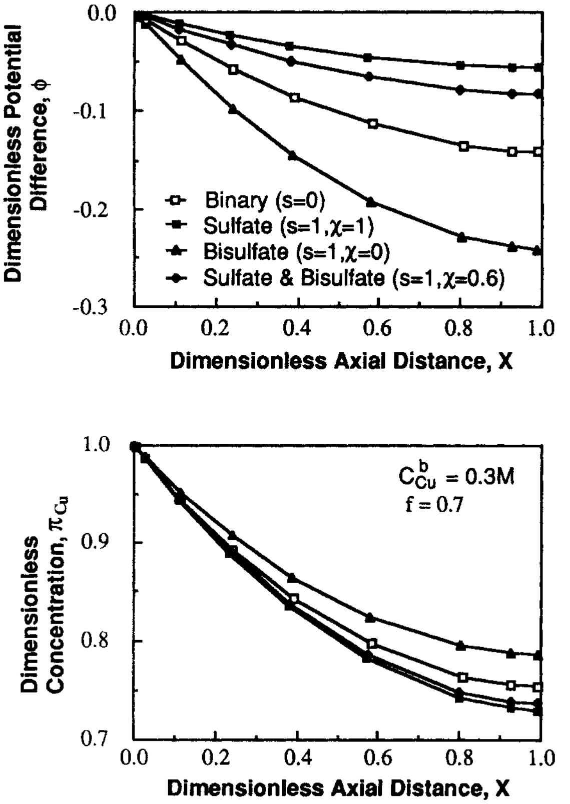

Figure 2. Typical profiles of dimensionless potential difference and cupric ion concentration within a through-hole.

$f = 0.7$ and $C^b_{Cu} = 0.3$ M A binary electrolyte ($s = 0$) is compared to a supporting electrolyte ratio of one with complete, partial ($\chi = 0.6$), and no dissociation of bisulfate ions.

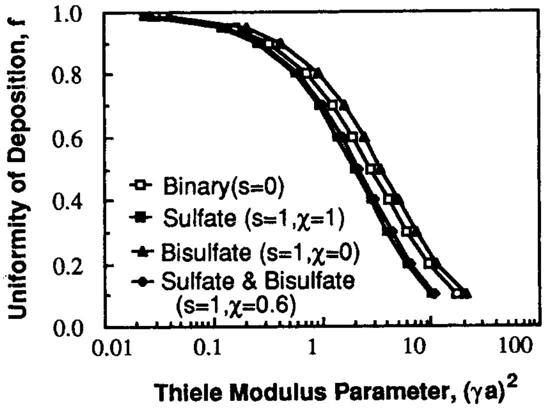

Figure 3. Dependence of the uniformity of deposition on the Thiele modulus parameter.

For a binary electrolyte, ($s = 0$), and a supporting electrolyte ratio of one with complete, partial ($\chi = 0.6$), and no dissociation of bisulfate ions.

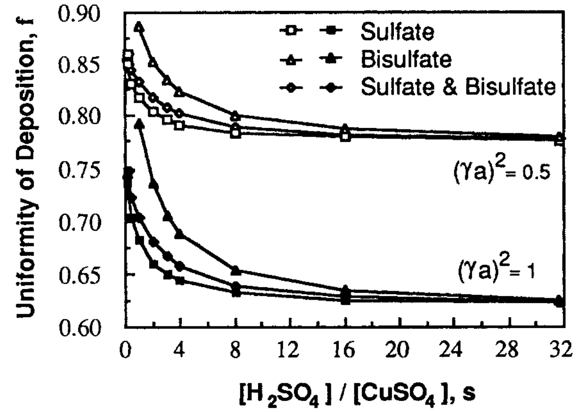

Figure 4. Dependence of the uniformity of deposition on the supporting electrolyte ratio.

For complete, partial, and no dissociation of bisulfate ions.

dissociation containing ions of charge +2, +1, and −2; and partial dissociation containing ions of charge +2, +1, −1, −1. In all cases, the uniformity of deposition for a fixed Thiele modulus parameter correlates well with the dimensionless microscopic ionic strength. Therefore, regardless of electrolyte composition, the uniformity of deposition for electroplating of through-holes containing stagnant fluid can be predicted from only two parameters, dimensionless microscopic ionic strength and Thiele modulus parameter.

