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## Simulation of Copper Electrodeposition in Millimeter Size Through-Silicon Vias

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Computational predictions of copper deposition in millimeter size through-silicon vias (mm-TSV) are presented based on localized breakdown of a co-adsorbed polyether-chloride suppressor layer. The model builds upon previous work on localized Cu deposition in microscale TSV and through-holes by incorporating 3D fluid flow calculations to more effectively evaluate chemical transport of cupric ion and additives, both of which are critical to adlayer formation and disruption within the via. Simulations using potentiostatic and potentiodynamic waveforms are compared to previously reported filling experiments. Alternatively, the utility of galvanostatic control and variations in fluid flow are explored computationally. For appropriate applied potential(s) or current, deposition is localized to the via bottom, with subsequent growth proceeding in a bottom-up fashion. Selection of inappropriate current or potential waveforms, or forced convection conditions that supply insufficient cupric ion to the bottom of the via, results in prediction of voids. Simulations of deposition in via arrays (4 × 1) predict non-uniform growth across the arrays, with the passivation of individual vias associated with minor variations in convective flow and/or numerical perturbations in the simulation, that reflects the critical nature of the bifurcation process.

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Electrochemical deposition is widely used in the fabrication of interconnects for microelectronic devices ranging from nanometer on chip metallization to millimeter features used in printed circuit board and related packaging applications. Across all length scales, copper electrodeposition in high-aspect ratio cavities is an important processing step. Presently, electrodeposition in fully metallized, sub-micron scale features employs a multicomponent combination of additives (i.e., suppressor, accelerator, and leveler) to enable void-free trench and via filling.<sup>1-11</sup> Competitive adsorption between species that accelerate and inhibit the metal deposition reaction along with their enhancement or depletion in response to area change are central to superconformal feature filling. At larger length scales, such as in microscale through-silicon via (TSV) and through-hole (TH) features used in 3D chip stacking and circuit boards, reactant depletion effects become important factors in filling behavior. This is most apparent in electrolytes where a single suppressor additive enables almost ideal bottom-up electrodeposition as demonstrated for copper in microscale TSV and TH features.<sup>12–18</sup> Using different molecules, the suppressor-only approach has been extended to Ni,<sup>19,20</sup> Co,<sup>21</sup> and Au<sup>22,23</sup> filling of TSV. For larger millimeter scale features, metallization has typically relied on through-mask deposition, which patterns a thick insulating material over a conducting surface that enables bottom-up, void-free filling in the patterned cavities.<sup>24,25</sup> The common backplane requires an etch step after dissolution of the patterned material to develop electrically isolated structures. Recently, a suppressor-only electrolyte was used to achieve robust, void-free filling of near millimeter scale vias (600  $\mu$ m deep and 125  $\mu$ m diameter) where all surfaces, including the sidewalls, were fully metallized prior to filling by Cu electrodeposition.<sup>26-28</sup> Filling of the mm-TSV exhibited behavior like that observed in microscale features; namely, localization of deposition at or near the bottom of the feature that is dependent on potential and suppressor concentration. However, for these larger mm-TSV features, forced convection has an important influence on local concentration of metal ion and additives within the recessed feature that is essential to successful filling.

For suppressor-only electrolytes, electroanalytical measurements demonstrate that inhibition of Cu deposition derives from co-adsorption of halide with polyether macromolecules that serves to limit coordination of  $Cu^{2+}$  to the electrode surface. Polarization at sufficiently negative potentials results in disruption of the chloride-polyether adlayer, thereby permitting active electrodeposition.<sup>12-14,27,29-3</sup> The breakdown process depends on the concentrations of both additives as well as the applied potential: deactivation involves a combination of desorption and/or incorporation of the adlayer components into the growing deposit. In cyclic voltammetry measurements, potential-driven breakdown gives rise to positive feedback with sharply accelerated copper deposition that leads to significant voltammetric hysteresis. Post-experimental correction for ohmic losses produces a voltammogram with an S-shaped, negative differential resistance where a decrease in driving force is associated with an increase in reaction rate, thus the moniker "S-NDR." Once the critical overpotential for suppressor breakdown is exceeded the system bifurcates into passive and active zones.<sup>12–14,29,34,35</sup> Rapid acceleration beyond the critical potential combined with the inverted nature of the S-NDR means that the potentiostat control loop convolves the interface potential and iR losses in the electrolyte to maintain the overall applied potential as the activated electrode area develops. The potentiodynamic response and resulting morphological evolution is quite complex, reflecting the nonlinear nature of the system. Alternatively, galvanostatic control enables the rate of breakdown to be controlled in a somewhat more linear fashion. The two different control loops result in different morphological evolutions of the electrode during bifurcation into passive and active zones as detailed in a recent publication.<sup>36</sup> On macroscale planar electrodes the localized regions of active deposition give rise to Turinglike patterns where the deposit shape and size is intrinsically related to the differing time scales for chemical diffusion and electrode polarization.<sup>12,37,38</sup> Importantly, for topographically engineered electrodes, such as TSV or TH, bifurcation is biased such that active deposition occurs preferentially where the additive flux is most constrained by geometry (i.e., the TSV bottom or TH middle).

