

## Microvia Fill Process Boundary Control

R. Tenno\*, A. Pohjoranta\*\*

\*Aalto University, School of Electrical Engineering, PO Box 15500, Aalto, Finland  
(e-mail: robert.tenno@aalto.fi)

\*\*VTT Technical Research Centre of Finland, PO Box 1000, 02014 VTT, Finland  
(e-mail: antti.pohjoranta@vtt.fi)

---

*Abstract.* This paper presents an exponentially stabilizing boundary control for the microvia fill process. The control accounts for the mass balance of the copper ions in the electrolyte and for the surface mass balance of the deposition-blocking additives, both modeled with a diffusion mass transfer model in a shape changing domain. With simulations based on real-world data, it is shown that by applying the control, the microvia fill process can be speeded up (in the example case by ca. 15%) without endangering product output quality.

*Keywords:* electrodeposition control, distributed parameter system, boundary control

---

### 1. INTRODUCTION

Multilayered printed circuit boards are basic building elements of microelectronic devices. They enable packing the electronic components of the device within a significantly smaller footprint than if only a single-layer board was used. 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 manufacturing of multilayered boards. The microvia fill process takes place in an electrolytic copper plating bath, where the copper plating rate at different sites of the board is significantly affected by surfactant chemicals (additives) added in the bath. To control the process in practice, the cell current is adjusted and a compromise between the production speed and product quality has to be made. Production speed increases as the cell current is increased but this also increases the risk 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 related to the copper electroplating process with additives have been carried out by Moffat et al. (2001-2007), Josell et al. (2007), Wheeler et al. (2003), Dow et al. (2003-2008), Andricacos et al. (1998), Vereecken et al. (2005), West et al. (2000-2001), Cao et al. (2001), as well as others. The referred work mainly focused on developing several fill process models in the sub-micron (integrated chip) scale. A model of microvia filling, used in the current work, was developed by Pohjoranta and Tenno, (2007-2011), and preliminary work on the process control algorithm has been carried out by Tenno (2012) and Tenno and Pohjoranta (2012).

### 2. THE MICROVIA FILL PROCESS MODEL

For brevity, explanations of most parameters and symbols are omitted from the text and, instead, gathered in Appendix A, Tables 1-2, respectively.

*The electrochemical system* The copper electrolysis system model builds on the  $\text{Cu}/\text{Cu}^{2+}$  electrochemical reaction whose rate is considered directly proportional to the current density  $i_c$  ( $\text{A}/\text{m}^2$ ) on the cathode surface where the reaction takes place. The current density is given by the Butler-Volmer equation (1), as a function of the electrode overpotential  $\eta$  (V) and the activity of the reacting species  $a_a$  (anodic) and  $a_c$  (cathodic, no dim.)

$$i_c = i_0 \left( a_a \mu_a e^{k\alpha_a \eta} - a_c \mu_c e^{k\alpha_c \eta} \right) \quad (1)$$

The coefficients  $\mu_a$ ,  $\mu_c$  in (1) are used to implement the effects of the surfactant chemicals on the rate of the copper reduction reaction. In our case only  $\mu_c$ , i.e., the term affecting the cathodic reaction is essential, and the oxidation reaction is not considered ( $\mu_a = 1$ ). The activity  $a_c$  can be expressed through the copper ion concentration as described in Pohjoranta and Tenno (2007).

The mass transfer of species within the diffusion layer (i.e. a bounded domain  $\Omega \subset R^3$  with smooth Lipschitz boundary in the electrolyte and at the cathode surface) is described by (2).

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) \quad (2)$$

The considered species  $i$  include the  $\text{Cu}^{2+}$  ion as well as the additive species (suppressor, accelerator, leveler), which are not charged. It is considered that due to the continuous agitation of the microvia fill bath electrolyte, species' concentration in the bulk of the bath have a constant bulk concentration  $c_i = c_{i,bulk}$  at  $\partial\Omega_{bulk}$ , and the mass transfer has to be modeled explicitly only within a thin layer of electrolyte (the diffusion layer) close to the electrode surface where diffusion is assumed to dominate species' mass transfer.