The diffusion limit of uniformity of deposition as a function the dimensionless ionic strength is indicated by the horizontal dashed lines shown in Figure 5. At dimensionless, high ionic strengths, the results of the general model approach those of the diffusion-limited model. This is expected, because the migration term becomes smaller than the diffusion term at high ionic strengths. A diffusion-limited model of plating without convection will thus give a lower bound for the uniformity of deposition as a function of the Thiele modulus parameter. The results of diffusion-limited models, however, are within a factor two of the value obtained under optimum conditions and therefore provide a very good order-of-magnitude estimate of the results expected of models of coupled diffusion and migration. If the dimensionless ionic strength in the bulk solution is greater than 25, the solutions of the diffusion equation provide an accurate approximation of the general equations for plating without convection.

An empirical correlation to account for the sulfuric acid concentration effect on the cupric ion activity coefficient was included in the reaction rate, Eq. 26. To examine the effects of including the sulfuric acid concentration factor, the uniformity of deposition is plotted vs. the bulk sulfuric acid concentration in Figure 6. The uniformity decreased by approximately 0.01 for each increase of 1 M sulfuric acid, which is a relatively small effect. Therefore, the empirical correction to the kinetics for the effect of sulfuric acid concentration on the cupric ion activity is insignificant for modeling of through-hole plating.

Typical cupric ion concentration and potential difference profiles for Butler-Volmer kinetics and adsorption kinetics are shown in Figure 7 to compare electroplating without additives to plating with additives to the bath. In this application of the model, a neutral additive species has been assumed. The adsorption effects of potential-dependent plating additives are discussed elsewhere (Hazlebeck, 1989). The concentration and potential difference gradients are much larger for adsorption kinetics than Butler-Volmer kinetics. This is expected because adsorption kinetics are less dependent on cupric ion concentration than Butler-Volmer kinetics and are independent of the potential difference. An important aspect of the adsorption kinetics profile is that at a uniformity of 0.70, the concentration of cupric ions at the center of the through-hole is negligibly small. A perfectly adsorbing additive would promote a completely uniform deposition while the concentration was nearly zero at the center of the through-hole. The rate would then be limited by the maximum mass transport rate, which is calculated by assuming a cupric ion concentration of zero at the center of the through-hole.

The deposition uniformity also can be correlated with the Thiele modulus parameter, $(\gamma a)^2$, for adsorption kinetics. As there are no kinetic data available to determine actual values of the adsorption constants K_{ad} and K_o, a value of π_o and uniformity of deposition were specified instead. From Eq. 37 it can be

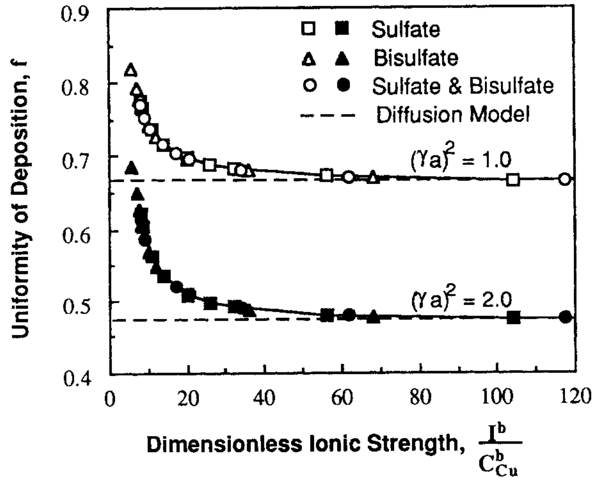

Figure 5. Dependence of the uniformity of deposition on the dimensionless ionic strength.

For various supporting electrolyte compositions.

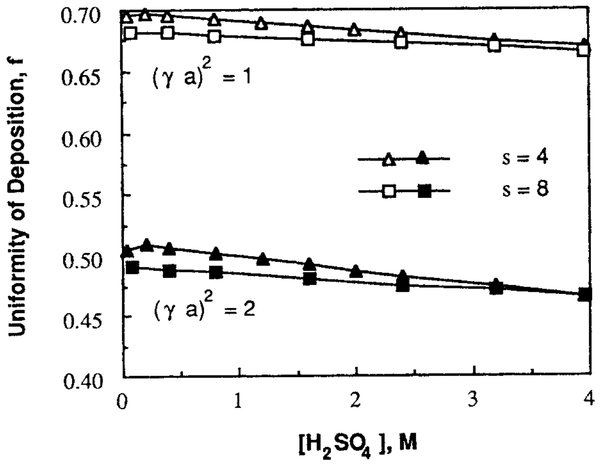

Figure 6. Dependence of the uniformity of deposition on the concentration of sulfuric acid in the bulk solution.