A two-additive halide-suppressor model has been developed to describe deposition in Cu S-NDR systems.<sup>14,36,39</sup> The co-adsorption model limits suppressor (e.g., poloxamine) coverage to no more than that of chloride ( $\theta_P \leq \theta_{Cl}$ ) and demonstrates favorable comparison to experimental voltammetry in low chloride electrolytes (<80  $\mu$ mol·l<sup>-1</sup>) on rotating disk electrodes (RDE) in 1D simulations<sup>14</sup> and for both

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cyclic voltammetry and galvanodynamic sweeps in 2D simulations of microelectrodes.<sup>36</sup> The latter study also captures the temporal observations of the active/passive bifurcation on the 25  $\mu$ m diameter disk electrodes. Additionally, kinetics obtained from the RDE studies enabled the model to describe feature filling dynamics in microscale annular TSV and a priori predict the filling of TH features.<sup>14,39</sup>

The present study uses the two-additive S-NDR model to simulate Cu deposition in millimeter scale TSV features. Whereas prior predictions of S-NDR features used a 2D-axisymmetric geometry and fixed boundary layer to model purely diffusive chemical transport, these simulations incorporate convective flow in the actual 3D geometry. This is done in keeping with experimental results demonstrating the need for forced convection to obtain effective bottom-up filling in large features from this electrolyte. Symmetry of the substrate also makes clear that the imposed flow is responsible for observed asymmetrical deposition in the latter stages of filling. Simulations of mm-TSV feature filling under potentiostatic and potential stepped waveforms are compared to experimental results published for Cu filling in a  $1 \text{ mol} \text{ L}^{-1}$  CuSO<sub>4</sub>,  $0.5 \text{ mol} \text{-L}^{-1} \text{H}_2\text{SO}_4$  electrolyte containing 80  $\mu \text{mol} \text{-L}^{-1}$  NaCl and  $40 \ \mu \text{mol} \cdot \text{L}^{-1}$  poloxamine suppressor. The feature filling experiments involved a three-step procedure. The recessed via patterned wafer fragments were wetted with ethanol, then transferred and immersed in the electroplating cell at a small overpotential,  $\approx -0.02$  V where negligible copper deposition occurred, for two minutes to allow electrolyte to exchange with the ethanol before stepping to the deposition potential to initiate feature filling; further details can be found in Ref. 26. Additional simulations explore galvanostatic deposition and the influence of convective flow on feature filling. Finally, the S-NDR theory is applied to deposition in multi-feature arrays, with observations of non-uniform growth in individual vias arising from slight variations in the local environment reflecting the critical nature of the relationship between transport-driven suppression and potential-driven activation.