The initial conditions for (2) is  $c_i = c_{i,bulk}$ , i.e. species are in their bulk concentration. The mass flux of the plated  $Cu^{2+}$  ions and the current density over cathode boundary are coupled by (3).

$$\mathbf{n} \cdot 2F(D_{Cu} \nabla c_{Cu}) = i_c \quad (3)$$

The boundary condition on the cathode boundary for the additives ( $i = [supp, acc, lev]$ ) is taken as the first order consumption reaction at the cathode boundary.

$$\mathbf{n} \cdot (D_i \nabla c_i) = k_i^{cons} c_i \quad (4)$$

Constant concentration  $c_i = c_{i,bulk}$  at the bulk solution boundary and zero flux (symmetry) conditions are assumed on other boundaries for all species.

The additives affect the via-fill process in proportion to their surface concentration  $\Gamma_i$  on the cathode surface. The surface concentration normalised with its maximum value  $\Gamma_i^{max}$  to obtain the surface coverage  $\theta_i = \Gamma_i / \Gamma_i^{max}$ , whose behaviour is modelled with equation (5).

$$\frac{\partial \theta_i}{\partial t} = -\theta_i (\nabla_T \cdot \mathbf{v}_T) - \theta_i (\nabla_T \cdot \mathbf{n})(\mathbf{v} \cdot \mathbf{n}) + D_{s,i} \nabla_T^2 \theta_i + N_i^{ads} - N_i^{des} + N_i^{cons} \quad (5)$$

The boundary conditions for (5) are point conditions (in a 2D model) and a symmetry condition was used in this work.

Equation (5) accounts for changes in the surfactant's surface coverage  $\theta_i$  due to the following phenomena (from left to right, on the right-hand side of (5)):

- (i) surface deformation in the surface tangential direction (i.e. for surface stretching and compression)
- (ii) surface deformation due to the movement of a curved surface in its normal direction
- (iii) diffusion of the surfactant along the surface due to a surface concentration gradient
- (iv) other processes such as adsorption, desorption and consumption are collected in the source terms  $N_i^p$

Several formulations 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), and the most appropriate formulation depends on the chemical system in question. In this work, equations (6)-(9) are used for the adsorption (*ads*), desorption (*des*) and consumption (*cons*) of the additives.

$$N_{supp}^{ads} = k_{supp}^{ads} c_{supp} (1 - \theta_{acc} - \theta_{supp}) \quad (6)$$

$$N_i^{ads} = k_i^{ads} c_i (1 - \theta_i) \quad (7)$$

$$N_i^{des} = k_i^{des} \theta_i \quad (8)$$

$$N_i^{cons} = \frac{k_i^{cons}}{\Gamma_i^{max}} \theta_i \quad (9)$$

Initially, the surface coverage of the accelerator and the leveler are small  $\theta_{acc}(0, \cdot) \ll 1$ ,  $\theta_{lev}(0, \cdot) \ll 1$  but the coverage of the suppressor is high  $\theta_{supp}(0, \cdot) \approx 1$ .

The coupling of the copper plating current and the surfactant additives' coverage is made through the coefficient  $\mu_c = (1 - \theta_{supp})(1 - \theta_{lev})$  in (1) which therefore represents the additives' blocking effect on the copper reduction rate.

*The domain and boundary shaping* In electrodeposition, the cathode surface moves as metallic copper is deposited, which means that the involved species' diffusion path length changes locally during the process. Furthermore, the surfactants' effect on the deposition rate in feature filling processes has been shown to be related to the electrode surface curvature by Moffat et al. (2004). The electrode surface movement must thus be included in the via fill process by a means that effectively alters the geometry of the modeled domain during the computation. In this work, the arbitrary Lagrange-Eulerian (ALE) method was utilized. The ALE method is a node tracking method, where the shape of the modeling domain is tracked explicitly. Tracking of the deforming domain is based on creating a mapping between the deformed and a reference (fixed) 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 in the reference coordinate systems, respectively. To carry out calculations of phenomena that occur in the deformed domain, 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 equation

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

for velocity  $\mathbf{v}$  as part of the entire equation system (a.k.a. Laplace smoothing). The determinant  $\det(\mathbf{F})$  yields the scaling factor between the two coordinate systems, which scales the infinitesimal integration element used in solving the electrochemical system (1)-(9).

