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Microvia Superfilling Process Control

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Abstract. Electrochemical thermodynamics is the foundation of the microvia fill process, whose model represents the mass conservation of species (copper ions and surfactants) in the condition of moving boundary. The shape of via changes due to the deposed metallic copper, whose growth depends on the blocking effect of surfactants, which in turn depends on the boundary curvature. The via filling process is controlled through the boundary by adjusting the electric current flowing through the bath system. Maximizing the current raises the via fill process speed but ends up in depletion of the copper ions at the bottom of via causing an incomplete via fill (poorly fabricated board). In this paper the problem is solved by adjusting the concentration of copper ions to a reference value near the panel surface of the plated board. The stabilizing control is proposed based on the developed via fill model. By applying the control, the via fill process can be sped up by ca. 20% and the via dimple minimized 5% without risking product output quality.

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Keywords: electrodeposition, distributed parameter system, boundary control

1. INTRODUCTION

Microvia filling, a process in which the interconnections between adjacent circuit layers are formed, is a key step in the series of sub-processes required in fabrication of multi-layered printed circuit boards (PCB). The microvia fill process takes place in a copper plating bath, where the plating rate at different sites of the board is significantly affected by surfactant chemicals added in the bath. To control the process in practice, the cell current is adjusted and a compromise between the plating productivity and product quality must be made. Production speed increases as the cell current is increased but this also increases the risk of depleting the electrode of copper ions, which would deteriorate product quality. This paper presents one approach to solve the said conflict of interests by controlling the cell current based on the copper ion concentration on the plated board surface.

Significant research efforts of the copper electroplating process with surfactants have been carried out by Moffat et al. (2001-2007), Josell et al. (2007), Wheeler et al. (2003), West et al. (2000-2001), Dow et al. (2008), as well as others, although, most of the referred work focuses on developing the fill process in the sub-micron scale. A model of microvia filling (larger scale), used in Section 2, was developed by Pohjoranta and Tenno (2007, 2011), and preliminary work on the process control has been carried out by Tenno and Pohjoranta (2012, 2016).

2. THE MICROVIA FILL PROCESS MODEL

Equations (1)-(11) summarize the basic electrochemical and thermodynamic phenomena of the microvia fill process that take place in the non-bulk electrolyte moving coordinates subdomain.

For brevity, explanations of common symbols are omitted from the text and, instead, gathered in Table 1.

The electrochemical system The copper redox system model builds on the Cu/Cu^{2+} electrochemical reaction whose rate is proportional to the current density i_e (A/m^2) on the electrode surface where the reaction on the anode and cathode, $e=a,c$ takes place. The current density is given by the Butler-Volmer kinetics (1), as a function of the electrode overpotential η (V) and the activity of the reacting species a, and the blocking effect of the surfactants μ.

$$i_e = i_{0,e}\left(a_{a,e}\mu_{a,e}e^{k\alpha_{a,e}\eta_e} - a_{c,e}\mu_{c,e}e^{k\alpha_{c,e}\eta_e}\right) \quad (1)$$

The activity of anodic $a_{a,a} \equiv a_a$, and cathodic $a_{c,c} \equiv a_c$ reactions are essential, they are expressed as the ratio of the copper ion concentration and reference concentration c^0_{Cu}.

$$a_e \approx \left(\frac{c_{Cu,e}}{c^0_{Cu}}\right)^{0.446} \quad (2)$$

The blocking effect of the cathodic reaction is essential $\mu_{c,c} \equiv \mu_c$. The rest of the coefficients $\mu_{\dots,a} = \mu_{a,c} = 1$ and $a_{c,a} = a_{a,c} = 1$ are not considered. The electrode overpotential is defined as difference of the electrode potential $\Delta\phi_e$ from the equilibrium potential $\Delta\phi_{eq,e}$ as given in $\eta_e = \Delta\phi_e - \Delta\phi_{eq,e}$. The equilibrium potential for the electrode is obtained based on the standard equilibrium potential and the thermodynamic state of the electrode as in the Nernst equation $\Delta\phi_{eq,e} = \Delta\phi^0_{eq,e} + k^{-1}\ln a_e$.

