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An ALE Model for Prediction and Control of the Microvia Fill Process with Two Additives

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A computational model for examining the microvia fill process as encountered in the multilayered printed circuit board industry is presented. The model includes mass transfer of both copper and the additive species present. The additives' mass balance is considered between both the solution and the surface-adsorbed layer of additives, as well as on the shape-changing cathode surface.

This paper presents a computational model of the via fill process applied in multilayered printed circuit board (MLB) manufacturing. The via fill process, i.e., electrolytic filling of microscopic via holes with copper, is a technology obtaining increasing interest due to continuously growing interconnect packaging density, decreasing size scale, improving apparatus, as well as tightened production quality and yield demands. Overviews and experimental studies regarding the via filling process have been published, but there are still few process models in the application domain of microvia filling. Such a model is not only a good tool to more precisely examine the process at hand, but it also enables optimization and control of the process operating parameters on the production line where the technology is applied.

Fortunately, via filling as applied in MLB manufacturing is closely related to the filling of trenches and vias in microchip manufacturing, because recently the latter has been more extensively studied and modelled than the former. Some notable differences between the processes in MLB manufacturing and microchip manufacturing exist; however, the most obvious difference being the hundredfold difference in scales of dimension and plating time. Process conditions on an MLB production line are also different from those on a microchip line.

In all the referred studies, the exact chemical composition of the plating system is known, which often is not the case for the applicant of an industrial MLB production line. In particular, the concentration and composition of additive chemicals in the plating bath is usually proprietary information of the chemistry supplier and thus not available to the production-line applicant. This lack of information can be compensated for by assuming that the chemicals in the plating solution behave in some typical manner, which can then be modelled by implementing characteristic effects such as differential copper reduction rate caused by consumption on cathode accompanying by diffusion-limited mass transfer of additives or the curvature enhanced accelerator accumulation effects. The model documented here is based on such an approach.

The via-filling process is such by nature that modelling it requires tracking a moving front. The arbitrary Lagrange–Eulerian (ALE) method for solving moving boundaries in a finite element method (FEM) model is applied in this paper. These two methods (FEM and ALE) together enable easy configuration of varying model geometries of practically any initial size and shape. A weak formulation of the partial differential equation system is applied to overcome some stability problems related to computation of surface curvature and the ALE method. The ALE method has been successfully applied before in modelling deformation of solid bodies as well as to modelling interfacial fluid flows with insoluble surfactants on the interface, but in the case at hand, the surfactants are soluble and the interface is one between a solid and a liquid phase and thus is different.

The model given here is in many aspects based on Ref. 14, but several improvements have been made on the additive consumption and surface chemical mechanisms, as described later on.

The presented principles are implemented as a relatively simple, computational finite element (FE) model, and the modelling results are compared to a series of data from via fill tests made on a similar system that is being modelled. Model sensitivity to parameters is studied on behalf of selected parameters, directly related to the surfactant chemistry.

System Model Overview

A thorough description of the physical system and a derivation of the electrode Eq. 1 is given in Ref. 14, and only a brief overview is presented here. All parameter values and physical properties are given as proportional values related to a certain reference set of parameter values (Table I), used to fit the model with the experimental data available. The reference values correspond to typical operating parameters on an MLB production line.

The system under inspection consists of two copper metal electrodes and a plating bath with aqueous CuSO₄ and H₂SO₄ (mol/m³). The additive system is specified below in the text. Direct current is used for plating, and the plating current density (A/m²) is controlled by a galvanostat. On the cathode, the current density is modelled with a modified bidirectional Butler–Volmer equation, which is assumed to be symmetric in respect to the electrodes and thus obtains the form of

\[
\frac{\partial c}{\partial t} = -2 \frac{\mu_{\text{Add}}}{\mu_{\text{Cu}}} \frac{k_i}{a_0} \sinh(kBH)
\]

where \( a_0 \) is the cathodic apparent transfer coefficient of the electrochemical reaction \( \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \) and \( a_0 \) is that for the anodic reaction. \( B \) is a shorthand, \( \beta = a_0a_0/(a_0 + a_0) \), \( t_0 \) is the system exchange current density, and \( k \) is \( zCe_F/RT \) for the system where \( zCe \) is 2, \( F \) is Faraday’s constant, \( T \) is absolute temperature (K), and \( R \) is the ideal gas constant.

