# Electrochemical Deposition in Deep Vias

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*Copper is used as interconnects on chips. It is laid down in deep vias by electrodeposition. For the simple case, the rate of electrodeposition on the shoulders is much greater than that at the bottom, and the via-mouth closes during the process and a bubble is captured inside. Approximate solutions to the electrodeposition process, when the transport is diffusion controlled and when it is reaction controlled, are obtained. It is shown that bubbles are easily captured in diffusion-controlled systems, but no bubbles are captured in the reaction-controlled system. However, the diffusion-controlled system has very low currents, low electrodeposition rates, and low production rates, and the reaction-controlled system has even lower rates. Based on these, the existing solutions to the bubble-capture problem are briefly reviewed to suggest that inducing natural convection appears most promising.* © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 354–358, 2006

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## Introduction

The very large integrated systems (VLSI) and the ultralarge integrated systems (ULSI) are generally made up of transistors and interconnects on a chip.[1] The interconnects are $<100$ $\mu$m in width, and the obvious thrust at present is to go to even smaller dimensions. The other path for improvement has been to look at better materials. Aluminum with 0.5% copper, to discourage electromigration, has been in use. Copper is the material of choice because of both its higher conductivity and higher resistance to electromigration. A breakthrough in the fabrication of copper interconnects has recently been made.

The details of dual damascene channels for fabricating copper interconnects have been described by May and Sze.[2] However, in the present work, only a single deep via is considered. The via surface is lined with copper using physical vapor deposition (PVD). This surface is then used as a cathode to electrodeposit copper. The electrolytes are typically a 2 M copper sulfate solution, often including an indifferent electrolyte, which is present at very high strengths. It can be imagined that in real systems the density of vias on a chip is large and varies on the chip surface. Although this gives rise to spatially varying demands on the operating conditions,[3] this aspect will be ignored.

A simple via is shown in Figure 1. The liquid outside the via is assumed to be well stirred and at a uniform concentration $c_b$. Inside the via, the concentration diminishes as the electrode is approached. Along with changes in the concentration, there are also changes in the electric potential. The potential rapidly rises from a value of zero at the cathode, called the inner Helmholtz plane, to some value at the outer Helmholtz plane. The Helmholtz layer is about a molecule thick.[4] Under this model, the potential in the well-stirred bulk is a constant.[5] Because of the large ionic strength of the electrolyte, the electrostatic double layer is in collapsed form and can be ignored. Thus the potential in the via is governed by the Laplace equation.[6] Reaction takes place at the outer Helmholtz layer.[4,7] For electrodeposition of copper at the cathode from the copper sulfate solution, the kinetics following elementary reaction is

$$r_{\mathrm{Cu}^{++}} = k_c e^{\beta U} c_{\mathrm{Cu}^{++}} - k_a e^{-(1-\beta)U} \tag{1}$$

where $k_c$ and $k_a$ are the rate constants for the cathodic (forward) and anodic (backward) reactions, respectively, and $\beta$ is the transfer number, usually around 0.5. The backward reaction arises from dissolution of copper cathode. $U$ is the dimensionless potential at the outer Helmholtz plane.

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The interest here lies in obtaining a description of how the thickness of deposited copper varies with time. The reason is that because the mouth of the via is narrow, the electrodeposition on the shoulders could close the mouth before the bottom moved up. Solving such a moving boundary problem with a "free" surface is difficult. Two special cases are considered. In the first, the transport is assumed to be diffusion controlled. In that case the interfacial concentration of the reactant is zero. Because the reaction rate is not evaluated, it is not necessary to calculate the electric potentials. In the second case, the transport is assumed to be reaction controlled. It should be mentioned here that the problem of trench-filling (and in greater details than considered here) was previously analyzed numerically by Georgiadou et al.[8] The solutions are restricted with deposition rates used as a parameter. The numerical nature of the solution makes it difficult to compare reaction rates to diffusion rates. Their goal was to study the effects of additives (discussed in the last section) along with the newer insight gained from the present work.