The standard equilibrium potential $\Delta\phi^0_{eq,e}$ of the Cu^{2+} redaction reaction is 0.34 V, which is in proportion to the Gibbs free energy change of $\Delta G^0 = -2F\Delta\phi^0_{eq,c} = -65.61$ kJ/mol.

The current densities i_e and plating areas A_e of the electrodes are coupled by the total current, which at both electrodes is equal (opposite signed) $A_a i_a + A_c i_c = 0$. Similarly, the applied voltage E or work $W = 2FE$ (J) of the filling bath system

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equals to the sum the overpotentials and the ohmic voltage drop ΔU_{ohm} between electrodes $E = \eta_a - \eta_c + \Delta U_{ohm}$.

The mass transfer of species within the diffusion layer (bounded open set $\Omega \subset R^2$ between the bulk electrolyte and the cathode surface) is given by the diffusion model (3).

$$\partial_t c_j = \nabla \cdot \left(D_j \nabla c_j \right) \quad (3)$$

The considered species *j* includes the Cu^{2+} and Cl^- ions as well as the surfactants (suppressor: brightener PEG, accelerator: career SPS and leveler JGB), which are not charged. Due to the continuous agitation of the via fill bath electrolyte, species' concentration in the bulk of the bath have a constant bulk concentration $c_j = c_{j,b}$ on $\partial\Omega_b$, and the mass transfer has to be modeled explicitly only within a thin layer of electrolyte (the diffusion layer Ω) close to the cathode surface on $\partial\Omega_c$ where diffusion is assumed to dominate mass transfer. Since, a supporting electrolyte is used, the mass transfer of the copper ions by migration is insignificant related to diffusion.

The initial conditions for (3) is $c_j = c_{j,b}$, i.e. species are in their bulk concentration. The mass flux of the copper ions and the current density over cathode boundary $\partial\Omega_c$ are coupled in (4).

$$\mathbf{n} \cdot 2F \left(D_{Cu} \nabla c_{Cu} \right) = i_c \quad (4)$$

The boundary condition on the cathode boundary for the surfactants (*j* = *supp, acc, lev*) depends on the concentration of the surfactant close to the surface as well as on adsorption to the surface.

$$\mathbf{n} \cdot \left(D_j \nabla c_j \right) = k_j^{cons} c_j + \Gamma_j^{\max} N_j^{ads} \quad (5)$$

Consumption flux of the suppressor species is larger than for other additives. Consequently, the concentration of suppressor species is lower on the cathode surface and especially low in via compared to the concentration of other species.

Constant concentration $c_j = c_{j,b}$ at the bulk solution boundary $\partial\Omega_b$ and zero flux conditions (symmetry) are assumed on two other boundaries $\partial\Omega_{sym}$ for all species.

Subdomain Ω boundary is union of the mentioned above boundaries: $\partial\Omega = \partial\Omega_b \cup \partial\Omega_{sym} \cup \partial\Omega_c \cup \partial\Omega_{sym}$. Due to the deposit growth, the cathode is a moving boundary $\partial\Omega_c(t)$ and the shape of the subdomain is under constant deformation $\Omega(t)$.

The surfactants affect the via-fill process in proportion to their surface concentration Γ_j on the cathode boundary $\partial\Omega_c$. The surface concentration is normalised with its maximum value $\Gamma_j^{\max}$ to obtain the surface coverage $\theta_j = \Gamma_j / \Gamma_j^{\max}$, whose behaviour is explained with equation (6).

$$\partial_t \theta_j = D_{s,j} \nabla_T^2 \theta_j - \theta_j \left(\nabla_T \cdot \mathbf{v}_T \right) - \theta_j \left(\nabla_T \cdot \mathbf{n} \right) \left(\mathbf{v} \cdot \mathbf{n} \right) + N_j \quad (6)$$

The boundary conditions for (6) are point conditions (in a 2D model) and a symmetry condition was used in this work.