The coupling between the ALE solution and the electrochemical part is formed by the electrode boundary velocity, which is given as boundary condition for (10). 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

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

Other boundaries move with the same velocity as the flat cathode surface. Further information of the ALE system implementation is given in Pohjoranta and Tenno (2011).

### 3. THE PROCESS CONTROL

The main goal of the microvia fill process control is to maximize production while retaining product quality, with a set of process and product parameters being given. 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.

The plating process control is implemented by adjusting the cell current. However, the microvias form only a fraction of the whole plated board surface and therefore the cell current essentially corresponds to the plating rate on the flat surface of the board. Although the current density inside the vias is high due to the additives, only a small fraction of the overall cell current goes through the vias and so the control signal (cell current density) can be computed in a single, representative point on the flat board surface. The aim is to obtain such a cell current that the copper concentration on the flat surface is preserved at a desired (as low as possible) level without causing depletion of  $\text{Cu}^{2+}$  ions inside the via.

*The control target* To re-cap, the goal of the control is to bring the (unobserved) boundary concentration  $c(t,0)$  of copper ions at the 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 ( $c(t,x) \approx 0$ ). The target concentration  $c_d$  is given as a constant, which simplifies the control problem. From here on, the control problem is considered in a single dimension and formulated as the following diffusion process boundary control problem.

$$c(0,x) = c_b \quad (12)$$

$$\frac{\partial c(t,x)}{\partial t} = D \frac{\partial^2 c(t,x)}{\partial x^2} \quad 0 \leq x \leq \delta \quad t > 0 \quad (13)$$

$$D \frac{\partial c(t,x)}{\partial x} \Big|_{x=0} = \frac{i_c(t)}{2F} = u(t) \quad (14)$$

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

Furthermore, only the copper ion is considered in the control model and therefore, the species' subscripts are omitted.

*The boundary control* It is simple to prove that the proportional control (16)

$$u(t) = -K_p (c(t,0) - c_d) \quad (16)$$

brings the copper ion concentration in (12)-(15) close to the desired level  $c_d$ . The bigger 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, which can be removed entirely if the target concentration is scaled (to a lower value) by (17). Since the

static error  $c_d^0$  is known and constant it can be removed effectively without integration of control errors.

$$c(t,0) - c_d \rightarrow \frac{D}{D + K_p \delta} (c_b - c_d) \equiv c_d^0 \quad (17)$$

The obtained control is an exponentially stabilizing feedback control.

*The control mapping* The relations between the microvia fill process and the control are sketched in Fig. 1 The control is computed by (16) as  $u(t) = u(t, p_{bx}, p_{by})$  in a representative point  $(p_{bx}, p_{by})$  on the flat board surface and scaled to obtain the current density  $i(t) = 2Fu(t)$ . Then the control is applied point-wise in the control model to find the required electrode overpotential  $\eta(t, x_b, y_b)$  on the cathode boundary by solving the Butler-Volmer equation (1). Then, the found overpotential is used to calculate (with (1)) the current density distribution  $i(t, x_b, y_b)$  over the whole cathode, including inside the via, the current density obtained so is finally used for validating the control signal  $u(t, p_{bx}, p_{by})$ .

The last part of the state-to-control mapping must include all mass transfer and shape evolution processes and should be implemented in dimensions higher than one, at least in two dimensions as was also done in this study.