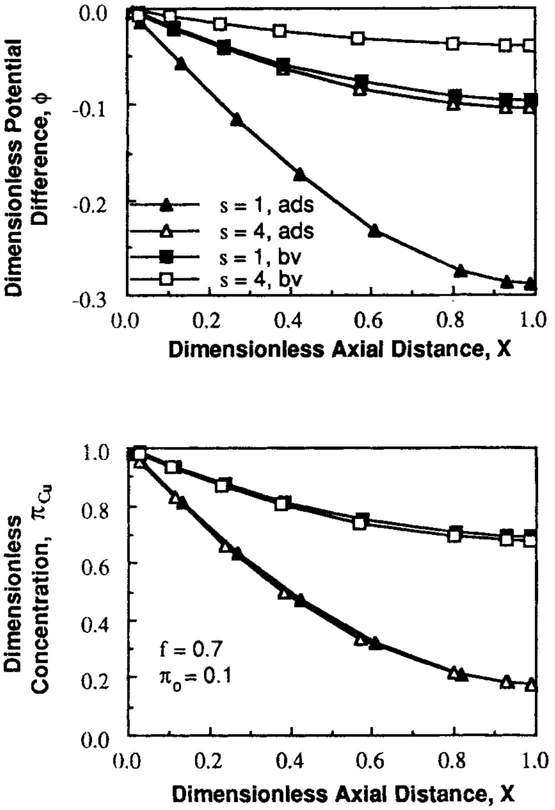

Figure 7. Typical profiles of dimensionless potential difference and cupric ion concentration.

Within a through-hole without additives (Butler-Volmer kinetics, bv) and with additives (adsorption kinetics, ads).

seen that the limits of the adsorption kinetic relationship are either zero-order or first-order kinetics with respect to cupric ion concentration. Smaller values of π_o would yield a more uniform deposition. The dependence of uniformity on Thiele modulus parameter for Butler-Volmer kinetics and for adsorption kinetics with $\pi_o = 0.1$ is shown in Figure 8. The trends of the dependence of uniformity on Thiele modulus parameter and supporting electrolyte ratio are similar for both types of kinetics. Both are limited by the same rate as they approach zero uniformity. The advantage of using an additive with adsorption kinetics is that the uniformity remains high until the maximum rate of mass transport is reached. To plate at a higher rate would require the use of forced convection in the through-hole. Although a reaction order of 0.865 from the empirical relationship of Cabán and Chapman (1977) in Eq. 30 was used to generate the curve for additive-free copper deposition kinetics in Figure 8, the results by using a reaction rate order of one are nearly identical (Hazlebeck, 1989). Therefore, as a simplification, the uniformity of copper deposition could be determined by the analytical expression in Eq. 47.

Deposition uniformity as a function of bulk copper sulfate concentration for $i_{x=0} = 2.25\ \mathrm{mA/cm^2}$, $a = 5$, $D = 0.1\mathrm{mm}$, and $s = 1$ is illustrated in Figure 9. As expected, the uniformity of deposition increases as the bulk copper sulfate concentration increases. The sharp decrease in uniformity for low-bulk copper sulfate concentrations indicates the importance of well-mixed bulk phase to insure that the bulk concentration is identical for all through-holes in a circuit board panel. For adsorption kinetics, the uniformity is relatively independent of bulk concentration at high copper sulfate concentrations, but decreases quickly to very low uniformity at low copper sulfate concentrations. The leveling of the curve at high concentrations occurs because the rate of deposition is less dependent on the cupric ion concentration. The sharp decrease in uniformity at low concentrations occurs because the maximum mass transport rate is approached.