Equation (6) accounts for changes in the surfactant's surface coverage θ_j due to the following phenomena (from left to right, on the right-hand side of (6)):

(i) diffusion of the surfactant along the surface due to a surface concentration gradient
(ii) surface deformation in the surface tangential direction (i.e. for surface stretching and compression)
(iii) surface deformation due to the movement of a curved surface in its normal direction (i.e. bottom up growth)
(iv) surface adsorption, desorption and consumption fluxes collected in the source term $N_j = N_j^{ads} - N_j^{des} + N_j^{cons}$

Several models for the adsorption and desorption as well as consumption processes are given in the literature Moffat et al. (2004), Wheeler et al. (2003), Dow et al. (2008), West et al. (2000). In this work, equations (7)-(9) are used for the adsorption (*ads*), desorption (*des*) and consumption (*cons*) fluxes of the surfactants.

$$N_{supp}^{ads} - N_{supp}^{des} = k_{supp}^{ads} c_{supp} \left(1 - \theta_{supp} + \theta_{acc} \right) - k_{supp}^{des} \theta_{supp} \quad (7)$$

$$N_j^{ads} - N_j^{des} = k_j^{ads} c_j \left(1 - \theta_j \right) - k_j^{des} \theta_j \quad (8)$$

$$N_j^{cons} \Gamma_j^{\max} = \left(k_j^{cons} - k_j^{debris} \right) c_j \quad (9)$$

The adsorption and desorption fluxes (8) represent a Langmuir isotherm, which depends on the volumetric concentration c_j of surfactants at the surface multi-layer. This concentration c_{supp} of the suppressor species in (7) is essentially lower inside via compared to the concentration at the panel surface layer. Correspondingly, the surface coverage θ_{supp} is lower inside via than on the panel surface and approximately $1 - \theta_{supp} + \theta_{acc} \approx 1$, meaning the site is well accessible to deposition. The situation is vice versa at the panel surface where coverage of suppressor is high and $1 - \theta_{supp} + \theta_{acc} \approx 0$, meaning that the surface is nearly blocked. The involved accelerator species are specially adsorbed, which allow copper deposition. They negate the effect of suppressor species by prohibiting them from adsorbing to the surface by occupying suitable sites, thus confining the effective coverage from $1 - \theta_{supp}$ to $1 - \theta_{supp} + \theta_{acc}$ in terms (7) of suppressor adsorption. This effect is significant in the panel surface layer where the free site of suppressor species $1 - \theta_{supp} \approx 0$ is imporous and consequently, small values of coverage of the accelerator species have stronger effect than in the via surface layer were the free site $1 - \theta_{supp} \approx 1$ is porous.

The coupling of the copper plating current and surfactants occurs through the free sites of the suppressor and leveller specie $\mu_c = \left(1 - \theta_{supp} \right) \left(1 - \theta_{lev} \right)$ in (1), which therefore represents blocking effect on the copper reduction rate.

The subdomain and boundary shaping In electrodeposition, the cathode surface $\partial\Omega_c(t)$ moves as metallic copper is deposited, which means that the involved species' diffusion path length changes essentially in the via and the blocking effect of surfactants depends on the curvature of surface as they move along the surface. The electrode surface movement is thus included in the via fill model by a means that effectively alters the geometry of the modeled subdomain during the computation. The moving interface (level set) method and the deformed mesh (arbitrary Lagrange-Eulerian, ALE) method

are often used. In this work the ALE method was utilized, which is a node tracking method, where the shape of the modeling subdomain is tracked explicitly. Tracking of the deforming subdomain is based on creating a mapping between the deformed and a reference coordinate system. The mapping is obtained as the deformation gradient $\mathbf{F} = \partial \mathbf{x} / \partial \mathbf{X}$, where $\mathbf{x}$ and $\mathbf{X}$ are the location in the deformed and reference coordinate systems, respectively. To carry out calculations of phenomena that occur in the deformed subdomain, their describing equations are transformed back to the reference system by using the inverse $\mathbf{F}^{-1}$ of the deformation gradient. The node points of the deformed mesh $(\mathbf{x})$ are obtained by integrating the mesh velocity $\mathbf{v}$ in time, with the initial condition $\mathbf{x} = \mathbf{X}$. The mesh velocity $\mathbf{v}$ is obtained by solving the Laplace (smoothing) equation (10).

$$\nabla^2 \mathbf{v} = 0 \qquad (10)$$

The determinant $\det(\mathbf{F})$ yields the scaling factor between the two coordinate systems, which scales the infinitesimal area element used in integration in the variational method for solving the electrochemical system (1)-(9). The electrode boundary moves due to the growth of the deposited copper layer and the movement velocity in the boundary normal direction is thus given by (11).

$$\mathbf{v} \cdot \mathbf{n} = i_c \frac{M_{Cu}}{2F \rho_{Cu}} \qquad (11)$$

Although the ALE method transforms the fixed geometry processes into the deformed geometry, it cannot handle all geometry deformations. Remeshing partly helps but only up to topological changes, thus excluding e.g. a void buried in the via or the via wall colliding with itself is not possible.