#### **Computational Methods**

Finite element method (FEM) computations are used to simulate copper electrodeposition in millimeter-scale through-silicon vias. The computational geometry, shown in Fig. 1, includes a full 3D cylindrical via ( $D_{\rm via} = 125 \ \mu m$  and  $H = 600 \ \mu m$ ) with a surrounding square region of the field ( $W_{cell} = 250 \ \mu m$ ). A reference electrode and counter electrode are combined in a common plane at a distance  $L_{RE}$  above the boundary layer  $\delta$ . Electrolyte occupies the internal volume and forced convection occurs within the boundary layer marking the transition to the unperturbed bulk electrolyte. A constant velocity,  $U_x$ , is imposed at the left-hand boundary of the simulation domain and at the top of the boundary layer whose thickness is estimated from rotating disk electrode theory, i.e., 22  $\mu$ m for  $U_x = 40 \text{ cm} \text{ s}^{-1}$  (400 rpm equivalent at a distance of 1 cm from the center of rotation).<sup>40</sup> The concentration of each species (Cu<sup>2+</sup>, Cl<sup>-</sup>, and polymer) is set equal to that of the bulk solution  $(C_i^o)$  at these boundaries. The lateral boundary conditions emulate filling a 1D array of such vias that is periodic in the ydirection. A fluid outlet condition of constant pressure is imposed at the right-hand boundary. The electric potential is set equal to zero at the reference/counter electrode positioned 1 cm away from the TSV field. The concentration  $C_i$  and flux  $N_i$  of each species in the electrolyte domain are described by the full convective-diffusive Nernst-Planck equation, including electromigration from potential  $(\phi)$  gradients, by

$$\frac{dC_i}{dt} = -\nabla \cdot \vec{N}_i = -\nabla \cdot (-z_i u_{m,i} F C_i \nabla \phi - D_i \nabla C_i + C_i \vec{u}) \quad [1]$$

given the species' charge  $z_i$ , diffusion coefficient  $D_i$ , Faraday's constant *F*, and mobility  $u_{m,i}$  calculated by the Einstein relationship



Figure 1. Schematic of 3D geometry used in the S-NDR model to simulate filling in mm-scale through-silicon vias. Relevant boundaries and dimensions are indicated. Via diameter and height are 125  $\mu$ m and 600  $\mu$ m, respectively. A constant fluid velocity is imposed in the x-direction at the left-hand boundary and at the boundary layer plane,  $\delta$ . A constant pressure outlet condition is imposed at the right-hand boundary. Dimension values can be found in Table I.

$$u_{m,i} = \frac{D_i}{RT}.$$
 [2]

The velocity field,  $\vec{u}$ , is computed independently from species migration (Eq. 1) by solving the Navier–Stokes equation

$$\frac{d\vec{u}}{dt} + (\vec{u} \cdot \nabla)\vec{u} = -\frac{1}{\rho_f}\nabla p + \frac{\mu_f}{\rho_f}\nabla^2\vec{u}$$
[3]

where the flow is assumed to be laminar and incompressible. The pressure field p is obtained by enforcing the incompressibility constraint,

$$\nabla \cdot \vec{u} = 0 \tag{4}$$

Here,  $\rho_f$  and  $\mu_f$  are the fluid density and viscosity, respectively, the values taken from semiempirical relationships derived from measurements of copper sulfate—sulfuric acid electrolytes.<sup>41</sup> Free convection is ignored in this treatment except for a subset of simulations probing the impact of imposed inlet velocity presented in Fig. 5. In these particular simulations, buoyancy transport driven by cupric ion depletion near the via bottom is evaluated using the semiempirical relationships for density and viscosity from Ref. 41:

$$\rho_f = 1.01856 + 0.00238 M w_{Cu} C_{Cu} + 0.00054 M w_{H_2SO_4} C_{H_2SO_4} - 0.00059 T(^{\circ}C)$$
[5]

$$\mu_{f} = 10^{-6} (1592 + 0.0108 (Mw_{H_{2}SO_{4}}C_{H_{2}SO_{4}})^{2} + 2.373 Mw_{H_{2}SO_{4}}C_{H_{2}SO_{4}} + 29.93 Mw_{Cu}C_{Cu} + 76.48 (Mw_{Cu}C_{Cu})^{1/2}) \exp \frac{1890}{T(K)}$$
[6]

where  $Mw_i$  is the molecular weight of each species (in g·mol<sup>-1</sup>), *T* is the temperature (units denoted in the parentheses), and density and viscosity have units of g·cm<sup>-3</sup> and cP, respectively. The simulated electrolyte assumes full dissociation of CuSO<sub>4</sub> and NaCl, reasonable for the relevant concentrations of Cu<sup>2+</sup> and Cl<sup>-</sup>, ignoring hydronium, sulfate, bisulfate and sodium species. The poloxamine suppressor is assumed to be neutral in charge ( $z_p = 0$ ). Diffusion coefficients listed in Table I for Cu<sup>2+</sup>, Cl<sup>-</sup>, and TET are taken or estimated from literature sources.<sup>14,42-46</sup>