As a first approximation, the cavity in the via is such that the deposit reduces the half-width from $B$ to $\xi$ and the depth from $D$ to $z_0$. Under quasi-static conditions, the concentration satisfies $\nabla^2 c \cong 0$. For the diffusion limited system, the solution is

$$c = \frac{4c_b}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\cos(q_n x)[\cosh(q_n z) - \coth(q_n z_0)\sinh(q_n z)] \quad (2)$$

where $q_n = (2n + 1)\pi/(2\xi)$. An important feature here is that $\xi(z, t)$ is being assumed to be a constant, as is $z_0(t)$. Equation 2 can be simplified further. There is one part that is an even function of $x$, which is multiplied by a function of $z$ that drops to zero at $z_0$. A polynomial approximation is

$$c = c_b\left(1 - \frac{z}{z_0}\right)\left[1 - \left(\frac{x}{\xi}\right)^2\right] \quad (3)$$

which, although it preserves the basic effects (and much of the boundary conditions), does not satisfy the conservation of species equation all that well. More features can be brought in to make the approximation look better[9] but Eq. 3 is adequate

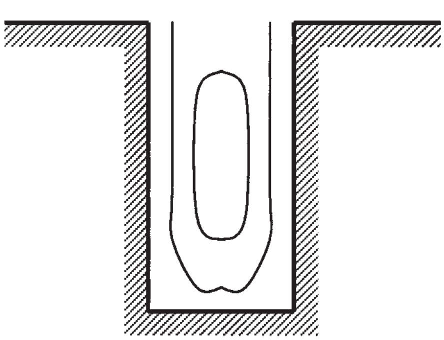

**Figure 1. View of how the deposited layer increases with time to capture a bubble inside a trench.**

The surface of the trench is the cathode.

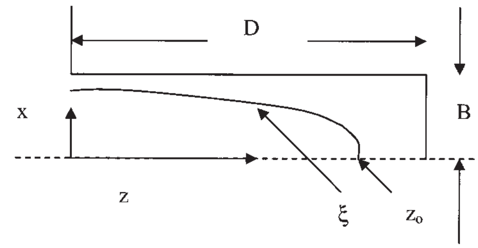


**Figure 2. Coordinate system used.**

The trench is shown as horizontal. Half of the trench is shown. The mouth is to the left.

for the present purposes. Later (and iteratively) the variations in $\xi$ and $z_0$ will be accounted for. In particular, the condition that $\partial\xi/\partial z = -\infty$ at $z = z_0$ will be used. The bounding surfaces described by $\xi(z, t)$ and $z_0(t)$ are shown in Figure 2. For a reaction limited system, the solution is simple: $c = c_b$. It will be assumed that the potential is also uniform and equal to that in the bulk. This assumption is less easy to justify, but is made as a necessary simplification.

## Diffusion-Controlled Transport

The concentration at the interface is $c_i = 0$. The unit normal to the surface is written as

$$\mathbf{n} = \frac{1}{\alpha}\mathbf{e_x} - \frac{1}{\alpha}\frac{\partial\xi}{\partial z}\mathbf{e_z} \quad (4)$$

where $\alpha = \sqrt{1 + (\partial\xi/\partial z)^2}$ and $\mathbf{e_x}$ and $\mathbf{e_z}$ are unit vectors in the $x$- and $z$- directions. Using Eq. 3

$$\mathbf{n}\cdot\nabla c|_{x=\xi} = -\frac{2c_b\alpha}{\xi}\left(1 - \frac{z}{z_0}\right) \quad (5)$$

is obtained. The jump species balance at the interface is

$$c_0\left(-\frac{1}{\alpha}\frac{\partial\xi}{\partial t}\right) = c_i\left(\mathbf{n}\cdot\mathbf{v} - \frac{1}{\alpha}\frac{\partial\xi}{\partial t}\right) - D\mathbf{n}\cdot\nabla c|_\xi \quad (6)$$

where $c_0$ is the concentration of the deposit, $c_i$ is the concentration of $Cu^{++}$, $\mathbf{v}$ is the velocity in the liquid phase, and $D$ is the diffusivity of $Cu^{++}$. Substituting Eq. 5 into Eq. 6 and setting $c_i$ to zero, leads to

$$\frac{\partial\xi}{\partial t} = -\frac{2Dc_b\alpha^2}{\xi c_0}\left(1 - \frac{z}{z_0}\right) \quad (7)$$