3. THE PROCESS CONTROL

The main goal of the via fill process control is to maximize plating productivity while retaining product quality. It is anticipated, that the case-specific maximal plating rate is obtained when the copper ion concentration at the cathode surface is driven to such a level that mass transfer of the copper ions to the cathode is maximized but the surface is still not depleted of copper ions. If depletion would occur, product quality would deteriorate. Although the control problem is a maximization problem with constraints, a simpler regulation problem is solved in practice and only a constant current control is applied.

More relevant controls (18) and (20) are developed below.

Simple control Since the major part of the plating area is a panel surface a simpler goal of control can be considered, which is to bring the (unobserved) boundary concentration $c(t,0)$ of copper ions at the flat cathode surface to level c_d, which is as low as possible to maximize mass transfer of copper to the cathode without running to depletion $c(t,0) \approx 0$ inside via. This problem can be solved in a single dimension and formulated as the following diffusion process boundary control problem:

$$c(0,x) = c_b \qquad 0 < x < \delta \qquad (12)$$

$$\partial_t c(t,x) = D\partial_{xx}^2 c(t,x) \qquad 0 < x < \delta \quad t > 0 \qquad (13)$$

$$D\partial_x c(t,x) = u(t) \qquad x = 0 \quad t > 0 \qquad (14)$$

$$c(t,\delta) = c_b \qquad (15)$$

In (14), $u(t)$ is the flux-type control (mol/m^2/s). Only the copper ion is considered in the system (12)-(15) and therefore, the species' subscripts are omitted, for brevity.

This has been found in (Tenno, 2016) that the simple proportional control (16) brings the copper ion concentration in (12)-(15) close to the desired level c_d.

$$u(t) = -K_P\left(c(t,0) - c_d\right) \qquad (16)$$

The larger the control gain K_P is, the closer and faster the controlled concentration comes to the desired level c_d. However, such a proportional control leaves a static control error (17), which can be removed if the target concentration is aimed to a lower value $c_d - \varepsilon_d \equiv c_d^0$, with offset ε_d.

$$c(t,0) - c_d \to \frac{D}{D + K_P \delta}\left(c_b - c_d\right) \equiv \varepsilon_d \qquad (17)$$

Solving the problem (12)-(16), the unobserved boundary concentration $c(t,0)$ in (16) can be eliminated and then the proportional control can be expressed in the form of convolution integral, which is a nonlinear stabilizing feedback. (18)

$$u(t) = -K_P\left(c_b - c_d^0\right) - \frac{K_P}{\sqrt{\pi D}} \int_0^t \frac{u(\tau)}{\sqrt{t-\tau}} \left(1 + 2\sum_{n=1}^{\infty} (-1)^n e^{-\frac{n^2\delta^2}{(t-\tau)D}}\right) d\tau$$

Proof The change of variables, Laplace transform, Efros' theorem, convolution theorem and direct integration techniques has been applied on the system (12)-(16) to prove (17), (18) in (Tenno, 2016).

The panel surface A_f is 10-100 times large than the via bottom A_v area for all vias togethers on a PCB (normal and high density vias are considered). Consequently, the plating area A in bath is approximately equal to the panel surface area with vias $A \approx n(A_f + A_v)$ or without vias $A \approx nA_f$ multiplied with the number n of submerged PCBs. The mass flux $u(t)$ scaled by the plating area equals to the total current $I(t)$ (A) that passes the bath system.

$$I(t) = 2FAu(t) \qquad (19)$$

This simple control (19) can be implemented in a galvanostatic mode, i.e. the controlled-current technique in which the cell voltage becomes dependent on the applied current. The system of control is depicted in Fig. 1.