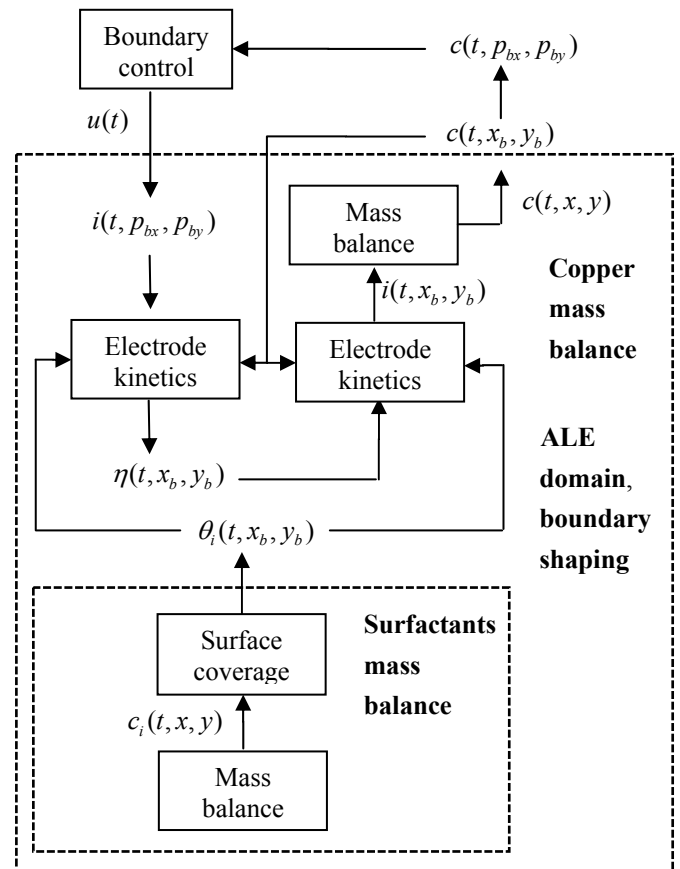


Fig. 1. The state-to-control mapping, where  $(x_b, y_b)$  is any point on the cathode surface and  $(x_{bx}, y_{by})$  is the reference point on flat cathode surface.

*The practical controls* The feedback boundary control (16) can be expressed as the model-based feed-forward control (18) or past control (20) that does not require concentration measurements on the boundary. Equation (18) is a model-based control that reads

$$u(t) = -K_p(c_b - c_d) \times \left( \frac{D}{D + K_p \delta} + 2K_p D \sum_{n=1}^{\infty} \frac{e^{-\mu_n^2 D t}}{\delta K_p^2 + K_p D + \mu_n^2 \delta D^2} \right) \quad (18)$$

In (18),  $\mu_n$  are the roots of the transcendental equation (19).

$$\frac{D}{K_p} \mu + \tan(\mu \delta) = 0 \quad (19)$$

These roots can be found with the fixed point iteration method that is a fast method in this particular case. For example, convergence to three-digit accuracy occurs in ca. 10 steps. The sequence of roots increases rapidly  $\mu_n \rightarrow \infty$ ,  $n = 1, 2, \dots$  and the sum in (18) converges in ca. 50 steps.

The system is stable for any gain  $K_p > 0$ . The lack of dynamics between the boundary concentration and current density in (16) makes the system stable provided that the system is stable in open loop, which is the case in natural diffusion processes ( $D > 0$ ) like here.

*Proof outline for (17)* The change of variables and separation of variables techniques are applied on (13)-(16) to prove (17).

The proportional control (16) can also be expressed as dependent of the past controls  $u(\tau)$  scaled to the current measurements  $i(\tau) = 2Fu(\tau)$  that are available in a via-fill process,

$$u(t) = -K_p(c_b - c_d) - \frac{K_p}{\sqrt{\pi D}} \int_0^t \frac{u(\tau)}{\sqrt{t-\tau}} \left( 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\frac{n^2 \delta^2}{(t-\tau)D}} \right) d\tau \quad (20)$$

The sum in (20) can be computed recursively and then integrated with past controls. However, the dynamics that exist between the boundary concentration and current density in the case of past controls (20) makes the system unstable for a large gain  $K_p$ , which introduces a dynamic feedback. In the case of a (“gentle”) control with a relatively small gain, the system is stable. In Fig. 2 the proportional control (16) is compared with the past control (20). If  $K_p = 10^{-4}$  m/s, the controls coincide rather well except for a short initial period which is insignificant in the via fill application (where  $D = 4 \times 10^{-10}$  m<sup>2</sup>/s,  $\delta = 10^{-4}$  m). The past controlled system loses stability if the control gain is, for example, 10 times larger but the proportionally controlled system is still stable.

