Publication P1


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A microvia-fill model is formulated for control-design purposes of the via-fill process in 100 μm scale. The formulas required to model a Cu–Cu-electrode electroplating system with generic additive-type chemicals in both single-directional and bidirectional processes are given in detail. The model relies on principles familiar from a submicrometer-scale via-filling model known as the curvature-enhanced accelerator accumulation model. Additive coverage is modeled based on a simplified method based on local surface-area computation and an analytical formula for surfactant coverage is given. A galvanostatic control law that does not require computing cell voltage is derived. The model also considers the Cu(II)-ion activity vs Cu(II)-ion concentration. A finite element method-based implementation, applying the arbitrary Lagrange–Eulerian method to compute geometry changes, is tested and compared to via-fill experiment results.

A Method for Microvia-Fill Process Modeling in a Cu Plating System with Additives

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The damascene electroplating process for creating copper interconnections on microchips has been known and industrially applied for about a decade now.\(^1\) Important characteristics of this process are suppressed growth on the planar chip surface and the so-called bottom-up fill of nanometer-scale chip features.

The mentioned characteristics are also observed in the process of microvia filling by electroplating, applied in the printed circuit board (PCB) industry. Interstitial interconnects are made on multilayered PCBs by first drilling holes on an individual board layer and then filling these holes with copper by applying the via-fill electroplating process.

Deposit growth suppression is generally obtained by adding suppressor additives, typically large-sized polymer molecules in combination with chloride ions, to the electrolyte.\(^2\) Superconformal fill and bump formation above the electroplated features occurs when so-called accelerator additives are used.\(^3\) Instead of being controlled by the applied plating voltage, due to using additive chemicals, the copper plating process becomes at least partially, if not fully, controlled by chemical phenomena occurring on the surface being plated. These chemical phenomena are additive-consuming reactions as well as adsorption and desorption of the additive chemicals, and modeling the originally purely electrochemical system relies partially on also modeling the additive chemical behavior.

There are studies in which information of the incorporations of additives into the copper deposit\(^3,4\) as well as negligible incorporation of additives.\(^5\) Also, chemical consumption of additives on the cathode in a nickel-plating process has been reported.\(^5\) In any case, models and theories that explain levelling by additives rely on the suppressing species being somehow consumed on the cathode.\(^1,7,8\) Consumption of the inhibiting species results in a steady-state mass flux to the cathode, causing the inhibitor concentration to be higher on the planar surface, which in turn manifests as more suppressed deposition outside the features than inside them.

The accelerator chemicals by some means negate the effect of the suppressing additives. In Ref. 2 it is reported that the accelerator species replaces the adsorbed inhibitor complex, causing the suppressing effect to thus be nullified at these sites. Studies show that incorporation of sulfur-containing accelerator species occurs but is negligible.\(^9,10\) though other reports have also been published.\(^11,12\)

Hence, while the suppressing species is assumed to be markedly consumed at the cathode (resulting in diffusion-limited mass transfer), the accelerating species is assumed to mainly remain segregated at the cathode surface. This phenomenon, combined with the accelerator’s capability to replace the suppressing species, where competitively present, leads to accelerator accumulation at regions where the surface shrinks. The mechanism for superfill relying on the aforementioned principles is entitled the curvature-enhanced accelerator coverage (CEAC) mechanism.\(^13\)

Several models for submicrometer-scale processes relying on diffusion-limited mass transfer of additives, variation in adsorption rate of additives, and the CEAC mechanism have been published, among others by Andricacos et al., Moffat et al., and Cao et al.\(^1,14-16\) However, the models in these reports disregard some effects important for the electrode current-density model, such as the effect of activity of reduced species, and they do not reveal explicitly what potential terms are discussed in which occasion. Further, the concept of an adsorbed accelerator’s coverage and the coverage dependence of cathode surface movement, additive flux, and additive bulk concentration is left unspecified; the required equations are not given.

This paper elucidates these points and presents a robust model created for use in industrial microvia-fill plating applications, where laboratory-level accuracy in conditions cannot be obtained and laboratory analyses cannot be continuously carried out. The computational implementation of this model relies on the finite element method (FEM) and applies the arbitrary Lagrange–Eulerian (ALE) method for implementing the moving domain geometry. The ALE method is versatile, well documented, and far simpler to apply in varying situations than many ad hoc methods. A computation method for local surface area is developed for implementing the CEAC effect. The model does not rely on any specific additive reaction mechanisms or additive compound data but only models additives based on their eventual effect on the via-fill process. This is because in practical applications, process operators seldom have the needed information of the additives’ chemical composition. The system is operated under continuous galvanostatic control and plating time is the primary operating parameter.

A set of data relevant to our case study is represented in this paper.