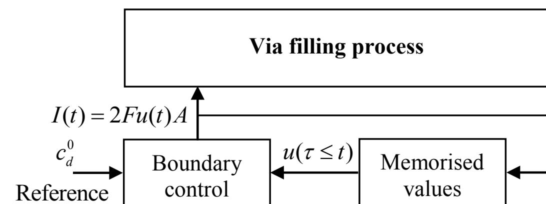

Fig. 1. The robust control is efficient in the initial transient period but less efficient in the later period.

This control is robust because a small number of model parameters (with possible uncertainties) are used in the total current computation. This control is efficient in the initial transient period (time optimal) and better than a constant current control. However, the proposed control is constant after the transient period and is not as efficient as initially because a crucial information on the state of via is missing in the 1D model (12)-(15). In advanced control (20) this issue is fixed. To fix the problem, it is essential to know that there is a widespread concentric belt around the via mouth with the transient characteristics that range between the panel surface and via characteristics (current density, concentrations of species and other). Consequently, the via-affected area A_w is wider than just the via bottom area A_v. Their difference is ca. 5 times. Consequently, the efficient panel surface area A_f is only 2-20 times larger than the via-affected area A_w. Although, the fraction of via-affected area is small the current density inside vias is ca. 5 larger than the current that passes the panel surface due to the blocking effect of surfactants. Simple evidence that confirms this argument is a larger total current observed in the potentiostatic control mode when the PCB with vias is compared against the PCB without vias.

Advanced control Preserving the structure of proportional control (16) (which is similar in the case of 2D rectangular) we return to the large via fill model in two dimensions (1)-(11). Replacing $c(t,0)$ in (16) with $c_{Cu}(t,x_f,y_f)$ computed from the large model and replacing the desired target with the corrected target c_d^0, one has the control that depends on the state of via.

$$u(t) = -K_P\left(c_{Cu}(t,(x_f,y_f)) - c_d^0\right) \tag{20}$$

In (20), the spatial variables in extra brackets (x_f,y_f) designate any or fixed reference point $p_f \equiv (x_f,y_f)$ on the panel surface, $p_f \in \partial\Omega_f \subset \partial\Omega_c$. This control can be scaled up to the total current for the bath as explained in (19).

The control system sketched in Fig. 2 proceeds as follows. Select any reference point on the panel surface $(x_f,y_f) \in \partial\Omega_f$. Initially the copper ion concentration is equal to the bulk electrolyte concentration $c_{Cu}(0,(x_f,y_f)) = c_{Cu,b}$. The control $u(t) = u(t,(x_f,y_f))$ is computed based on the concentration $c_{Cu}(t,(x_f,y_f))$ by (20) in the selected reference point $(x_f,y_f) \in \partial\Omega_f$ on the panel surface and then scaled up from the mass-flux to the current density $i(t) = 2Fu(t)$ that is applied point-wise $i_c(t,(x_f,y_f)) = i(t)$ in the model to obtain the required electrode overpotential $\eta(t,(x_f,y_f))$ by solving the Butler-Volmer equation (1) as equation for inversed kinetics. All these are scalar variables. Then, the found overpotential is used to calculate (with (1)) the current density distribution $i_c(t,x_c,y_c)$ over the whole cathode, including inside the via. This current is a distribution because the activity and blocking effect coefficients are distributed variables. This current is used further to calculate the copper concentration in the diffusion layer $c_{Cu}(t,x,y)$ including concentration at the cathode boundary $c_{Cu}(t,x_c,y_c)$ and at the panel surface boundary $c_{Cu}(t,x_f,y_f)$. Obviously, at the selected reference point the concentration is the same as everywhere else at the panel surface boundary $c_{Cu}(t,(x_f,y_f)) = c_{Cu}(t,x_f,y_f)$ and in the next instant of computing this point-wise concentration is used again as update in the control rule (20). Before that, one must computer all the other mass transfer and via shape evolution processes shown in Fig. 2.