Uniformity of deposition as a function of current density with and without additives is illustrated in Figure 10 for a process with a through-hole diameter of 0.1 mm, an aspect ratio of 5, a bulk cupric sulfate concentration of 0.9 M, and a supporting electrolyte ratio of 1. An additive with adsorption kinetics allows the plating of a smaller-diameter through-hole without convection. Typical through-holes of multilayer printed circuit boards are four to eight times larger in diameter than 0.1 mm used in this calculation. This increase in diameter would make the rate four to eight times lower at a particular uniformity. Therefore,

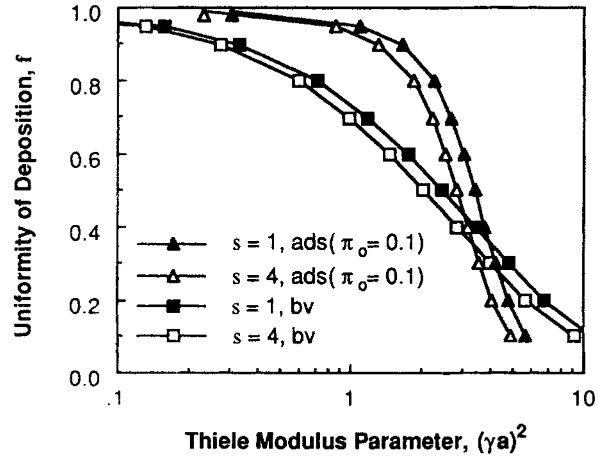

Figure 8. Dependence of uniformity of deposition on the Thiele modulus parameter.

Without additives (Butler-Volmer kinetics, bv) and with additives (adsorption kinetics, ads).

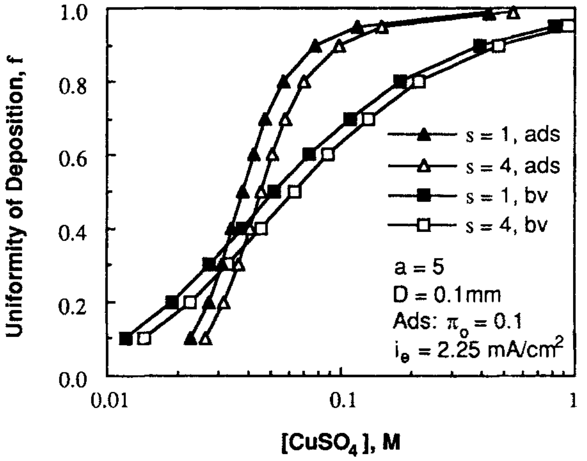

Figure 9. Dependence of uniformity of deposition on the cupric ion concentration

In the bulk solution without additives (Butler-Volmer kinetics, bv) and with additives (adsorption kinetics, ads).

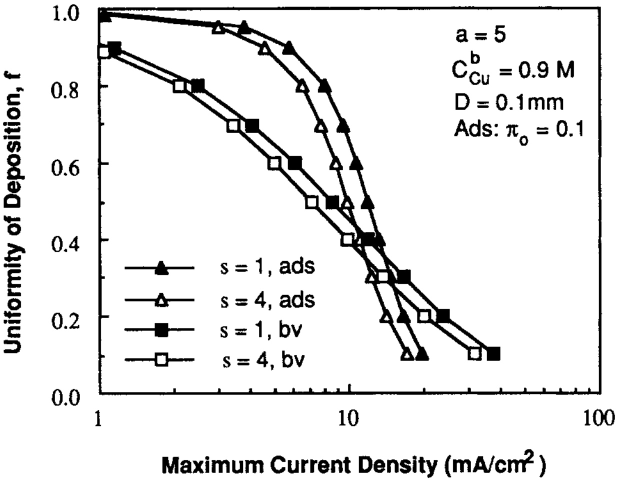

Figure 10. Dependence of uniformity of deposition on the maximum current density.

Without additives (Butler-Volmer kinetics, bv) and with additives (adsorption kinetics, ads).

plating through-holes of multilayer printed circuit boards without convection in the through-hole is not practical. There are holes which need to be plated in devices such as magnetic recording heads which have even smaller diameters than the size considered in Figure 10. These holes could be plated at higher rates than the through-hole considered in Figure 10.

Conclusions

General and diffusion-limited mathematical models have been developed to describe copper plating of a through-hole without considering convection within the through-hole. The models relate plating uniformity in the through-hole to the applied potential difference, current density, bulk electrolyte composition, through-hole dimensions, extent of bisulfate dissociation, and deposition kinetics. Although only heterogeneous reaction kinetics are considered in this investigation, both homogeneous and heterogeneous reactions can be considered in the general model. The effects of additives to the plating bath were investigated by considering adsorption kinetics and comparing with results from Butler-Volmer kinetics. The diffusion-limited model provides a lower bound to the uniformity of deposition as a function of the Thiele modulus parameter and is a good order-of-magnitude estimate of plating under the optimum conditions.