Near the entrance, it is assumed that $|\partial\xi/\partial z| \ll 1$, by reason of which $\alpha \approx 1$, and that $z \ll z_0$. This leads to

$$\xi\frac{\partial\xi}{\partial t} = -\frac{2Dc_b}{c_0} \quad (8)$$

and on integration to

$$\xi^2 = B^2 - \frac{4Dc_b}{c_0} t \tag{9}$$

near the entrance. Near the bottom of the via, $|\partial\xi/\partial z|$ is very large and thus $\alpha^2 \approx (\partial\xi/\partial z)^2$. As $z \rightarrow z_0$ and $\xi \rightarrow 0$, the zero-over-zero term

$$\frac{\left(1 - \frac{z}{z_0}\right)}{\xi} \approx -\frac{1}{z_0}\frac{\partial z}{\partial \xi}$$

using L'Hospital rule. Finally, the chain rule that

$$\frac{\partial \xi}{\partial t} = -\frac{\partial \xi}{\partial z}\frac{dz_0}{dt}$$

can be used. When these results are substituted into Eq. 7

$$z_0 \frac{dz_0}{dt} = -\frac{2Dc_b}{c_0} \tag{10}$$

is obtained, which on integration, leads to

$$z_0^2 = D^2 - \frac{4Dc_b}{c_0} t \tag{11}$$

A comparison of Eqs. 9 and 11 shows that the via mouth closes faster than the time taken for the bottom to rise to the top, and thus a bubble will be captured.

The nonlinear equation, Eq. 7, is difficult to solve. It is assumed that the slopes $|\partial\xi/\partial z|$ are small, and thus $\alpha \approx 1$. This reduces the order of the equation in $z$ by one and the resulting equation

$$\frac{\partial \xi}{\partial t} = -\frac{2Dc_b}{\xi c_0}\left(1 - \frac{z}{z_0}\right) \tag{12}$$

cannot satisfy the boundary condition that $\xi = 0$ at $z = z_0$, but can satisfy the initial condition that $\xi = B$ at $t = 0$. Using Eq. 11 in Eq. 12 and integrating

$$\frac{\xi}{B} = \left\{1 - \left(\frac{D}{B}\right)^2\left[T + 2\frac{z}{D}\left(\frac{z_0}{D} - 1\right)\right]\right\}^{1/2} \tag{13}$$

and

$$\frac{z_0}{D} = (1 - T)^{1/2} \tag{14}$$

result, where $T = (4Dc_b/c_0)t$. By using Eq. 14 it is possible to define a dimensionless time at $z_0 = 0$, that is, when the bottom reaches the top, as

$$T_D = 1 \tag{15}$$

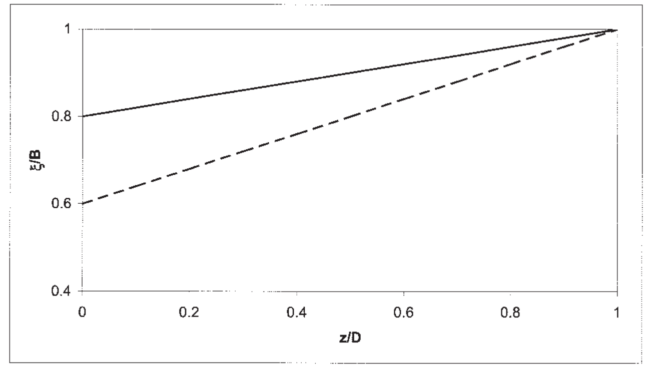


**Figure 3. Solution given by Eq. 12 is shown for $T = 1 \times 10^{-3}$ (dashed) and $T = 0.5 \times 10^{-3}$ (bold).**

The profiles look exactly like the only case shown by Georgiadou et al.,[8] which has no additive (their Figure 7c).

Equation 13 can be used to define a dimensionless time when the mouth $z = 0$, closes, that is, $\xi = 0$, as

$$T_B = \left(\frac{B}{D}\right)^2 \tag{16}$$

Obviously $T_B \ll T_D$ when $B \ll D$. That is, the mouth will close and the via will envelop a bubble. For $B/D = 1/20$, $T_B = 2.5 \times 10^{-3}$ and the value of $z_0/D = 0.9987$ at that time. That is, the bottom has hardly moved when the mouth closes. For this $B/D$, Figure 3 shows the deposit thicknesses at two different times.