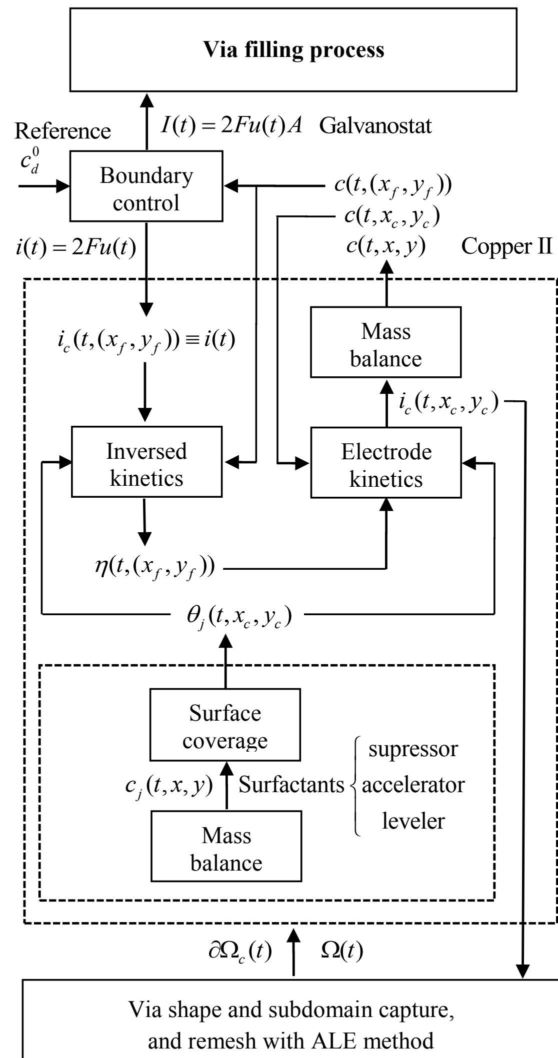

Fig. 2. The advanced boundary control depends on the state of via that is evaluated at the same time with control.

Remark 1. This advanced control (20) is less robust than the simple control (18) because more parameters are involved in the state of via evaluation but their role in total current is limited as the via-affected area is small compared to the panel surface area and this reduces losses of the firmness in the case of parametric uncertainties.

Remark 2. In principle, the copper concentration inside via can be controlled directly, for instance, stabilised at half of the reference level c_d compared to the level for stabilisation at the panel surface. However, the flux-type control (20) cannot be converted to the total current as simply as explained in (19).

Remark 3. The anodic reaction as well as the electrode potential on which the cathodic overpotential depends is not needed to specify in this control approach. This simplifies the control algorithm and makes it less exposed to the parametric uncertainties.

3. CONTROL APPLICATION

The shape of the via and the copper concentration field in the modeled electrolyte subdomain at four instants during the constant current controlled process is shown in Fig. 3. It is seen that the computed via shape is close to the measured cross-section displayed in Fig. 4.

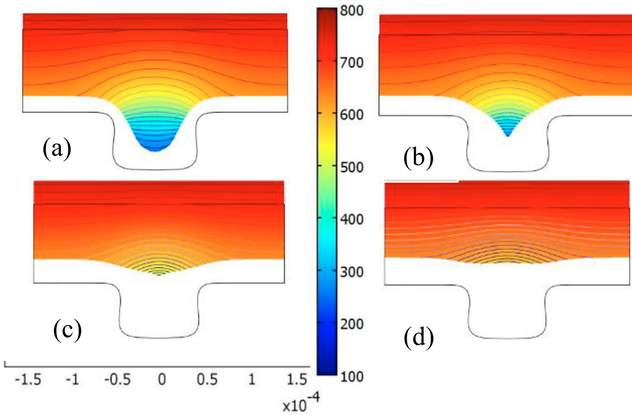

Fig. 3. Simulated evolution of the microvia shape and the copper concentration (mol/m^3) during the constant current fill process. The time instants are (a) 24, (b) 36, (c) 48, nad (d) 60 minutes.

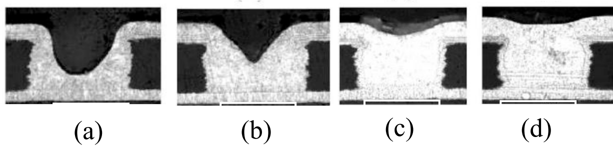

Fig. 4. Measured microvia cross-sections during the fill process.

The advanced boundary control (20) was used to calculate the actuator signal for the microvia fill process modeled with the process model discussed in Section 2. The reference concentration $c_d = 595$ mol/m^3 was applied for calculation of the control with (20).