The Electrode Reaction Model

The industrial system considered in this paper consists of two copper electrodes; the plated board, acting as cathode, is from the start copper coated, and metallic copper pellets, acting as anode, create the source for copper. The electrochemical reaction occurring in opposing directions on both electrodes is the copper reduction-oxidation reaction

\[ \text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu} \quad [1] \]

The system is a dc-plating system, thus the polarity of the copper electrodes always stays the same. Therefore, the analytical treatment of the electrodes can be simplified by, instead of always considering the board to be plated and the copper metal pellets as electrodes, considering only the cathode and anode, correspondingly. The current density \( i \) corresponding to the reaction rate of Eq. 1 at each electrode can be expressed with the Butler–Volmer equation

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In Eq. 2, the subscript e denotes the electrode in question (a = anode, c = cathode) and the a and c subscripts already in Eq. 2 denote whether the term refers to the anodic or cathodic subpro-
tession set value in the apparatus' galvanostatic control system, we
denoted previously in the text. The anodic current density included in the estimate to match concentration and activity at
dropped. The scheme of copper pellets used for the cathode is given by the Nernst equation

\[ E_{\text{Cu}} = \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}^+}}{a_{\text{Cu}}} \right) \]

And the deposition process is driven by an external voltage source (dc) whose electromotive force is denoted by \( E \). The individual electrodes' potentials (in reference to a reference potential) are denoted by \( \Phi_e \), and their difference equals \( E \).

\[ \Phi_a - \Phi_c = E \]  

(3)

Equation 4 and 5 are applied to calculate electrode over-
potentials and concentration effects. The reaction of copper ions in Eq. 9 is denoted as the reaction potential.

\[ i_c = -i_{\text{c,a}} R_A \left( \frac{a_{\text{Cu}^+}}{a_{\text{Cu}}} \right) e^{-k_A I_A} \]

(9)

The aforementioned two current densities (Eq. 6 and 7) are coupled by the electrode areas, \( A_a \) and \( A_c \) (m²), and total current flowing through the circuit \( I = I_A \) (amperes) as in Eq. 8

\[ i_{\text{c,a}} + i_{\text{c,c}} = 0 \]  

(8)

In order to further simplify the analysis, we assume that the apparent transfer coefficients and exchange current densities on each electrode are equal (\( \alpha_{\text{c,a}} = \alpha_{\text{c,c}} = \alpha_a \), \( \alpha_{\text{a,a}} = \alpha_{\text{a,c}} = \alpha_c \), and \( i_{\text{c,0}} = i_{\text{c,0,a}} = i_c \)). This is justified because the parameters mentioned correspond to the charge-transfer reaction in question, which on both electrodes is essentially the same. Further, the standard equilibrium potentials of reactions occurring on the anode and cathode are also assumed to be equal (but opposite signed) for the same reason \( \Phi_{\text{c,a}} = \Phi_{\text{c,c}} = \Phi_{\text{eq}} \). It is not clear how strongly differences in surface morphology impair the assumption validity.

Now, by applying Eq. 4 and 5 when calculating electrode over-
potentials (\( \Phi_e \)), formulating electrode potentials (\( \Phi \)) in terms of over-
potentials and \( E \), and then substituting these into Eq. 6 and 7 and further these into Eq. 8, we obtain an approximation for the cathode current density. Note, \( \beta = \alpha_a a_a / (\alpha_c + \alpha_a) \)
tration is denoted $c_{Cu}^{b}$, and this value is also used as the cupric ion concentration on the anode in Eq. 10

$$
\mu_{Cu} = \frac{a_{c} - a_{a}}{a_{a}} = \frac{c_{Cu}^{b}}{c_{Cu}^{a}} \left( \frac{c_{Cu}^{b} + c_{Cu}^{a}}{c_{Cu}^{a}} \right) ^{0.5554}
$$

[10]

This term corresponds to the increased overpotential requirement (inflicted via altered reaction equilibrium potential) as the Cu(II)-ion concentration on the electrode surface decreases during deposition.

The $i_{c}$ approximation (Eq. 9) works well for large applied voltages $E$. However, when the cell voltage approaches zero, Eq. 9 differs significantly from the original two-directional equation (Eq. 2). The $i_{c}$ approximation can be improved by assuming a symmetric system, i.e., estimating that the copper-pellet anode behaves as cathode similarly as the plated PCB and vice versa for the PCB as anode. This assumption yields the two-directional $i_{c}$ approximation

$$
i_{c} = -2i_{0}(k_{a} \mu_{a} A_{n}^{\alpha} \mu_{Cu}^{b} \sinh(k_{b}H))
$$

[11]

The galvanostatic control law is implemented by setting $i_{c} = i_{target}$ and solving $H$, which yields

$$
H = \frac{1}{k_{b}} \sinh^{-1}\left( \frac{i_{target}}{2i_{0}(k_{a} \mu_{a} A_{n}^{\alpha} \mu_{Cu}^{b})} \right)
$$

[12]

$H$ is the driving force for the electrode reactions and connects the control-system current-density set value with local cathode current density without the need to model the cell voltage $E$ as such. $E$ is, however, easily obtainable as $H + U_{Q}$ when the apparatus dimensions and electrolyte composition are known. When computing the model, the value of the denominator inside sinh$^{-1}$ is measured on the level PCB surface, which corresponds to the majority (>99%) of the surface area on the cathode. In the following, the chemical terms $\mu_{a}$ and $\mu_{Cu}$ are discussed.