The general model provides a vehicle for predicting operating conditions for plating through-holes uniformly. The effect of additives on deposition uniformity can be evaluated by incorporating the appropriate kinetic relationships in this model. Plating baths of other supporting electrolytes and copper compounds also may be examined using this model.

The uniformity of deposition was found to be dependent upon two dimensionless parameters: the Thiele modulus parameter and the dimensionless microscopic ionic strength. The aspect ratio has been perceived as the important geometrical factor used to judge the difficulty in achieving uniform plating in through-holes. However, the term L^2/D is the relevant geometrical parameter determined from the dimensionless groups, rather than the aspect ratio.

The results indicate that the plating rate of through-holes without convection is too low for use by the printed circuit board industry. However, "through-holes" for devices such as magnetic recording heads and solar cells have a much smaller diameter. In these circumstances, plating without convection becomes practical and inducing convection becomes difficult. This results from the dependence of the Thiele modulus on the diameter of the through-hole. The trends predicted for plating of through-holes without convection also are applicable to the plating of blind holes. There are significant differences in optimal processing conditions between plating with convection and plating without convection. When plating blind holes and very small diameter through-holes without convection, the following principles apply:

- The conductivity should be held as low as possible. To obtain a lower value of dimensionless microscopic ionic strength, a supporting electrolyte with a charge of -1 and $+1$ should be chosen, if available.
- The concentration and diffusivity of the ion to be deposited should be as high as possible.
- Additives which lower the dependence of rate on concentration should be used rather than those which lower the dependence on potential difference.
- The uniformity will depend on the Thiele modulus parameter and the dimensionless microscopic ionic strength. If the uniformity is too low, one or both of these parameters should be lowered. When making significant changes in the process, these parameters should be held constant to obtain the same uniformity.

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Notation

a = aspect ratio, L/D
C_i = concentration of species i
D = diameter of the through-hole
D_i = diffusivity of species i
$D_{r,i}$ = diffusivity of species i relative to species M, $D_{r,i}/D_M$
f = uniformity of deposition, $\mathcal{R}_c/\mathcal{R}_e$
F = Faraday's constant, 96,487 C/equiv.
i = current density
I = microscopic ionic strength, Eq. 15
K_{ad} = adsorption rate constant
K_d = dissociation constant for bisulfate ions
K_o = inverse of the kinetic adsorption coefficient
L = length of the through-hole
N_i = flux of species i
R = universal gas constant, 8.3141 J/mol · K
$\mathcal{R}_b$ = homogeneous rate of reaction
$\mathcal{R}_c$ = rate of deposition at the center of a through-hole
$\mathcal{R}_e$ = rate of deposition at an end of a through-hole
$\mathcal{R}_s$ = heterogeneous rate of reaction
s = ratio of sulfuric acid to cupric sulfate in the bulk solution
T = temperature, K
X = dimensionless axial distance, $2\,y/L$
y = axial distance in the through-hole
z_i = charge of species i

Greek letters

α = Tafel cathodic charge transfer coefficient
β = cupric ion concentration reaction rate order

γ^2 = Thiele modulus squared, $\mathcal{R}_e D/D_{\mathrm{Cu}}C^b_{\mathrm{Cu}}$
η = surface overpotential
η^* = concentration overpotential
$\xi(\phi)$ = dimensionless microscopic ionic strength, Eq. 14
π_i = dimensionless concentration of species i, C_i/C^b_M
π_o = dimensionless inverse of the kinetic adsorption coefficient
ϕ = dimensionless potential, $F(\Phi - \Phi_e)/RT$
Φ = potential difference in the solution
Φ_A = potential difference applied between the counter electrode and the through-hole
Φ_b = equilibrium potential difference for the conditions in the bulk of the solution
Φ_e = potential difference at the entrance to the through-hole
χ = extent of bisulfate dissociation
$\psi(\phi)$ = kinetic function, Eq. 13

Subscripts

ads = adsorption kinetics
bv = Butler-Volmer kinetics
Cu = cupric ion
c = center of the through-hole
e = entrance of the through-hole
H = hydrogen ion
$\mathrm{HSO_4}$ = bisulfate ion
$\mathrm{H_2SO_4}$ = sulfuric acid
i = all ionic species
j = all ionic species not involved in reactions
migr = electrical migration
M = deposited metal species
s = at the surface
$\mathrm{SO_4}$ = sulfate ion

Superscript

b = in the bulk solution

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