However, meanwhile the measured process data in Fig. 4 describe the process evolution with a constant current of 200 A/m^2 posed over the cell, in the boundary-controlled case the cell current fluctuates as illustrated in Fig. 5. At first, the current declines rapidly to the local negative minimum and then gradually rises to the local maximum and then again declines slowly (this latter decline is missing in the case of simple control (18)). These changes of the current density are caused by the bottle-neck situations inside via where the risk of the copper depletion (Fig. 7) is eliminated by actuation when a larger current is applied. On average, the controlled current is higher (230-280A/m^2) than the constant current of 200 A/m^2 applied in practice. As result, the deposition process reaches the 95% fill ratio level ca. 13 minutes sooner (20% shorter plating time) than with a constant current. Moreover, the via fill is rather accomplished as the via dimple < 1%, while in the case of constant current the dimple is 6%. The via fill ratios for both processes are shown in Fig. 6 along with measured ratios in the case of constant current.

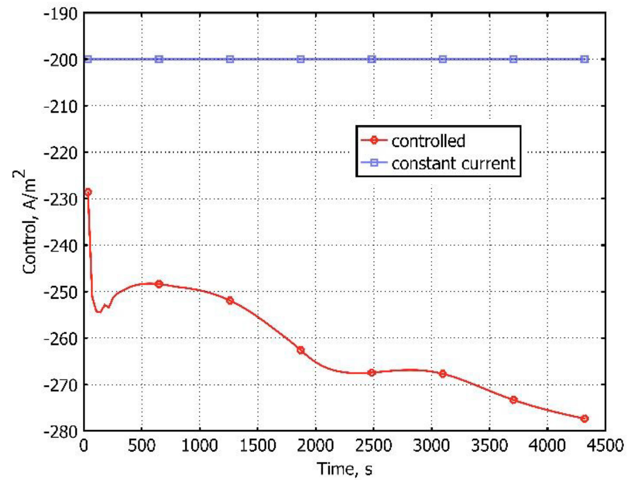

Fig. 5. The constant current (blue, square) and the boundary controlled current (red, circle) applied to the via fill process.

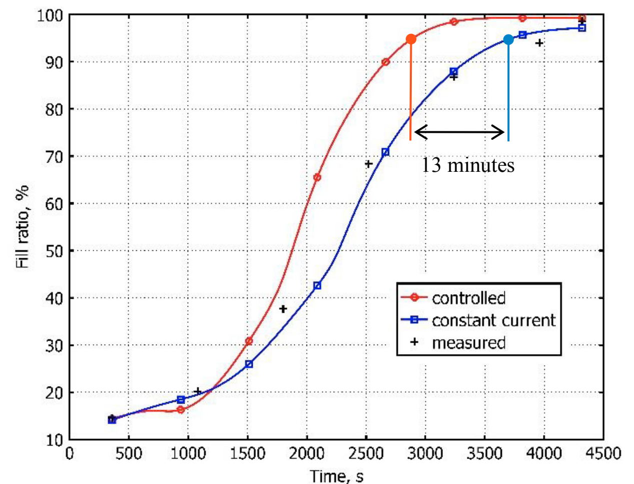

Fig. 6. The via fill ratio during the fill process when constant (blue, square) and boundary controlled (red, circle) plating current is used.

The control induced current inside via is significantly higher than the control signal itself; compare Figs. 5 and 7.

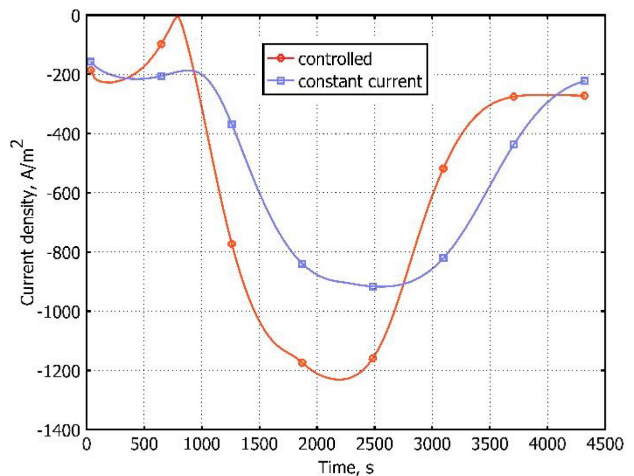

Fig. 7. The current density is highest in the via (centrum). The risk of depletion at 700 s is eliminated by the applied larger control.