**Additive Chemistry**

The electrode equation (Eq. 11) contains terms that depict effects of surface chemical phenomena on the electrodes. These effects are brought to the system by additive chemicals added to the electrolyte, in order to improve superform fill characteristics of the process. The effects are local in microscopic scale, altering dramatically the local current density within the microvia, around its mouth, and on the level board surface, compared to the situation without additives.

Though it is clear that these chemicals affect both the anode and cathode of the electrolysis apparatus, most of their influence on the copper deposition reaction comes via the cathode, where the deposition of copper takes place. Therefore, we initially assume that no significant surface chemical effects are brought to the system through the anode and denote $\mu_{a} = 1$.

On the cathode, $\mu_{Cu}$ must contain effects of all additives included in the bath, which typically are of at least two kinds, (i) a suppressor, decreasing the current density everywhere on the cathode and (ii) a suppressor-negating, and therefore deposition “enhancing,” surface deformation-dependent additive, which affects sites where the local cathode surface shrinks or expands.

In addition to (i) and (ii), there often is a halide, typically chloride, added to the solution. In this paper, the halide additive is considered to influence the reduction reaction jointly with either of the additives (as presented, e.g., in Ref. 18 and 19), and therefore its specific investigation is omitted.

The additives (i) and (ii) are called the suppressor, denoted with the subscript Supp, and the accelerator, denoted with the subscript Acc.

The additives’ effect is assumed to be based on a simple interrelation mechanism. In this mechanism the suppressor additive is assumed to attach rather weakly on the cathode surface and therefore its effect can be negated by the accelerator additive, which is assumed to have a stronger bond with the cathode surface. Further, the accelerator additive’s strong attachment to the cathode surface is assumed to lead to the CEAC effect. These assumptions correspond to the physical and chemical adsorption and reaction phenomena, currently considered as the basis for the copper-plating electrolyte additives’ affecting mechanisms and presented in, e.g., Ref. 20.

The mass-conservation law, formulated as Eq. 13 for additive $i$, is the basis for additive mass-transfer analysis on the cathode surface

$$
d(n_{i}^{a}) \frac{dt}{dt} = \int_{A} (N_{i}^{ads} - N_{i}^{des})dA
$$

[13]

Here $d/dt$ denotes a total derivative and $n_{i}^{a}$ is the amount (mol) of species $i$ (adsorbed) on a copper surface with area $A$. $N_{i}^{ads}$ is the adsorption flux of species $i$ from the electrolyte to the cathode surface (mol/m²s) and $N_{i}^{des}$ is the desorption flux of species $i$ (mol/m²s) from the same surface. Adsorption is considered to comprise all flux of species $i$ to the surface, whereas desorption includes all phenomena that remove surface-adsorbed species $i$ from the surface back to the solution. Applying Eq. 13 on a small surface area $A_{s} (m^{2})$ we get

$$
d(n_{i}^{a}) \frac{dt}{dt} = A_{s}(N_{i}^{ads} - N_{i}^{des})
$$

[14]

Assuming first-order reaction mechanisms behind adsorption and desorption, the total flux (Eq. 14) can be written in terms of species $i$’s surface concentration $\Gamma_{i}$ and area $A_{s} (n_{i}^{ads} = A_{s} \Gamma_{i})$. For the accelerator additive the equation becomes

$$
d(A_{s} \Gamma_{Acc}^{i}) \frac{dt}{dt} = A_{s}[k_{Acc}^{ads} \Gamma_{Acc}^{sat} - \Gamma_{Acc}^{i}] - k_{Acc}^{des} \Gamma_{Acc}^{i}
$$

[15]

and for the suppressor additive$^{20,21}$

$$
\frac{d(A_{s} \Gamma_{Supp}^{i})}{dt} = A_{s}[k_{Supp}^{ads} \Gamma_{Supp}^{sat} - \Gamma_{Supp}^{i}] - k_{Supp}^{des} \Gamma_{Supp}^{i}
$$

[16]

The $\Gamma_{i}$ and $\Gamma_{i}^{sat}$ are the surface concentration of species $i$ and its surface concentration at saturation (mol/m²). $c_{i}$ is the species’ molar concentration (mol/m³) in the cathode surface vicinity, $k_{Acc}^{ads}$ and $k_{Acc}^{des}$ are (reaction) rate coefficients for adsorption and desorption of species $i$ (mol/m²s, 1/s).

Equations 15 and 16 elucidate the relationship between the suppressor and accelerator. In essence, a surface-adsorbed suppressor species can be displaced by an accelerator species residing close to the copper surface, but the opposite is not possible.

The derivative of $d(A_{s} \Gamma_{i})/dt$ can be expanded as a Stokes derivative, as in

$$
\frac{d(A_{s} \Gamma_{i})}{dt} = \frac{\partial(A_{s} \Gamma_{i})}{\partial t} + \gamma_{i} \cdot \nabla(A_{s} \Gamma_{i})
$$

[17]

where $\gamma_{i}$ is the surface velocity. The layer of surface-adsorbed species tends to move identically to the surface itself, as long as compression of adsorbed species does not force the adsorbed layer to diverge from the metal surface.