*Proof outline for (20)* The change of variables, Laplace transform, Efros’ theorem, convolution theorem and direct integration techniques are applied on (12)-(15) to prove (20).

A rigorous proof is presented in a forthcoming paper and is omitted from here for the sake of brevity. Further information

of both the process model and the control is currently found in Pohjoranta and Tenno (2014) although there, in contrast to this paper, a stochastic control model is considered.

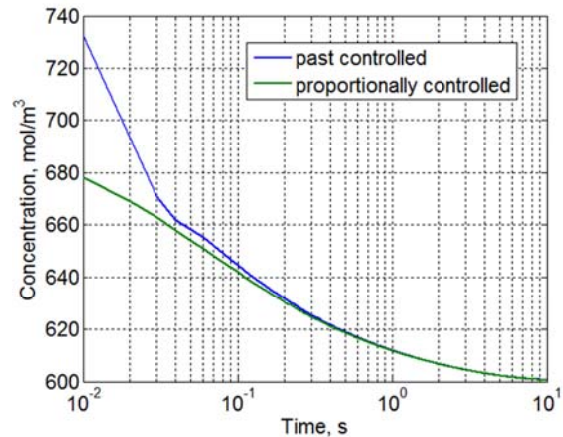


Fig. 2. The results of the proportionally controlled (16) and past controlled (20) processes are almost identical except for a short initial period of 0.04 sec (insignificant).

### 3. CONTROL APPLICATION

The boundary control is used to calculate the actuator signal for the microvia fill process modeled with the process model discussed in Section 2. The setpoint concentration  $c_d = 600$  mol/m<sup>3</sup> was applied for calculation of the controls with (16).

The shape of the via and the Cu<sup>2+</sup> concentration field in the modeled electrolyte domain at four time instants during the controlled process is shown in Fig. 3. It is seen that the modelled via shape is close to the measured shape displayed in Fig. 4. However, meanwhile the measured process data in Fig. 4 describe the process evolution with a constant current of 215 A/m<sup>2</sup> posed over the cell, in the controlled case the cell current fluctuates as illustrated in Fig. 5. At first, the current changes rapidly but soon it gradually approaches a constant value. On average, the controlled current is slightly higher (240-270 A/m<sup>2</sup>) than the constant current of 215 A/m<sup>2</sup>. As result, the deposition process reaches the 90% fill ratio level ca. 10 minutes sooner (a ca. 15% shorter plating time) than with a constant current. The via-fill ratios for both processes are shown in Fig. 6.

Despite posing a larger current through the cell, the control is safe because the concentration inside the via does not go below 100 mol/m<sup>3</sup>, illustrated in Fig. 7. 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 given.

### 5. CONCLUSION

A microvia fill process can be controlled with a relatively simple exponentially stabilizing boundary control. The control is applied as a state-to-control mapping, and is based on stabilizing the copper concentration at a single point on the flat cathode surface, which maximizes the microvia filling rate yet ensuring production quality. The process control

allows (in the example case ca. 15%) faster via filling than in the regular case of constant plating current.