Despite posing a larger current through the cell, the control is harmless because the concentration inside the via does not go below 100 mol/m^3, illustrated in Fig. 8.

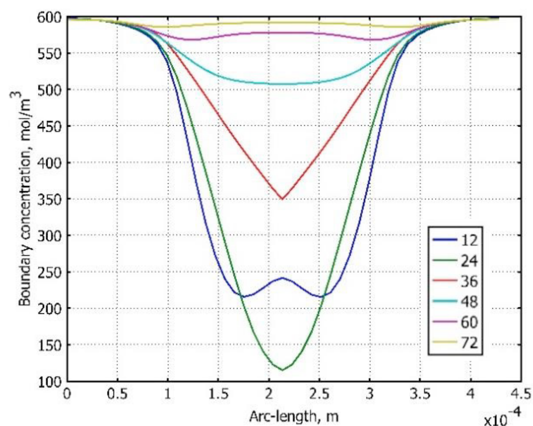

Fig. 8. The copper concentration inside the via and at the panel surface during the controlled via fill process. The electrode is not depleted as the concentration inside the via is above 100 mol/m^3 throughout the process. The time instants are 12, 24, … 72 minutes.

Clearly, the process could be optimized further, and the result obtained here is case-specific. By iterating with the developed control algorithm, it is straightforward to find the optimal means for carrying out the plating process in whichever case comes to question when the process model and parameters are established.

5. CONCLUSION

A microvia fill process can be controlled with a relatively simple exponentially stabilizing boundary control that depends on the processes inside via and maintains the boundary concentration on the panel surface of PCB at given reference. This control maximizes the via filling rate and minimizes the via dimple - it allows ca. 20% faster plating and 5% more complete vias (dimple <1%) than these in the regular case of constant current plating.

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Table 1. List of symbols

Symbol	Description	Unit
A, A_e	Total plating area of all PSBs submerged in the bath or electrode surface area	m^2
A_f, A_v, A_w	Flat area of single board, via bottom area or via current affected area	m^2
a_a, a_c	Activity of Cu^{2+} ion anodic or cathodic reactions	–
α_a, α_c	Apparent transfer coefficient for the anodic or cathodic reactions	–
c, c_{Cu}	Copper ion concentration	mol/m^3
c_{Cu}^0	Reference concentration 10^3 of the Cu^{2+}	mol/m^3
c_j	Concentration of species *j*	mol/m^3
$c_{j,b}$	Bulk concentration of species *j*	mol/m^3
D	Diffusivity of the Cu^{2+} ion	m^2/s
D_j	Diffusivity of species *j*	m^2/s
$D_{s,j}$	Surface diffusivity of surfactants *j*	m^2/s
δ	Thickness of the diffusion layer	m
η_e	Surface overpotential at electrode *e*	V
F	Faraday's constant, 96485	As/mol
$\mathbf{F}$	Deformation strain gradient	–
$\Gamma_j, \Gamma_j^{\max}$	Surface concentration of surfactants *j* and its maximum value	mol/m^2
I	Applied current of the plating bath	A
i_e, i_c	Electrode or cathodic current density	A/m^2
i_0	Exchange current density	A/m^2
K_p	Control gain	m/s
k	Temperature voltage 2F/R/T = 77.85	1/V
k_j^p	Coefficient of species *j* due to process *p*	
M_{Cu}	Copper atomic weight	g/mol
μ_c	Surfactants blocking effect	–
N_j^p	Surface mass transfer flux of surfactants *j* due to process *p*	mol/m^2/s
ρ_{Cu}	Copper density	kg/m^3
θ_j	Surface coverage of surfactants *j*	–
u	Boundary control (flux)	mol/m^2/s
$\mathbf{v}$	Mesh movement velocity (vector)	m/s
$\mathbf{x}, \mathbf{X}, x$	Location at deformed and reference coordinate systems in 2D and 1D model	m
∇_T	Surface tangential differential operator	–