The derivatives in Eq. 17 essentially represent the equation of continuity for a compressible fluid, where the surface-adsorbed additive species is considered as the fluid and, as said, the equation is based on the law of mass conservation. The same phenomenon can also be described in terms of density, which in this case is surface concentration, simplifying the expression somewhat to

$$
\frac{d\rho_{i}}{dt} + \Gamma_{i} \cdot \nabla \gamma_{i} = \gamma_{i} \cdot \nabla \Gamma_{i}
$$

[18]

Computationally, the derivatives on the surface in Eq. 18 are problematic due to numeric instability. In order to model the mass balance on the cathode surface and to couple it with mass-transfer
phenomena in the stagnant diffusion layer, it is useful to approximate the surface-concentration behavior based on the species' volumetric concentration in the electrolyte very close to the surface. This can be done by solving $\Gamma_i$ from the flux equations by applying the following ideas.

**Balance between adsorption and desorption.**—The balance between adsorption and desorption of additive species is reported to be reached within seconds to hundreds of seconds.\(^5\) Even at the slowest reported values, the adsorption-desorption phenomenon can be considered fast in respect to the microvia-fill process (often lasting over an hour). Therefore, the assumption that adsorption and desorption are always in balance during the process is justified.

**Consumption of suppressing species on cathode.**—Based on measurements (Table V, Ref. 22) it is clear that both additives are somehow consumed during the plating process. It was also observed at the case-process that the anode material has a significant effect on the accelerator additive consumption; (but not on the suppressor additive consumption): using an insoluble anode material can up to double accelerator consumption in the plating bath. In studies it is also reported that chemicals commonly applied as accelerators in copper plating baths have the ability to not be consumed on or to not be incorporated into the copper deposit but remain segregated and floating on the copper surface.\(^2\) This allows for the following assumptions: (i) the suppressor species is consumed on the cathode surface and therefore there exists a mass flux of suppressor from the bulk to the cathode, and (ii) the accelerator is not significantly consumed on the cathode surface (but somewhere else).

The balance assumption of adsorption and desorption fluxes does not, however, mean that their difference equals the flux that removes the species from the system, $N_i$. Thus we denote

$$N_i^{\text{ads}} - N_i^{\text{des}} = N_i$$

For convenience it is useful to introduce the term proportional surface coverage denoted with $\theta_i$, where $\theta_i = \Gamma_i/\Gamma_i^{\text{sat}}$ and $\theta_i = 1$. Also, the notion $\hat{k}_i = k_i^{\text{add}}/k_i^{\text{des}}$ is used from here on. Then we simplify the equations containing surface concentration as follows.

First, the accelerator flux over the cathode boundary is concluded to be negligible, $N_{\text{Acc}} = 0$, which enables solving $\theta_{\text{Acc}}$ from Eq. 15. The zero-flux conclusion also means that the surface coverage of the accelerator on the cathode can be approximated by a constant ($\theta_{\text{Acc}}$) that is a function of accelerator bulk-solution concentration

$$\theta_{\text{Acc}} = \frac{\hat{k}_{\text{Acc}}^{\text{b}}}{\hat{k}_{\text{Acc}}^{\text{c}} + 1}$$

Second, due to consumption, the net flux of the suppressor species at the cathode must be away from the solution, and by assuming a first-order reaction for suppressor consumption, the suppressor flux can be simplified as

$$N_{\text{Supp}} = \hat{k}_{\text{Supp}} \frac{A_0}{A_i}$$

However, as described in Eq. 16 and mentioned in Ref. 23, the accelerator has the ability to displace suppressor species from and remain segregated on the cathode surface, and these must be accounted for in the model equations. The second ability results in accumulation of the accelerator species where the cathode surface diminishes locally (and dilution where surface expands, correspondingly). This phenomenon, combined with the ability of the accelerator to remove the suppressor species from the cathode surface when both are present, can be implemented in the model, so that the suppressor consumption flux is increased where the accelerator accumulates due to locally diminishing surface area. Chemically, this would correspond to the situation where the displacement of the suppressor species by the accelerator species produces decomposed suppressor debris that cannot affect anymore and is thus consumed and that the suppressor is only consumed through a mechanism like this. In the computational model, this phenomenon can be accounted for by complementing the $N_{\text{Supp}}$ term with the change of local cathode area, $A_i$, relative to the same local area initially, $A_i^0$, yielding

$$N_{\text{Supp}} = \hat{k}_{\text{Supp}} \frac{A_0}{A_i}$$

This formulation is also mathematically in correspondence with Eq. 18, where the surface velocity derivatives are essentially another form of expressing the local surface-area change. Now by denoting the suppressor flux over the cathode boundary equal to the mass balance on the cathode surface, we can solve the suppressor surface concentration in terms of its volumetric concentration in the electrolyte close to the cathode from Ref. 23

$$\hat{k}_{\text{Supp}} \frac{A_0}{A_i} = \hat{k}_{\text{Supp}} \frac{\Gamma_{\text{Supp}} - \Gamma_{\text{Supp}}^{\text{sat}}}{\Gamma_{\text{Acc}}^{\text{sat}} - \Gamma_{\text{Acc}}} = k_{\text{Supp}} \Gamma_{\text{Supp}}$$