Due to the high concentration of  $CuSO_4$  and the  $H_2SO_4$  supporting electrolyte, potential in the electrolyte ( $\phi$ ) is well approximated by Laplace's equation

$$\nabla^2 \phi = 0, \qquad [7]$$

which neglects potential variation in solution arising from unbalanced ionic gradients. The current density  $\vec{j}$  associated with the Cu<sup>2+</sup> flux through the electrolyte is given by Ohm's law

$$\vec{j} = -\kappa \nabla \phi. \tag{8}$$

with the conductivity of the electrolyte ( $\kappa$ ) set as 15.26 S·m<sup>-1</sup>. A zero flux symmetry condition is imposed at all sides of the cell ( $W_{cell}$ ) for gradients of solution potential

$$\frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial y} = 0.$$
 [9]

consistent with a cell in the x-direction and symmetry of the periodic 1D array in the y-direction, the latter being a suitable approximation even for isolated features until the deposit emerges from the via and spreads on the free surface. Consistent with the symmetry of the periodic 1D array in the y-direction, zero flux conditions for the species' concentrations in solution are imposed only at the sides parallel to the inlet flow

$$\frac{\partial C_i}{\partial y} = 0.$$
 [10]

Accumulation of adsorbates on the electrode follows Langmuir adsorption kinetics with deactivation of suppression related to metal deposition involving a combination of desorption and/or incorporation into the growing deposit. Evolution of the fractional chloride coverage  $\theta_{Cl}$ , defined as the surface concentration divided by the saturation coverage, is described by

$$\frac{d\theta_{Cl}}{dt} = k_{Cl}^+ C_{Cl} (1 - \theta_{Cl}) - k_{Cl}^- \theta_{Cl} v \qquad [11]$$

where  $k_{Cl}^+$  is the adsorption rate constant,  $C_{Cl}$  is the chloride concentration at the evolving metal/electrolyte interface,  $k_{Cl}^-$  is the deactivation rate constant, and v is the metal deposition rate. Likewise, evolution of the fractional poloxamine coverage,  $\theta_P$ , is described by

$$\frac{d\theta_P}{dt} = k_P^+ C_P(\theta_{Cl} - \theta_P) - k_P^- \theta_P v \qquad [12]$$

where the poloxamine is restricted to adsorption on top of halide covered sites and thereby implicitly subject to the requirement that  $\theta_P$ cannot exceed  $\theta_{Cl}$  through adsorption. The fractional chloride and poloxamine coverages are further limited to values between 0 and 1. Values for  $k_i^+$  and  $k_i^-$  listed in Table I are estimated from model fits to the S-NDR voltammetry with the fitting procedure focused on capturing the critical potential for the onset of suppressor breakdown as a function of suppressor and halide concentration.<sup>14,32</sup> In previous efforts with sub-100  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolytes, the critical breakdown potential was shown to be far more sensitive to the rate constant for Cl<sup>-</sup> adsorption and consumption relative to that for the polymer. Going further, we note that once a fully developed Cl<sup>-</sup> polyether adlayer exists, Cl<sup>-</sup> consumption into the solid by the second term in Eq. 11 can lead to the first term in Eq. 12 effectively becoming a desorption term.

The metal deposition rate is assumed to be a function of the suppressor coverage  $\theta_P$  (or equivalently, coverage of the polyetherchloride bi-layer), metal ion concentration  $C_{Cu}$ , and overpotential  $\eta$  at the interface, thus

$$v(\theta_P, C_{Cu}, \eta) = \frac{\Omega}{nF} \frac{C_{Cu}}{C_{Cu}^{\theta}} [j_{\theta=0}(\eta)(1-\theta_P) + j_{\theta=1}(\eta)\theta_P] \quad [13]$$

The current densities on unsuppressed  $(j_{\theta=0})$  and suppressed  $(j_{\theta=1})$  surfaces for the two electron reduction of Cu<sup>2+</sup> to its metallic form are translated into growth velocity, v, using Faraday's constant ( $F = 96,485 \text{ C} \cdot \text{mol}^{-1}$ ), the ionic charge n, and the molar volume  $\Omega$  of solid copper. This simple form captures suppression arising from the polyether coverage (as limited by chloride coverage). The current densities ( $j_{\theta=0,1}$ ) are assumed to exhibit the conventional exponential dependence on overpotential  $\eta$  by

$$\dot{j}_{\theta=0,1}(\eta) = \dot{j}_{\theta=0,1}^{o}(e^{\frac{(1-\alpha_{\theta=0,1})F}{RT}\eta} - e^{-\frac{\alpha_{\theta=0,1}F}{RT}\eta}).$$
 [14]