The \( \mu_0 \) terms are (dimensionless) chemical terms which depict the effect of the additives as well as that of the copper(II) ion concentration on the cathode surface

\[
\mu_{\text{Add}} = 1 - \theta_{\text{Supp}}
\]

\[
\mu_{\text{Cu}} = \frac{c_{\text{Cu}}}{c_{\text{Cu}}} \left( \frac{c_{\text{Cu}}}{c_{\text{Cu}}} + \frac{c_{\text{Cu}}}{c_{\text{Cu}}} \right)^{-0.5554}
\]

In Eq. 2 \( \theta_{\text{Supp}} \) is the suppressor additives’ proportional surface coverage on the cathode. \( c_{\text{Cu}} \) is the \( \text{Cu}^{2+} \) ion concentration and \( c_{\text{Cu}}^0 \) that

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in the bulk solution. \( c_{\text{lim}}^{\text{Cu}} \) is a limit concentration below which all \( \text{Cu}^{2+} \) solutions are considered infinitely dilute.

\( H \) in Eq. 1 is the electromotive force between the electrodes, reduced of the voltage drop due to resistivity of the electrolyte, and it is determined by the plating system galvanostat, based on the desired cathode current density, \( i_{\text{target}} \). Because the vast majority of the cathode (\(-99.8–100.0\%) is flat copper metal surface, whose area is known, \( i_{\text{target}} \) corresponds well to the current density on the flat copper surface where the modelling geometry does not essentially change. Hence, \( H \) can be calculated by setting \( i_c = i_{\text{target}} \) in Eq. 1 on the flat copper surface and solving \( H \) as follows

\[
H = \frac{1}{k} \sinh^{-1} \left( \frac{i_{\text{target}}}{2i_k k_{\text{Add}}} \left( \frac{\mu_{\text{Add}}}{\mu_{\text{Cu}}} \right) \right)
\]

Equation 4 enables solving the model without explicitly computing reaction overpotentials of copper reduction and oxidation. A convenient form for the cathode current density in various locations on the cathode surface, in reference to that on the flat copper surface (i.e., the control current density, \( i_{\text{target}} \)) is thus obtained

\[
i_c = \left( \frac{\mu_{\text{Add}}}{\mu_{\text{Add}}/\mu_{\text{Cu}}} \right) i_{\text{target}}
\]

Mass transfer of \( \text{Cu}^{2+} \) ions follows the Nernst–Planck system of diffusion and migration and mass transfer of the additives in the solution is modelled based on Fick’s law of diffusion. The electro-neutrality condition and mass transfer of \( \text{H}^+, \text{HSO}_4^-, \) and \( \text{HSO}_4^{2-} \) ions not computed yet is compensated for in Ref. 14.

Only a two-dimensional cross section of the diffusive liquid layer above the plated microvia is actually modelled. The model is configured to be axially symmetric, with the axis of symmetry running through the via center. The modelling domain geometry can be seen in Fig. 1 on the left. The horizontal top boundary (i) is the interphase between the agitated bulk solution, where convective mass transfer dominates, and the stagnant solution layer next to the cathode surface, where diffusive mass transfer is dominant. The vertical right and left boundaries (ii) are considered symmetry boundaries, i.e., they represent symmetry surfaces between adjacent vias. The bottom boundary (iii) is the moving cathode surface that is being plated.

In the stagnant solution layer, mass transfer of all species is modelled by the Nernst–Planck equation (dilute solution model)

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot \left( -D_i \nabla c_i + \frac{z_i F}{RT} \nabla \phi \right)
\]

where \( c \) is concentration (mol/m\(^3\)), \( t \) is time (s), \( D \) is the diffusion coefficient (m\(^2\)/s), \( z \) is the electron number, \( F = 96485 \text{ AS/mol} \), \( R = 8.314 \text{ J/mol/K} \), and \( \phi \) is the electric potential (V). For further details of Eq. 6 refer to Ref. 14.

Boundary conditions for mass transfer in the solution domain are set as (i) constant concentration on the bulk solution boundary, (ii) zero mass net flux over the symmetry boundaries, and (iii) removal of species on the cathode boundary according to rate of reduction of \( \text{Cu}^{2+} \) ions (Eq. 1) or the additives (Eq. 7), respectively.