As described in Eq. 11, the cathode current density is proportional to the cathodic chemical term $\mu_c$, which here is actually assigned the complement of $\theta_{\text{Supp}}$. Hence, $\mu_c = 1 - \theta_{\text{Supp}}$, yielding

$$\mu_c = 1 - \frac{k_{\text{Supp}} \Gamma_{\text{Supp}}}{1 + k_{\text{Supp}} \frac{A_0}{A_i} \frac{\hat{k}_{\text{Supp}}}{\hat{k}_{\text{Supp}}^{\text{c}}}}$$

Equations 24 and 11 show explicitly what factors the cathode current density depends on.

**Computational Implementation**

In addition to the cathode current and the additive chemical effects, there are two more phenomena related to the problem that introduce equations to be solved in both time and space: (i) the electric field equation and (ii) mass transfer of species. The modeling domain is selected as the stagnant diffusion layer, within one via diameter toward all directions from the via mouth. The domain is assumed to be radially symmetric (around the via center axis) and thus modeling is done only in two dimensions, denoted with $x$ (or $X$) and $y$ (or $Y$).

The electric field intensity $\phi$ in the model domain satisfies the Laplace equation

$$-\nabla \cdot \sigma \nabla \phi = 0$$

where $\sigma$ is a function of the concentration of the main charge carriers, that are the $\text{Cu}^{2+}$, $\text{HSO}_4^-$, $\text{SO}_4^{2-}$, and $\text{H}^+$ ions, according to Eq. 26

$$\sigma = \frac{\mu^2}{RT} \sum_i c_i \chi_i D_{\text{f},i}$$

The electroneutrality condition can be fulfilled by means other than including it in the system of equations; (i) because hydrogen and hydrogen sulfate ions do not take part in reactions on the electrodes, their concentration stays constant over the domain, and (ii) approximating that the sulfate ion concentration accounts for electroneutrality required by copper-ion concentration changes enables using only the copper-ion concentration value to implement the electroneutrality condition where needed.

Values for diffusivities of nonreacting species are based on literature values and are kept constant in the domain. Cu(I) diffusivity is estimated using literature data and conductivity measurements. The diffusivity estimates for ionic species are initially based on conductivity data for binary, aqueous CuSO$_4$ and H$_2$SO$_4$ solutions found in Ref. 17. Then the initial estimates for each species are weighted with their diffusivities at infinite dilution and finally fitted with conductivity measurements done on the industrial plating electrolyte. For nonionic species the Einstein–Stokes and Wilke–Chang\(^2\) equations are applied, depending on the species’ assumed molecule size. The estimates obtained this way are given in Table II.
When computing the sulfate-ion contribution to $\sigma$, the Cu(II)-ion concentration is used instead of sulfate-ion concentration to account for electroneutrality effects. Further, bulk concentrations of HSO$_4^-$, SO$_4^{2-}$, and H$^+$ ions brought to the system by sulfuric acid are used.

Mass transfer of Cu(II) ions and suppressor molecules is considered to be nonconvective and thus the Nernst–Planck equation without electroneutrality is applied

$$-\frac{\partial c_i}{\partial t} = \nabla \cdot \left( D_i \nabla c_i + \frac{z_i F}{RT} D_i^c \nabla \phi \right)$$  \hspace{1cm} \text{[27]}

where $z_i$ is the electron number (no dim.) and $D_i$ the diffusivity (m$^2$/s) of species $i$.

**Boundaries.**—The modeling domain is restricted by four boundaries: (i) the diffusion layer-to-bulk solution boundary, (ii) the cathode boundary, and (iii) two symmetry boundaries, orthogonal to (i) and (ii).

Boundary conditions on these boundaries are set in order to solve the given partial-differential equations. As for Eq. 25, the electric-field-intensity equation, on the boundary toward the bulk solution (i) the electric potential is restricted to a value calculated based on bulk solution conductivity $\sigma$, the diffusive layer thickness $\delta$, and the requested plating current density target value $i_{\text{target}}$

$$\phi = \frac{\delta}{\sigma} i_{\text{target}}$$  \hspace{1cm} \text{[28]}

On the cathode (ii), the electric-field equation is restricted by the cathode current density

$$\mathbf{n} \cdot (-\sigma \nabla \phi) = i_c$$  \hspace{1cm} \text{[29]}

and on the symmetry boundaries (iii) the current density over them is set to zero

$$\mathbf{n} \cdot (-\sigma \nabla \phi) = 0$$  \hspace{1cm} \text{[30]}

Similar to Eq. 27, mass transfer, on the bulk solution boundary (i) the volumetric concentrations of species are set to equal their bulk concentrations

$$c_i = c_i^0$$  \hspace{1cm} \text{[31]}

On the cathode (ii) the species’ mass flux restricts the mass-transfer equation

$$\mathbf{n} \cdot (-D_i \nabla c_i) = N_i$$  \hspace{1cm} \text{[32]}

where $N_{Cu} = i_c z_{Cu} F$ and $N_{Supp} = \frac{\rho_{Supp}}{\rho_{Cu}} A_0/A_c$.