The applied potential  $V_{app}$  is related to the overpotential at the working electrode through

$$V_{app} = \eta + \phi + E_{rev}$$
[15]

where the potential  $\phi$  within the electrolyte, evaluated at the electrolyte/deposit interface, captures the dissipative losses due to current flow through the electrolyte between the workpiece and the reference electrode. The overpotential driving electrodeposition is referenced to the reversible Nernst potential for the Cu<sup>2+</sup>/Cu reaction ( $E_{rev} = -0.38$  V vs SSE). The reference electrode position was selected so that the simulations had similar ohmic losses to those observed experimentally. The values of  $j_{\theta=1}^{o}$  and  $\alpha_{\theta=1}$  for the fully suppressed surface are obtained by fitting the negative-going voltammetric scans up to the onset of suppression breakdown.<sup>14</sup> The kinetics of metal deposition on polymer-free surfaces are known to be a function of halide coverage; however, for simplicity, the present work uses a single set of  $j_{\theta=0}^{o}$  and  $\alpha_{\theta=0}$  values for deposition on the polymer-free surface.

Table 1. Latameters for min-15 v simulation	Table	I.	Parameters	for	mm-TSV	simulations
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Parameter	Name	Units	Value	References
Electrochemical Cell Geometry				
mm-TSV diameter	$D_{via}$	$\mu$ m	125	_
mm-TSV height	H	μm	600	_
Cell width	$W_{cell}$	μm	250	_
Boundary layer thickness	δ	$\mu$ m	22	40
Reference/counter electrode distance	$L_{RE} + \delta$	cm	1	_
Electrolyte Parameters				
Bulk concentration Cu <sup>2+</sup>	$C_{Cu}^{o}$	$mol \cdot L^{-1}$	1	_
Bulk concentration Cl <sup>-</sup>	$C_{Cl}^{o}$	$\mu \text{mol} \cdot L^{-1}$	80	_
Bulk concentration polyether (Poloxamine Tetronic 701)	$C_P^o$	$\mu \text{mol} \cdot L^{-1}$	40	_
Diffusion coefficient $Cu^{2+}$	$D_{C''}$	$cm^2 \cdot s^{-1}$	$5  imes 10^{-6}$	42
Diffusion coefficient Cl <sup>-</sup>	$D_{Cl}$	$\text{cm}^2 \cdot \text{s}^{-1}$	$9 \times 10^{-6}$	14
Diffusion coefficient polyether (Poloxamine Tetronic 701)	$D_P$	$cm^2 \cdot s^{-1}$	$1 \times 10^{-6}$	44-46
Imposed inlet velocity	Ū,	$m \cdot s^{-1}$	0.4	_
Fluid density	$\rho_f$	kg⋅m <sup>-3</sup>	1182	41
Fluid viscosity	$\mu_f$	$kg \cdot (m \cdot s)^{-1}$	0.0024	41
Electrolyte conductivity	$\kappa$	$S \cdot m^{-1}$	15.26	Measured
Reversible Potential	$E_{rev}$	V	-0.38	Measured
Adsorbate Parameters				
Saturation chloride coverage	$\Gamma_{Cl}$	$mol \cdot m^{-2}$	$1.62 \times 10^{-5}$	14
Saturation suppressor coverage	$\Gamma_P$	$mol \cdot m^{-2}$	$9.2  imes 10^{-8}$	47
Chloride adsorption kinetics	$k_{Cl}^+$	$m^3 \cdot mol^{-1} \cdot s^{-1}$	20	
Chloride deactivation kinetics	$k_{Cl}^{-}$	$1 \cdot m^{-1}$	$1.5 \times 10^{7}$	14
Suppressor adsorption kinetics	$k_P^+$	$m^3 \cdot mol^{-1} \cdot s^{-1}$	2500	14
Suppressor deactivation kinetics	$k_P^-$	$1 \cdot m^{-1}$	$1 \times 10^7$	14
Initial chloride & polymer coverages	$\theta_{i,o}$		0	
Electrochemical Kinetics	1,0			
Unsuppressed Cu exchange current density	$j_0^o$	$A \cdot m^{-2}$	20	14
Suppressed Cu exchange current density	$i_1^o$	$A m^{-2}$	0.13	14
Unsuppressed charge transfer coefficient	$\alpha_0$	_	0.5	14
Suppressed charge transfer coefficient	$\alpha_I$	_	0.5	14
Cu ionic charge	n	—	2	_
Cu molar volume	Ω	m <sup>3</sup> ·mol <sup>−1</sup>	$7.1 \times 10^{-6}$	_
Miscellaneous				
Applied potential (potentiodynamic case)	$V_{app}$	V	-0.51 to $-0.56$	_
Applied current (galvanostatic case)	i <sub>app</sub>	$mA \cdot cm^{-2}$	-4.4	_
Pretreatment time	t <sub>pre</sub>	S	120	—
Pretreatment potential (potentiodynamic case)	$V_{pre}$	V	-0.40	—
Pretreatment current (galvanostatic case)	i <sub>pre</sub>	mA·cm <sup>-2</sup>	-0.044	—
Temperature	Т	K	293	_