The electric potential \( \phi \) in the solution layer is computed based on the electric-field equation \(-\sigma \nabla \phi = 0\). The electric-field equation is restricted on the model domain boundaries by a known potential on the bulk solution boundary, zero current over the symmetry boundaries, and a defined current density on the cathode (Eq. 1).

The mass transfer of surfactants on and over the evolving cathode surface are described next.

The Additives

There are two types of additives included in the system model, the suppressor and the accelerator additive. No leveller additive is considered. The suppressor inhibits copper reduction (as described by Eq. 2), and the accelerator can prohibit the suppressor from adsorbing on the cathode (as given in Eq. 9) and thus effectively cancels the suppressor’s effect.

A first-order consumption reaction of additives is assumed to continuously remove additive species from the vicinity of the cathode, thus causing an additive flux from the bulk solution to the cathode surface and eventually away from the solution. Hence, the additives’ mass balance between the electrolyte solution and the cathode surface is given as a mass flux (Eq. 7), where \( i \) is either the suppressor (Supp) or the accelerator (Acc)
Here, $k_{\text{conc}}^i$ is the rate of the consumption reaction of additive $i$ in the vicinity of the cathode surface, and $\Gamma_1^{\text{diff}}$ is the maximum surface concentration of species $i$. The additive adsorption flux $N_{\text{ads}}^i$ has to be multiplied by $\Gamma_1^{\text{diff}}$ in order to scale flux of proportional surface coverage to actual mass flux. As is seen in Eq. 9 and 10, these fluxes are formulated in terms of proportional surface coverage of associated species.

The consumption of additives is assumed to be due to either (electro)chemical decomposition on the cathode surface or physical incorporation into the copper deposit. The mass balance of additives adsorbed and remaining on the cathode surface is based on the mass-conservation law and is given by

$$\frac{\partial \theta_i}{\partial t} = N_{\text{ads}}^i - N_{\text{des}}^i - D_i^i \nabla_i^2 \theta_i - \nabla_i \cdot \theta_i (\nabla_i \psi_i)$$

Equations similar to Eq. 8 are derived in a different form in, e.g., Section 5 in the same paper. In Eq. 8 $t$ is time, $\nabla_i = \nabla^\perp_i$ is the tangential differential operator, and $\psi_i = (1 \cdot \nabla^\perp_i)$ is the tangential velocity of the cathode surface, obtained as the orthogonal projection of the surface velocity $\psi$ on the surface, whose tangent vector is $t$. The $N_{\text{ads}}^i$ and $N_{\text{des}}^i$ terms describe the adsorption and desorption fluxes of species $i$ to and from the surface. $D_i^i$ is the diffusivity of $i$ along the surface. The tangential differential operator yields the gradient of surface variables $\nabla_i \psi$.

Equations 8 and 7 together realize the following principles, according to which the mass balance of the additives is assumed to form:

1. The additives adsorb on the cathode surface and a once-adsorbed additive particle is assumed to desorb from the surface in such a form that it can never be effective again (destructive desorption). Hence, desorption here models removal of additive species assumed to occur on the cathode boundary via incorporation to the deposit or electrochemical breakdown.

2. The accelerator additive may surpass the suppressor additive on the cathode as shown in Eq. 9 but the contrary is not possible (Eq. 10).

3. The adsorbed additives move with the moving surface and, due to surface curvature, the amount of adsorbed additives per unit area (the additive surface concentration) tends to decrease on convex surfaces and increase on concave surfaces. This phenomenon is represented by the right-most term in Eq. 8.

4. The additives move diffusively along the surface, against their surface concentration gradient $\nabla_i \theta_i$, represented by the third term in Eq. 8. The accelerator additive is not considered to have a direct catalytic effect on copper reduction, though this feature is straightforwardly admissible to the model.

Boundary conditions for the mass-balance equations on the cathode surface Eq. 8 are given by symmetry. Zero net mass flux of additives is assumed over the surface-layer boundaries.