On the symmetry boundaries (iii) the net mass flux is set to zero

$$\mathbf{n} \cdot (-D_i \nabla c_i) = 0$$  \hspace{1cm} \text{[33]}

where $\mathbf{n}$ is the boundary normal vector.

**FEM and ALE.**—FEM is applied to solve the system of equations introduced. In order to implement the moving boundary and effects brought to the system by changing geometry, the ALE transformation is applied.

The number one weakness of the ALE method is, as commonly known, its inability to tolerate changes in model topology during model solution. However, compared to methods that do allow topology changes or do not need a changing mesh (i.e., some custom methods or, e.g., the level-set method), the ALE method is well documented and far more applicable when fast and diverse modifications of via geometry have to be enabled as products and manufacturing techniques change.

In order to compute the local area term $A_i$ in the moving coordinate system, an extra equation is defined on the cathode boundary. Assuming radial symmetry of the modeling domain and setting the via center in the origin, each cathode boundary mesh element can be thought to represent the cross section of a belllike zone around the via center. The area of this belt thus becomes $A_{belt} = 2\pi r \delta$, where $r$ is the mesh boundary element length and $\delta$ the coordinate orthogonal to the symmetry axis. The behavior of local area $A_i$ during model solution can be accurately described in the 2D-modeling domain by the belt area $A_{belt}$ when it is scaled with its initial value $A_i^0$. As $x$ is a part of the ALE system solution, only $l$ needs to be found and Eq. 34 is applied for that

$$l = \frac{1}{2} (\delta x / \delta X)^2 + (\delta y / \delta Y)^2$$  \hspace{1cm} \text{[34]}

where $l$ is the initial mesh element length $l$, $(t = 0)$, which can be set by the modeler. The upper-case $X$ and $Y$ refer to the fixed coordinate system and the lower-case symbols $x$ and $y$ to the moving coordinate system, both required by the ALE method.

The cathode boundary movement $v_c$ is governed by Faraday’s law

$$v_c \cdot \mathbf{n} = -i_c \frac{M_{Cu}}{z_{Cu} F \rho_{Cu}}$$  \hspace{1cm} \text{[35]}

$M_{Cu}$ and $\rho_{Cu}$ are the molar mass (mol/kg) and density (kg/m$^3$) of copper. The bulk-solution boundary movement is restricted to equal that of the level board surface on the cathode and board-directional movement of the symmetry boundaries is prohibited, but otherwise the mesh movement is left free.

**Experimental.**

Parameters for the model were obtained from the literature and estimated based on experiments. Linear cyclic voltammetry experiments were conducted to identify parameters for the electrode equation (Eq. 11). Typical results of three tests (conducted with different electrolyte composition) and curves fitted to the data are shown in Fig. 2. The nonlinear least-squares method was applied to fit the electrode equation to the data and the identified parameters corresponding to Fig. 2 are listed in Table III.

Via-filling tests were conducted to obtain coarse quantitative data of the process characteristics. These experiments were carried out in conditions corresponding well to the production operating condi-
Table III. Values obtained for the electrode equation (Eq. 11) parameters.

<table>
<thead>
<tr>
<th>Test</th>
<th>$i_0$ (A/m²)</th>
<th>$\alpha_s$</th>
<th>$\alpha_e$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>8.971</td>
<td>0.284</td>
<td>0.199</td>
<td>0.110</td>
</tr>
<tr>
<td>Test 2</td>
<td>8.987</td>
<td>0.281</td>
<td>0.180</td>
<td>0.110</td>
</tr>
<tr>
<td>Test 3</td>
<td>8.610</td>
<td>0.273</td>
<td>0.165</td>
<td>0.103</td>
</tr>
</tbody>
</table>

Table IV. Initial composition of electrolyte used in plating test.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄</td>
<td>0.814 mol/L</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>1.05 mol/L</td>
</tr>
<tr>
<td>HCl</td>
<td>1.3 mmol/L</td>
</tr>
<tr>
<td>Additive A</td>
<td>1.26 ml/L</td>
</tr>
<tr>
<td>Additive B</td>
<td>16.6 ml/L</td>
</tr>
</tbody>
</table>

Table V. Electrolyte additive composition before and after a 90 min continuous plating test.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fresh (ml/L)</th>
<th>Plated (ml/L)</th>
<th>Change (ml/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive A</td>
<td>1.26</td>
<td>0.81</td>
<td>-0.71 (-35.7%)</td>
</tr>
<tr>
<td>Additive B</td>
<td>16.6</td>
<td>15.5</td>
<td>-1.74 (-6.6%)</td>
</tr>
</tbody>
</table>

Other required parameters such as the adsorption, desorption, and other reaction-rate coefficients are listed in Table VII. Many of these parameters are of relative nature and thus an accurate absolute value for them is less important. However, further experiments are required to increase the accuracy of the model.