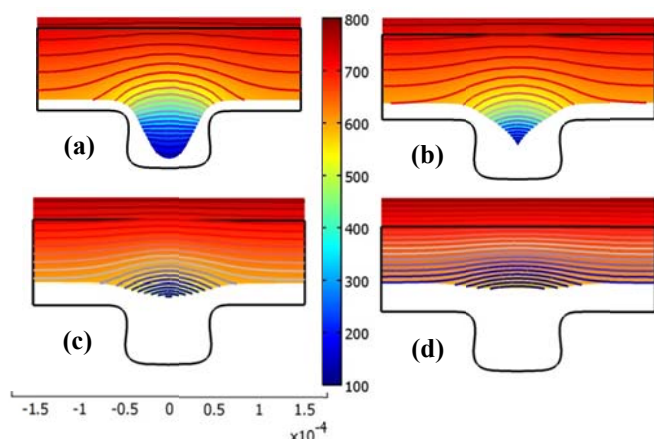


Fig. 3. Simulated evolution of the microvia shape and the copper concentration ( $\text{mol}/\text{m}^3$ ) field during the boundary controlled fill process. The time instants are (a) 24, (b) 36, (c) 48 and (d) 60 minutes. The length dimension is one meter.

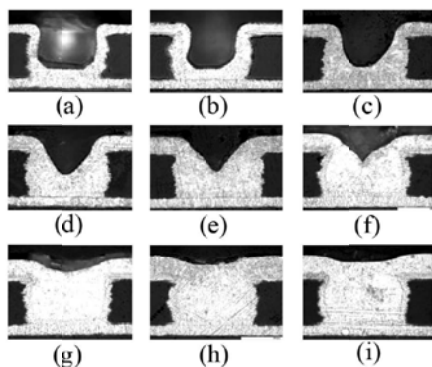


Fig. 4. Measured microvia shape evolution during the fill process. Time instants are (a)-(i), 12, 18, 24, 30, 36, 42, 48, 54, 60 minutes. Tenno and Pohjoranta (2008).

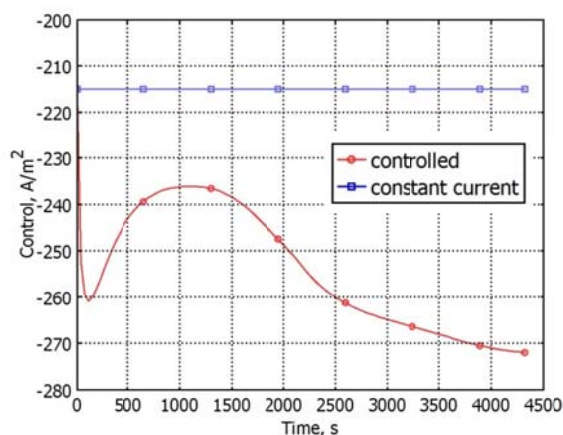


Fig. 5. The constant current (blue, square) and the boundary controlled current (red, circle) applied to the viafill process.

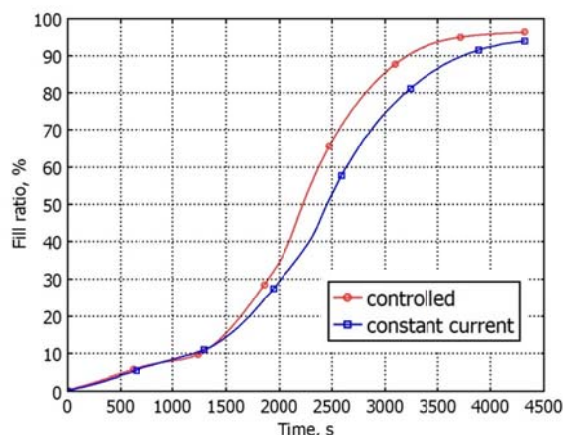


Fig. 6. The via-fill ratio during the fill process when constant (blue, square) and boundary controlled (red, circle) plating current is used.