The local current density at the electrode is equated to the Cu<sup>2+</sup> flux from the electrolyte onto the electrode interface (outward surface normal  $\hat{n}$ ) according to

$$\frac{1}{nF}\vec{j}_{Cu}\cdot\hat{n} = -(z_{Cu}u_{m,Cu}FC_{Cu}\nabla\phi + D_{Cu}\nabla C_{Cu} - C_{Cu}\vec{u})\cdot\hat{n}.$$
[16]

Similarly, the normal fluxes of chloride and polyether from the electrolyte to the interface are equated to the rates of their adsorption yielding

$$-(z_{Cl}u_{m,Cl}FC_{Cl}\nabla\phi + D_{Cl}\nabla C_{Cl} - C_{Cl}\vec{u}) \cdot \hat{n} = \Gamma_{Cl}k_{Cl}^{+}C_{Cl}(1 - \theta_{Cl})$$
[17]

and

$$(D_P \nabla C_P - C_P \vec{u}) \cdot \hat{n} = \Gamma_P k_P^+ C_P (\theta_{Cl} - \theta_P)$$
[18]

with saturation coverage values,  $\Gamma_i$ , estimated from literature.<sup>14,48,47,49</sup> As stated previously, the ( $\theta_{Cl} - \theta_P$ ) term captures the requirement that suppressor adsorption only occurs at chloride covered surface sites.

The full system of equations is solved numerically in 3D using a finite element method employed in the COMSOL Multiphysics version 5.5 software package and the default solver, implementing the following modules: tertiary current distribution, laminar flow, separate coefficient form boundary partial differential equations for both chloride and suppressor, and deformed geometry. 2D triangular mesh elements are more highly refined along the electrode interface, being a maximum of 25  $\mu$ m and minimum of 12.5  $\mu$ m on each side. 3D tetrahedral domain mesh elements within the boundary layer are no larger than 31  $\mu$ m on each side; mesh elements outside of the boundary layer are scaled between 31  $\mu$ m and 500  $\mu$ m moving from the workpiece surface toward the reference electrode. Default "boundary layer" mesh elements are also included along the electrode interface. Automatic remeshing is enabled, prompting remesh when the maximum mesh distortion parameter exceeds 4. A moving boundary smoothing parameter of 1, geometry shape order of 1, and Laplace mesh smoothing type are used in the deformed geometry module (see COMSOL documentation for detailed explanation on how these parameters impact moving boundary convergence). The system of equations is solved so that the overall charge imbalance (the fractional difference between the total integrated currents at the counter electrode and working electrode)

is less than 0.8%. The numerical evaluation error, thus, is acceptably small for much of the present work. To give a sense of the computational expense, typical simulations with 15000 domain, 3000 boundary, and 400 edge mesh elements take on the order of tens of hours to compute on a Dell Precision 3630 desktop computer with an Intel Xeon E-2186G CPU @ 3.80 GHz and 64 GB RAM using a Windows 10 Enterprise 64-bit operating system. More powerful computing and/or running in parallel on clusters can improve computation time.