Discussion and Model Improvement Requirements

Several details remain to be improved in the model. The first observation is that the deposit growth in a real filling process initiates from and is significantly more rapid in the via bottom corners than what the model estimates. Another deficiency in the model is its inability to predict the long incubation period of the copper deposit in the exact center of the via. However, a part of the difference in via-center deposit growth between model and experiment is caused by differences in growth measurement points; when modeling, the growth is measured in the exact center of the via; and when experimenting, growth is measured on the edge of the cross-sectioned via and always in the point of least growth.

The equations and approximations applied to calculate additive fluxes ($N_{\text{Supp}}, N_{\text{Acc}}$) and their corresponding proportional coverage values ($\theta_{\text{Supp}}, \theta_{\text{Acc}}$) are certainly not final but require deep further inspection. Improving these are expected to aid also in reducing the first mentioned error between the model and experiments.

The additive chemical model presented above is versatile for two reasons. (i) It does not discuss the composition of the deposition suppressing or accelerating species. The chemicals can be either some specific single chemicals or complex compounds formed by,
phenomena based on the phenomena in the liquid very close to the surface. Further, the dynamics of surface phenomena can be included in the model this way. In further studies, the theoretical model can obviously be made markedly more specific, but for control system purposes, a robust ad-hoc model is more likely to be preferred.

Conclusions

A FEM model that exploits the computational abilities of the ALE method was developed for monitoring the microvia-filling process, within and outside the microvias. A simplified coupling between

![Figure 5](Color online) The copper-deposit-thickness output by model compared against measured values.

![Figure 6](Color online) The microvia growth profile at various time instants as output by the model.

Table VI. The symbols, values, and units of parameters whose value is determined by the operating conditions. The relative value of additive concentrations refers to equal of the optimum additive concentration recommended by the technology provider.

<table>
<thead>
<tr>
<th>Operational parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_a$</td>
<td>780</td>
<td>mol/m$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{Cu}$</td>
<td>1000</td>
<td>mol/m$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{H_{2}SO_{4}}$</td>
<td>1000</td>
<td>mol/m$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{HSO_{4}}$</td>
<td>780</td>
<td>mol/m$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{H}$</td>
<td>1000</td>
<td>mol/m$^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c_{Supp}$</td>
<td>1</td>
<td>mol/m$^3$</td>
<td>Relative value</td>
</tr>
<tr>
<td></td>
<td>$c_{Acc}$</td>
<td>1</td>
<td>mol/m$^3$</td>
<td>Relative value</td>
</tr>
<tr>
<td></td>
<td>$d_{c}$</td>
<td>0.3</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>2.35</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$I_{Input}$</td>
<td>183</td>
<td>A/m$^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T$</td>
<td>298</td>
<td>K</td>
<td></td>
</tr>
</tbody>
</table>

Table VII. The symbols, values, and units of parameters whose value is either obtained by experiments, estimated based on experimental and literature data, or by fitting the model output with experimental data.

<table>
<thead>
<tr>
<th>Modelling parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{Cu}$</td>
<td>21.53</td>
<td>no dim.</td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>$c_{Cu}$</td>
<td>1000</td>
<td>mol/m$^3$</td>
<td>Chosen value</td>
</tr>
<tr>
<td></td>
<td>$c_{H_{2}SO_{4}}$</td>
<td>3.5</td>
<td>mol/m$^3$</td>
<td>Chosen value</td>
</tr>
<tr>
<td></td>
<td>$D_{Cu}$</td>
<td>2.4 $\ldots$ 3.8 $\times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td></td>
<td>$D_{H_{2}SO_{4}}$</td>
<td>3.5 $\ldots$ 5.5 $\times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td></td>
<td>$D_{H}$</td>
<td>6.87 $\times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>Estimated</td>
</tr>
<tr>
<td></td>
<td>$D_{Supp}$</td>
<td>4.62 $\times 10^{-9}$</td>
<td>m$^2$/s</td>
<td>Estimated, bulk solution value</td>
</tr>
<tr>
<td></td>
<td>$D_{Acc}$</td>
<td>5.95 $\times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>Estimated, bulk solution value</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>4.05 $\times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>Estimated, bulk solution value</td>
</tr>
<tr>
<td></td>
<td>$i_{0}$</td>
<td>21</td>
<td>A/m$^2$</td>
<td>Identified</td>
</tr>
<tr>
<td></td>
<td>$E_{Acc}$</td>
<td>$1 \times 10^{-5}$</td>
<td>m$^2$/mol</td>
<td>Fitted</td>
</tr>
<tr>
<td></td>
<td>$E_{Supp}$</td>
<td>$1 \times 10^{-3}$</td>
<td>m$^2$/mol</td>
<td>Fitted</td>
</tr>
<tr>
<td></td>
<td>$D_{H_{2}SO_{4}}$</td>
<td>$3 \times 10^{-5}$</td>
<td>m$^2$/s</td>
<td>Fitted</td>
</tr>
<tr>
<td></td>
<td>$D_{Supp}$</td>
<td>$6 \times 10^{-5}$</td>
<td>m$^2$/s</td>
<td>Fitted</td>
</tr>
<tr>
<td></td>
<td>$M_{Cu}$</td>
<td>0.06355</td>
<td>kg/mol</td>
<td>Literature data$^{17}$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{Cu}$</td>
<td>0.232</td>
<td>no dim.</td>
<td>Identified</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{H_{2}SO_{4}}$</td>
<td>0.170</td>
<td>no dim.</td>
<td>Identified</td>
</tr>
<tr>
<td></td>
<td>$\Gamma_{Supp}$</td>
<td>$3 \times 10^{-6}$</td>
<td>mol/m$^2$</td>
<td>Estimated based on literature$^{16}$</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$1 \times 10^{-4}$</td>
<td>m</td>
<td>Chosen value</td>
</tr>
<tr>
<td></td>
<td>$\theta_{Acc}$</td>
<td>$2.10 \times 10^{-6}$</td>
<td>no dim.</td>
<td>Fitted</td>
</tr>
<tr>
<td></td>
<td>$\rho_{Cu}$</td>
<td>8960</td>
<td>kg/m$^3$</td>
<td>Literature data$^{17}$</td>
</tr>
<tr>
<td></td>
<td>$\phi$</td>
<td>23 $\ldots$ 29</td>
<td>S/m</td>
<td>Estimated</td>
</tr>
<tr>
<td></td>
<td>$\phi_{eq}$</td>
<td>0.337</td>
<td>V</td>
<td>Literature data$^{17}$</td>
</tr>
</tbody>
</table>
the boundary element shape change and additive chemical concentration in the modeled electrolyte diffusion layer is applied to bring differential growth of the microvia, similar to that observed in microvia-filling tests. Differences between the experiment results and the model output prove a need for further model development, but for applications in process control a more specific and detailed model is hardly applicable. A galvanostatic control law is derived to drive the copper-deposition process as required by the process operator of, e.g., such industrial microvia-filling baths as described in the article.