Of course, the solution is not valid near the bottom where $|\partial\xi/\partial z|$ is large. In that case, in Eq. 7

$$\alpha \approx \left(\frac{\partial \xi}{\partial z}\right)^2 \quad \text{and} \quad \frac{\left(1 - \frac{z}{z_0}\right)}{\xi} \approx -\frac{1}{z_0}\frac{\partial z}{\partial \xi}$$

leading to

$$\frac{\partial \xi}{\partial t} = \frac{2Dc_b}{c_0 z_0}\frac{\partial \xi}{\partial z} \tag{17}$$

Defining

$$p = \frac{2Dc_b}{c_0}\int \frac{dt}{z_0}$$

Equation 17 becomes a wave equation for $z$ and $p$, leading to the solution

$$\frac{\xi}{B} = f(z + p) \tag{18}$$

where $f$ is an unknown function and $p$ works out to be $-z_0$. Initially $\xi$ is a step function, leading to the evaluation of $f$. The solution becomes

$$\frac{\xi}{B} = 1 - H(z - z_0) \tag{19}$$

where $H$ is the Heaviside step function, zero for negative arguments and one for positive arguments. The abrupt break between the solutions given by Eqs. 13 and 19 shows that it will be very difficult to match the two solutions using asymptotic analyses.[10]

## Reaction-Controlled Transport

In this case $c = c_b$ and $c_i = c_b$ and the potential is a constant. Consequently, the rate of deposition will be constant on the walls and the empty space will be driven out in the same instance, leaving behind a suture (shown in Figure 4). However, some complicating features may exist. For the present purposes, the reaction rate given by Eq. 1 is simplified to the form of $kc_b$. Now, according to some researchers,[5,11] the reaction rate is influenced by the curvature of the reacting surface

$$k = k_0 e^{2H\gamma/c_0RT} \tag{20}$$

where $H$ is the mean curvature and $\gamma$ is the surface tension. When the surface is convex outward, $H$ is negative and Eq. 20 demonstrates that the reaction rate is lowered. Conversely, the reaction rate is increased in the pits. This is the familiar action of leveling by surface tension. Because of surface tension, the pressure on one side of the interface is different from the pressure on the other side by $2H\gamma$, the Laplace pressure. The term in the exponential in Eq. 20 is simply the work done against this pressure during electrodeposition (over $RT$). Consequently, no sharp corners (infinite curvature) will exist. As a result, the deposit will look like that shown in Figure 5.

On the flat sides, the profile is given by

$$\xi = B - \frac{k_0 c_b}{c_0} t \tag{21}$$

Equation 21 can be used to obtain the time to close the mouth as $t_B = Bc_0/k_0c_b$. The radius of curvature of the base is $\xi$, and thus the bottom rises as

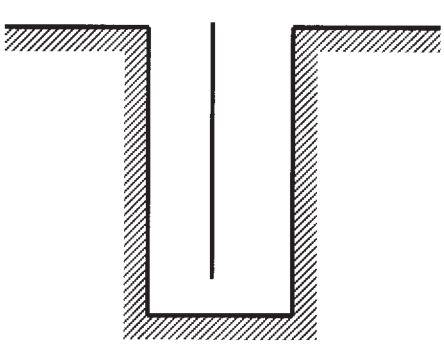

**Figure 4. View of reaction-controlled case at completion.**

The suture where the vacancy closes is shown.

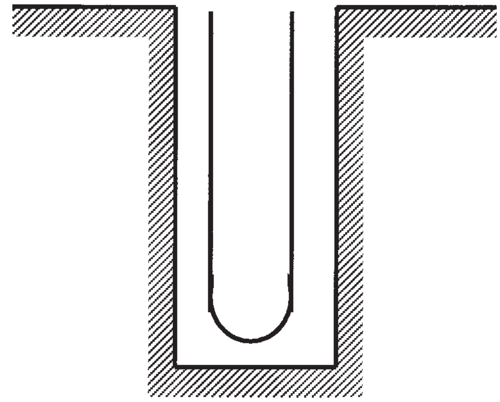

**Figure 5. View of the deposit when the system is kinetically controlled.**

$$\frac{dz_0}{dt} = -\frac{kc_b}{c_0} = -\frac{k_0 c_b \exp\left\langle 2\gamma \middle/ \left\{ c_0 RT \left[ B - \left(\frac{k_0 c_b}{c_0}\right) t \right] \right\} \right\rangle}{c_0} \tag{22}$$