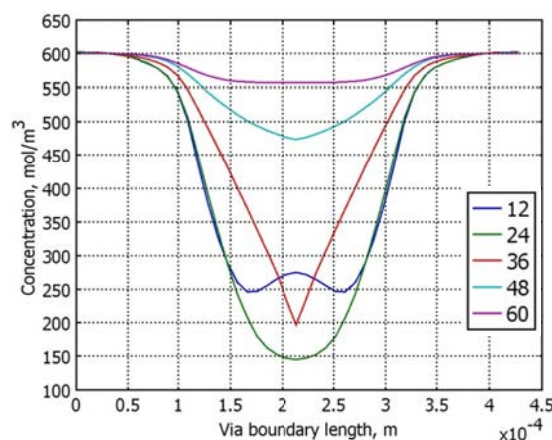


Fig. 7. The copper concentration inside the via and at the board surface during the controlled viafill process. The electrode is not depleted as the concentration inside the via is above  $100 \text{ mol}/\text{m}^3$  throughout the process. The time instants are 12, 24, 36, 48, and 60 minutes.

## REFERENCES

- Andricacos P.C., Uzoh C., Dukovic J.O., Horkans J. and Deligianni H. (1998). Damascene copper electroplating for chip interconnections. *IBM J. Res. Dev.*, **42**, 567-574
- Cao Y., Taephaisitphongse P., Chalupa R. and West A.C. (2001). Three-additive model of superfilling of copper. *J. Electrochem. Soc.*, **148**, C466-C472
- Dow W-P., Huang H-S. and Lin Z. (2003). Interactions between brightener and chloride ions on copper electroplating for laser-drilled via-hole filling. *Electrochem. Solid-State Lett.*, **6**, C134-C136
- Dow W-P. and Huang H-S. (2005). Roles of chloride ion in microvia filling by copper electrodeposition: I. Studies using SEM and optical microscope. *J. Electrochem. Soc.*, **152**, C67-C88
- Dow W-P., Yen M.-Y., Liao S.-Z., Chiu Y.-D. and Huang H-S. (2008). Filling mechanism in microvia metallization by copper electroplating. *Electrochim. Acta*, **53**, 8228-8237



- Josell D., Moffat T.P. and Wheeler D. (2007). Superfilling when adsorbed accelerators are mobile electrochemical/chemical deposition and etching. *J. Electrochem. Soc.*, **154**, D208-D214
- Moffat T.P., Wheeler D., Huber W.H. and Josell D. (2001). Superconformal electrodeposition of copper. *Electrochem Solid-State Lett.*, **4**, C26-C29
- Moffat T.P., Wheeler D., and Josell D. (2004). Superfilling and the curvature enhanced accelerator coverage mechanism. *Electrochem Soc. Interf.*, **13**, 46-52
- Moffat T.P., Wheeler D., Kim S.K. and Josell D. (2006). Curvature enhanced adsorbate coverage model for electrodeposition electrochemical/chemical deposition and etching. *J. Electrochem. Soc.*, **153**, C127-C132
- Moffat T.P., Wheeler D., Kim S.K. and Josell D. (2007). Curvature enhanced adsorbate coverage mechanism for bottom-up superfilling and bump control in damascene processing. *Electrochim. Acta*, **53**, 145-154
- Pohjoranta A. and Tenno R. (2007). A method for microvia-fill process modeling in a Cu plating system with additives. *J. Electrochem. Soc.*, **154**, D502-D509
- Pohjoranta A. and Tenno R. (2011). Implementing surfactant mass balance in 2D FEM-ALE models. *Eng. Comp.*, **27**, 165-175
- Pohjoranta A. and Tenno R. (2014). Microvia fill process model and control. *J. Math. Chem.*, **52**(5), 1414-1440
- Tenno R. and Pohjoranta A. (2008). An ALE model for prediction and control of the microvia fill process with two additives. *J. Electrochem. Soc.*, **155**, D383-D388
- Tenno R. and Pohjoranta A. (2009). Microvia fill process control. *Int. J. Control*, **82**, 883-893
- Tenno R. (2012). A stochastic model for electrodeposition process with applications in filtering and boundary control. *Int. J. Control*, **85**, 1807-1826
- Tenno R. and Pohjoranta A. (2012). Control of diffusion limited electrochemical redox processes: Simulation study. *IFAC J. Proc. Control*, **22**, 228-235
- Vereecken P.M., Binstead R.A., Deligiani H. and Andricacos P.C. (2005). The chemistry of additives in damascene copper plating. *IBM J. Res. Dev.*, **49**, 3-18
- West A.C. (2000). Theory of filling of high-aspect ratio trenches and vias in presence of additives. *J. Electrochem. Soc.*, **147**, 227-232
- West A.C., Mayer S. and Reid J. (2001). A superfilling model that predicts bump formation. *Electrochem. Solid-State Lett.*, **4**, C50-C53
- Wheeler D., Josell D. and Moffat T.P. (2003). Modeling superconformal electrodeposition using the level set method. *J. Electrochem. Soc.*, **150**, C302-C310