Acknowledgment

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List of Symbols

\( a \) activity, no dim.

\( A \) area, \( m^2 \)

\( A_c \) area of cathode surface segment, \( m^2 \)

\( \epsilon \) volumetric concentration, \( mol/l \)

\( D \) diffusivity, \( m^2/s \)

\( F \) Faraday's constant, \( 96485 \text{ As/mol} \)

\( i \) driving force of electrode reactions (sum of overpotentials), \( V \)

\( i_0 \) exchange current density, \( A/m^2 \)

\( k \) temperature, \( K \) or °C

\( k_\text{eq} \) reaction-rate coefficient, unit varies

\( k \) ratio of adsorption- and desorption-rate coefficients, \( m^3/mol \)

\( l \) 2D-mesh boundary element length, \( m \)

\( M \) molar mass, \( kg/mol \)

\( n \) number of moles, mol

\( R \) ideal gas constant, \( 8.314 \text{ J/mol/K} \)

\( t \) time, \( s \)

\( T \) temperature, \( K \) or °C

\( U_\text{Ohm} \) Ohmic drop of potential in bulk electrolyte, \( V \)

\( v \) velocity, \( m/s \)

\( X, Y \) coordinates in the fixed cartesian coordinate system, \( m \)

\( x, y \) coordinates in the moving cartesian coordinate system, \( m \)

\( \zeta \) electron number, no dim.

Greek

\( \alpha \) apparent transfer coefficient, no dim.

\( \beta \) system average apparent-transfer-coefficient, \( l \)

\( \Gamma \) surface concentration, \( mol/m^2 \)

\( \delta \) thickness of diffusion layer, \( m \)

\( \eta \) overpotential, \( V \)

\( \theta_{\text{supp}} \) proportional surface coverage of suppressor, \( 1 \)

\( \theta_{\text{acc}} \) steady-state estimate of proportional surface coverage of accelerator, no dim.

\( \mu \) chemical term, no dim.

\( \rho \) density, \( kg/m^3 \)

\( \sigma \) electrical conductivity, \( S/m \)

\( \phi \) potential, \( V \)

\( \phi_{\text{eq}} \) equilibrium potential, \( V \)

Superscripts

\( 0 \) value initially, at \( t = 0 \)

\( \text{ads} \) value of an adsorption-desorption phenomenon

\( \text{b} \) value in electrolyte bulk

\( \text{des} \) value of a consumptive phenomenon

\( \text{flux} \) value of total flux

\( \text{sat} \) value at saturation

\( \circ \) refers to standard value

Subscripts

\( e \) refers to electrode (\( a = \text{anode}, c = \text{cathode} \)) or “electrodes”

\( i \) refers to species (see below)

\( \text{Cu} \) \( Cu^{2+} \) ion

\( \text{SO}_4^{2-} \) ion

\( \text{H}_2\text{SO}_4 \) sulfuric acid, in bulk

\( \text{H} \) \( H^+ \) ion

\( \text{H}_2\text{SO}_4 \) sulfuryc, in bulk

\( \text{Acc} \) accelerator

\( \text{Supp} \) suppressor

\( s \) refers to a surface segment

References