where the mean curvature $H = 1/\xi$ has been used. Nondimensionalization and integration of Eq. 22 lead to

$$\frac{z_0}{B} = \frac{D}{B} - \int_0^T e^{E/(1-T)} dT \tag{23}$$

where $E = 2\gamma/c_0RTB$ and $T = t/t_B$. The time taken for the bottom to reach the top $T = T_D$ is given by

$$\int_0^{T_D} e^{E/(1-T)} dT = \frac{D}{B} \tag{24}$$

Because the integrant reaches a singularity at $T = 1$, it follows that $T_D < 1$ where $T_B = 1$. For small values of $E$, the integrant can be linearized to obtain

$$T_D - E \ln(1 - T_D) = \frac{D}{B} \tag{25}$$

The results also indicate that the bottom reaches the top before the sides close down.

## Results and Discussion

It appears from the previous sections that a bubble will always be trapped when diffusion is rate controlling. In contrast, no bubbles can be trapped if the system is kinetically controlled. This difference cannot be observed in the numerical solutions by Georiadou et al.[8] because they use deposition rate as a parameter with values that are sufficiently high that appear to keep the system in the diffusion-controlled regime. The kinetically controlled system will be observed only at low currents, which imply low deposition rates—and low deposition rates lower production. Even the diffusion-limited region that shows higher deposition rates gives rise to production rates that are still too small. As a result, the suggestion made by Georiadou et al.[8] of eliminating bubbles by using a surface active additive, although feasible, may not be the best solution. In their method, bubbles are eliminated by decreasing the deposition rates near the entrance. This slows the overall deposition rates below the diffusion-limited case. It is possible to understand the effect of the additive as a move toward a kinetically controlled process, which has been shown here as one where bubbles are not captured. In general, it is necessary to increase the deposition rates even beyond diffusion-controlled rates, and not capture bubbles.

There is one other effect not considered so far, that of natural convection. This is sometimes reported in electrodeposition and Nilson and Griffiths[12] mention relevant literature in their work. In Figure 1, it can be imagined that the concentration of copper sulfate is highest at the mouth and about zero at the bottom. It is also assumed that gravity is pointed downward. For a 2 M copper sulfate solution, it leads to a specific gravity of 1.17 at the mouth and 1.0 at the base. This gives rise to the buoyancy forces that drive the natural convection. Wooding[13] has shown that for natural convection to start in a capillary tube, the Rayleigh number must exceed a critical value. In simplified form, his result is

$$\frac{gb^4}{D\mu}\left(-\frac{\partial\rho}{\partial z}\right) > 67.9 \tag{26}$$

where $g$ is the acceleration arising from gravity, $b$ is the radius of the capillary, $D$ is the diffusivity of the solute, and $\mu$ is the viscosity of the solution. Using equivalent radius for the two parallel plates considered here, $b = 4B$. For $D = 10^{-5}$ cm$^2$/s, $\mu = 10^{-3}$ Pa·s, and $-\partial\rho/\partial z \cong 0.17/z_0$, one has $B^4/z_0 < 2.65 \times 10^{-8}$ cm$^3$. For $B = 25$ $\mu$m it implies $z_0 < 14.7$ $\mu$m and for $B = 10$ $\mu$m, $z_0 < 0.4$ $\mu$m for natural convection to appear. That is, in neither case is $z_0$ deep enough to be near $D$.

As apparent, the point behind examining natural convection is that once it starts, the role of diffusion is greatly reduced and high currents are obtained. Nilson and Griffiths[12] have shown in their calculations that natural convection leads to very high rates of mass transfer and deposition. Unfortunately, the available density gradients are not sufficiently high to start natural convection. As the via narrows, natural convection becomes less probable altogether. Although the calculations presented here are very approximate in some aspects and exaggerated in others, the basic idea that the natural convection fails seems reasonable nonetheless. The concept of natural convection is both important and intriguing, however, and one that will not occur at all in chemical vapor deposition (CVD) where bubbles are more easily trapped. Success at inducing it during the filling process, such as through heat of reaction or electric field, would have important consequences.

In effect it has been shown here why bubbles can become trapped in a quantitative manner. It is seen that the knowledge of the mechanism can help to provide solutions to prevent bubble formation, even though the suggested solution to the problem has not yet been fully developed.

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