Equations 9 and 10 show how the additives interact as described above

$$N_{\text{Supp}}^{\text{ads}} - N_{\text{Supp}}^{\text{des}} = k_{\text{Supp}}^{\text{ads}}c_{\text{Supp}}(1 - \theta_{\text{Supp}} - \theta_{\text{Acc}}) - k_{\text{Supp}}^{\text{des}}\theta_{\text{Supp}}$$

$$N_{\text{Acc}}^{\text{ads}} - N_{\text{Acc}}^{\text{des}} = k_{\text{Acc}}^{\text{ads}}c_{\text{Acc}}(1 - \theta_{\text{Acc}}) - k_{\text{Acc}}^{\text{des}}\theta_{\text{Acc}}$$

The Moving Geometry (ALE)

The computational model is implemented as a two-dimensional $(x,y)$ finite element model, applying the ALE method for solving the movement of the cathode surface and the whole geometry. Laplacian smoothing is applied for computing the moving mesh points. The initial geometry and mesh can be seen in Fig. 1.
The initial equation is first multiplied by the test function and then integrated by parts. The obtained term, which is a divergence of a scalar-with-vector product, is rearranged once. Finally, the divergence theorem is applied on the rearranged formulation and the obtained dot-product with the boundary normal is determined to be zero due to model symmetry. Applying the divergence theorem is justified, because the modelled surface is axially symmetric and thus in reality bounded.

Though the phrase “surface tangential velocity” is used extensively in the text, the material particles of the evolving-surface do not experience tangential movement, only movement in the direction of the surface normal. This is due to the nature of the metal-lattice growth process obtained by electrolytic deposition. The surface tangential velocity in the text refers to a feature of the numerical scheme used to model the evolving material front. Though nonphysical, this feature is numerical and can be utilized to model the relative movement between the evolving surface and a surface-attached surfactant layer “hovering” on top of the moving surface, the way it is applied in this model.

The deposition evolution estimated by the model with a set of parameters used to tune the model upon experimental data is given in Fig. 2. The images may be compared to the cross-sectional images of filled microvias in Fig. 3, obtained from via fill tests with increasing plating time. Similarly, Fig. 4 shows how the copper-deposit thickness grows during plating as estimated by the model and measured in the experiments. Figures 2-4 show that the model can be fit to correspond well to practical measurements. However, the model can clearly be seen to behave significantly more “sharply” in the center of the via than the practical via-filling process. This is presumably due to the singularity in the via center caused by axial symmetry, utilized in the model.

To illustrate that proportional surface coverage of the additive species on the cathode boundary remains within a physical range (i.e., [0,1]) during plating simulation, this is plotted on different time instants for both suppressor and accelerator additives in Fig. 5 and 6, respectively. The figures also show how the surface coverage of both additives gradually evens up toward the end of the plating process. According to Fig. 3, copper-deposit growth is first fastest in the via bottom corners and then in the via center, and the suppressor coverage distribution shown in Fig. 5 corresponds to this, showing lower-than-elsewhere surface coverage in the corresponding locations at corresponding times.

In the following, figures are used to illustrate the model-behavior dependence on various modelling parameters. The end-time fill ratio on top of the center of the microvia is used as criterion; the fill ratio is computed as usual, by dividing the copper-deposit thickness on
the microvia center axis by the sum of the copper-deposit thickness on the flat board surface and the board-substrate thickness.

The model responds to parameter changes and is stable in the required operating area. This enables proper tuning and parametrization of the model in case of process changes. Figure 7 shows how the simulation end-time via fill ratio changes when the bulk solution concentration of the given species is altered within ±50% of the normal value. The nonlinear behavior is evident, especially in respect to the suppressor additive. For instance, a too-high or too-low suppressor bulk solution concentration leads to uniform suppressor coverage on the cathode surface, manifesting as decreased end-time fill ratio.

Similarly, the model can be used to evaluate how the thermodynamical and surface-chemical properties of the additives would affect the fill result. In Fig. 8 the diffusivity of the examined species is varied around the currently applied value, in order to examine not only model sensitivity to error in diffusion coefficients but also to inspect how, e.g., the molecule size of the suppressor species might affect the fill process output through altered additive diffusivity.

By comparing Fig. 8 and 7, the linear effects of diffusion-limited mass transfer of especially the suppressor additive can be seen. An equal proportional alteration in either the diffusivity or the bulk solution concentration of the given species leads to a similar change in the simulated plating result. For Cu(II) species the correspondence is not as clear, because diffusivity of the Cu(II) ion is modeled as a nonlinear function of concentration.

To examine and illustrate how the fill output depends on four different surface-chemical properties of the additives, these parameters were varied within the range of ±50% from the assumed value.