Repeat simulations of the  $4 \times 1$  array result in differing growth profiles between each individual computation that reflect the critical nature of the S-NDR system. An extensive effort was made to explore and identify the cause and/or perturbation responsible for these variations. In the case of fluid flow orthogonal to the array (y-direction) the automatic re-meshing method implemented by COMSOL creates marginally different profiles upon re-mesh for each via, resulting in variation in the passivation time of individual vias in the latter stages of filling as discussed in the next section. However, other simulations did not have an obvious perturbation that could unambiguously account for the observed deviation between initially identical computations. Efforts to eliminate the variation in the commercial program included: reducing the solution tolerance, refining the mesh, switching the solver from *segregated* to fully coupled, adjusting automatic remeshing conditions, and limiting the maximum time-step to 1 s. All of these efforts increased the computation time without yielding identical results in replicate simulations.

#### **Results and Discussion**

Comparison to experimental through-silicon via filling.-Millimeter TSV that were cross-sectioned following 1 h of Cu deposition at the indicated applied potentials (vs a saturated sulfate reference electrode) are shown in Fig. 2a. The transition from passive to active Cu deposition is evident along the sidewalls of the TSV, the domain of active Cu deposition being larger at more negative potentials. The simulations in Fig. 2b qualitatively capture this experimental trend, predicting an upward shift of the activepassive transition along the sidewalls at more negative potentials. Significantly, the chloride concentration contours (color-map scaled to the bulk concentration shown on the right-hand side) approach zero at the location of the active-passive transition. Convective transport is predicted to have minimal influence on deposition at the bottom of the via as evident in the symmetric 0.1 normalized chloride contour line and relatively flat growth front after the first hour of deposition. Higher up in the via, the effect of forced convection is apparent in the slightly asymmetric chloride contours. The convection associated with an imposed velocity of  $40 \text{ cm} \cdot \text{s}^{-1}$ (400 rpm equivalent) effectively shifts the concentration profiles of diffusion-dominated transport of  $Cu^{2+}$  down the via by  $\approx 200 \ \mu m$ , vide infra. A color map of normalized  $Cu^{2+}$  concentration is shown in the unfilled space of the TSV (scale bar on the left-hand side), exhibiting maximum depletion of cupric ion at the via bottom to 70% of its bulk value for the most negative potential examined.

Figure 3a shows the temporal evolution of filling at -0.51 V for the indicated deposition times. After 1 h of deposition an activepassive transition occurs on the lower sidewall with an  $\approx 10 \ \mu m$ thick conformal deposit below. By the end of 2 h superconformal filling of the corner notches at the foot of the via is complete and a transition to bottom-up growth occurs that leads to the development of a concave v-shaped profile. A slight asymmetry is evident in the growth front after 4 h. The origin of symmetry breaking may be related to dispersion in the lithography, i.e., systematic variation of height and/or width of the "foot" around the vias, as convective transport is unlikely to impact the early stages of deposition at a depth of 448  $\mu m$  in the  $\approx 125 \ \mu m$  diameter via. Model predictions in Fig. 3b qualitatively capture the experimental observations, with deposition localized at the via bottom before 2 h followed by a transition to bottom-up fill. Simulations predict a slightly higher deposit profile after 6 h than is observed in the experiments. The difference reflects, in part, the deviation between the dimensions and geometry used for the simulations versus the actual features.

Previous studies of deposition with S-NDR systems have demonstrated complete feature filling by progressively stepping or ramping the potential to more negative values; this method shifts the sidewall active-passive transition point upward permitting gradual filling of the via without void formation.<sup>14,19,26</sup> An additional benefit of the potentiodynamic approach is that the growth front automatically passivates at a distance from the field defined by the increasing transport limited flux of suppressing additives and the applied potential. Figure 4 shows two such potential-stepped waveforms for experimental deposition in the mm-TSV; intervals were 1 h or 1.5 h, as indicated, from -0.51 V to -0.55 V in 10 mV steps, ending with 5 h at -0.56 V in each case. Simulations for the idealized cylindrical via and a via with a recessed concave foot at the bottom corner, representative of the actual features studied, are shown alongside the experimental cross-sections for each potentialstepped waveform. Localized conformal deposition below the active-passive sidewall transition is already evident by the end of the first stage of the stepped waveforms. As the potential is advanced to more negative values the position of the sidewall breakdown systematically shifts upward, accompanied by sustained motion of the bottom surface. Use of a longer fill time at each potential allows more complete filling of the active region in each step, such that by the end of deposition at -0.55 V the deposit height at the via center reaches  $\approx 180 \ \mu m$ , vs  $\approx 100 \ \mu m$  for the shorter potential steps. With the 1 h waveform, the upward shift of the active-passive transition at -0.56 V activates enough of the sidewall that Cu<sup>2+</sup> depletion retards deposition at the bottom of the as-yet unfilled region, with void formation being the end result. The extra 80  $\mu$ m of deposit at the via center from the 1.5 h waveform is sufficient to result in a void-free, nearly filled via by 12.5 h.