Appendix A. TABLES

Table 1. List of parameter values

Symbol	Cu <sup>2+</sup>	Supp	Acc	
$c_{i,b}$	755	0.005	0.01	mol/m <sup>3</sup>
$c_d$	600			mol/m <sup>3</sup>
$D_i$	$7 \times 10^{-5} e^{-0.001c}$	$5.9 \times 10^{-10}$	$4 \times 10^{-10}$	m <sup>2</sup> /s
$D_{s,i}$		$59 \times 10^{-7}$	$4 \times 10^{-6}$	m <sup>2</sup> /s

$\Gamma_i^{max}$		$44 \times 10^{-6}$	$2 \times 10^{-6}$	mol/m <sup>2</sup>
$k_i^{ads}$		4083	35	m <sup>3</sup> /mol/s
$k_i^{des}$		0.001	1.0	1/s
$k_i^{cons}$		$96 \times 10^{-5}$	$6 \times 10^{-5}$	m/s
$i_0$		21		A/m <sup>2</sup>
$\alpha_a, \alpha_c$		0.232	0.170	–
$\delta$		$10^{-4}$		m

Table 2. List of symbols

Symbol	Description	Unit
$\alpha_a, \alpha_c$	Activity of Cu <sup>2+</sup> ion toward the anodic or cathodic direction, Pohjoranta and Tenno (2007)	–
$\alpha_a, \alpha_c$	Apparent transfer coefficient for the anodic and cathodic reactions	–
$c$	Copper(II) ion concentration	mol/m <sup>3</sup>
$c_i$	Concentration of species $i$	mol/m <sup>3</sup>
$c_{i,b}$	Bulk concentration of species $i$	mol/m <sup>3</sup>
$D$	Diffusivity of the Cu <sup>2+</sup> ion	m <sup>2</sup> /s
$D_i$	Diffusivity of species $i$	m <sup>2</sup> /s
$D_{s,i}$	Surface diffusivity of additives $i$	m <sup>2</sup> /s
$\delta$	Thickness of the diffusion layer on the board	m
$\eta$	Surface overpotential at electrode	V
$F$	Faraday's constant, 96485	As/mol
$\mathbf{F}$	Deformation strain gradient	–
$\Gamma_i, \Gamma_i^{max}$	Surface concentration of additives $i$ and its maximum value	mol/m <sup>2</sup>
$i_c$	Cathodic current density	A/m <sup>2</sup>
$i_0$	Exchange current density	A/m <sup>2</sup>
$K_p$	Control gain	m/s
$k$	Shorthand for $2F/R/T$ , 77.85	1/V
$M_{Cu}$	Copper atomic weight	g/mol
$\mu$	Surfactants blocking effect	–
$N_i^p$	Surface mass transfer flux of additives $i$ due to process $p$	mol/m <sup>2</sup> /s
$\mathbf{n}$	Boundary outward normal vector	–
$R$	Ideal gas coefficient, 8.314	J/mol/K
$\rho_{Cu}$	Copper density	kg/m <sup>3</sup>
$T$	Temperature	K
$\theta_i$	Surface coverage of additives $i$	–
$u$	Boundary control	mol/m <sup>2</sup> /s
$\mathbf{v}$	Mesh movement velocity (vector)	m/s
$x$	Location in 1D model	m
$\mathbf{x}, \mathbf{X}$	Location at deformed and reference coordinate systems	m
$\nabla_T$	Surface tangential differential operator	–