The parameters in question are the reaction-rate coefficients of the adsorption ($k^{ads}$) and desorption ($k^{des}$) reactions as well as that of the possible decomposition reaction ($k^{cons}$), with consumption occurring on the cathode surface and also the assumed surface concentration of species on a saturated surface ($\Gamma^{sat}$). The results are shown in Fig. 9 and 10. The adsorption and desorption reaction-rate coefficients of additives were found to be statistically relevant to the output in simulations done on a similar model. Further, the cathode current density in another similar study was found to be most sensitive to these reaction-rate coefficients. However, neither of the previous studies, done for the microchip application domain, compared the model output to via-filling experiments.

A time-dependent FE solver with a direct UMFPACK linear system solver was used to solve the model. On a regular 2.1 GHz desktop PC the model requires ca. 200 s to solve, which makes it applicable for control applications on the production line. The computing time is adequately short compared to the process flow time, around an hour depending on conditions. The model provides a good basis for monitoring system development, and by improving parametrization as well as model geometry, computing time of the model can be reduced.
Conclusions

A versatile model for simulating electrophoresis of copper in the microvia-filling process applied in MLB production was presented. The model implements most relevant phenomena included in the process, and the ALE method applied to track the model boundary movement enables accurate modelling of geometries encountered in real MLB manufacturing applications. In order to compute mass transfer of surfactants on the cathode surface, the model relies on weak formulations of the associated PDEs. Without these formulations the necessary computations could not be executed. The model is compared against experimental results, and the effect on model behavior of a variety of relevant parameters is examined. The model is shown to be able to predict the end-point of fill and also the nonlinear evolution of the deposition process as well as being sufficiently stable for parameter tuning against experimental data.

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List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>c</td>
<td>volumetric concentration, mol/m³</td>
</tr>
<tr>
<td>D</td>
<td>diffusivity, m²/s</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant, 96485 C/mol</td>
</tr>
<tr>
<td>$H$</td>
<td>driving potential for electrode reactions, V</td>
</tr>
<tr>
<td>$i_0$</td>
<td>exchange current density, A/m²</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction-rate coefficient for consumption reaction of species $i$, m/s</td>
</tr>
<tr>
<td>$M_{Cu}$</td>
<td>molar mass of copper, 0.06355 kg/mol</td>
</tr>
<tr>
<td>$N_t$</td>
<td>mass flux, mol/m²/s</td>
</tr>
<tr>
<td>$N_i$</td>
<td>proportional mass flux in process*, 1/s</td>
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<tr>
<td>$R$</td>
<td>ideal gas coefficient, 8.314 J/mol/K</td>
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<tr>
<td>$r$</td>
<td>time, s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$X, Y$</td>
<td>coordinates in the fixed coordinate system, m</td>
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<tr>
<td>$z$</td>
<td>electron number, dimensionless</td>
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<td>$a$</td>
<td>apparent transfer coefficient, dimensionless</td>
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<td>$\alpha$</td>
<td>system’s apparent transfer coefficients’ harmonic mean, dimensionless</td>
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<tr>
<td>$\Gamma$</td>
<td>surface concentration, mol/m²</td>
</tr>
<tr>
<td>$\theta$</td>
<td>proportional surface coverage of surfactant, dimensionless</td>
</tr>
<tr>
<td>$\mu$</td>
<td>chemical term, dimensionless</td>
</tr>
<tr>
<td>$\rho_{Cu}$</td>
<td>density of metallic copper, 8960 kg/m³</td>
</tr>
<tr>
<td>$\phi$</td>
<td>electric potential, V</td>
</tr>
<tr>
<td>$\psi$</td>
<td>velocity of mesh, m/s</td>
</tr>
<tr>
<td>$\phi_t$</td>
<td>tangential velocity of cathode boundary, m/s</td>
</tr>
</tbody>
</table>

Superscripts

- $\text{ads}$ value related to adsorption
- $\text{b}$ value at bulk solution
- $\text{des}$ value related to desorption
- $\text{flux}$ value of consumptive flux
- $\text{s}$ value of surface-adsorbed element
- $\text{sat}$ value at saturation

Subscripts

- $i$ refers to species as below
- $\text{Cu}^{2+}$ ion
- $\text{Acc}$ accelerator
- $\text{Add}$ additive chemicals
- $\text{Supp}$ suppressor
- $T$ refers to a tangential property

References