Comparison of the simulation to the experimentally filled vias clearly reveals that the experimental vias have larger radii than the targeted value, the via radius increasing with depth due to dispersion during Bosch processing. While simulations were used to explore the impact of the foot, the effect of widening was not evaluated. In all simulations (both waveforms and geometries) deposition is initially localized toward the bottom of the via. The cylindrical vias transition to a v-notch profile sooner than the footed vias for which additional deposition volume is required at the bottom. Thus, the deposit height at the center of the cylindrical vias is higher at each potential than for the footed vias. This "lag" in the central deposit height is enough to create a seam in the simulated waveform with 1 h steps (the sidewalls impinge at 7.13 h) whereas the cylindrical via for the same waveform fills halfway up in a seamfree manner until passivation occurs. For the waveform with 1.5 h steps, passivation is predicted to happen at essentially the same midheight location with both geometries despite different evolution during the course of filling. Simulated profiles between 7.5 h and 12.5 h (not shown) indicate that the idealized geometry passivates at 8.75 h while the footed geometry passivates at 9.3 h, the difference being associated with the time needed to fill the foot. The model captures the experimental behavior very well from -0.51 V to -0.55 V. However, electrode passivation is predicted much earlier, i.e., farther down, than is observed experimentally. An analogous discrepancy was noted for Cu deposition in microscale annular TSV in an electrolyte of the same composition.<sup>14</sup> The deviations in that study also increased at more negative potentials, suggesting that other processes disruptive to passivation, effectively altering  $k_i^+$  and  $k_i^-$  of the additives, might be at play.

*Computational exploration of operating conditions.*—The influence of convection in terms of the substrate rotation rate on mm-TSV filling was not detailed in the recent experimental study. However, it was noted that rotation rates greater than 100 rpm were necessary to achieve effective localization of copper deposition to the via bottom, with 400 rpm being utilized for most filling



**Figure 2.** (a) Cross-sectioned mm-TSV after 1 h of Cu deposition at the indicated applied potentials in electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET (preceded by 2 min at -0.40 V where negligible Cu deposition occurs while the electrolyte mixes with the ethanol pretreated, wetted features). The patterned substrates were rotated like a helicopter blade at 400 rpm during deposition. Insets are 2× relative magnification. (b) Simulations from the S-NDR model for the above experimental conditions with an imposed inlet velocity  $U_x$  of 40 cm·s<sup>-1</sup>. Isocontours of chloride concentration are overlaid on color maps of copper concentration, both scaled by their respective bulk values. The simulations consider the idealized via pictured in Fig. 1, ignoring the foot in the experimental features.



**Figure 3.** (a) Cross-sectioned mm-TSV showing Cu filling after the indicated deposition times at -0.51 V in electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET (preceded by 2 min at -0.40 V where negligible Cu deposition occurs while the electrolyte mixes with the ethanol pretreated, wetted features). The patterned substrates were rotated like a helicopter blade at 400 rpm during deposition. Insets are 2× relative magnification. (b) Simulations from the S-NDR model for the experimental conditions with an imposed inlet velocity  $U_x$  of 40 cm·s<sup>-1</sup>. The simulations consider the idealized via pictured in Fig. 1, ignoring the foot in the experimental features.



**Figure 4.** Cross-sectioned mm-TSV (middle) and simulated deposit profiles (outside) showing the evolution of Cu filing during deposition at a sequence of potentials stepped from -0.51 V to -0.56 V in 10 mV increments. Deposition times were 1 h (left) or 1.5 h (right) at each potential from -0.51 V to -0.55 V, finishing with 5 h at -0.56 V, for total deposition times of 10 h and 12.5 h, respectively. The electrolyte contained 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. The patterned substrates were rotated like a helicopter blade at 400 rpm during deposition. Simulations were done for idealized cylindrical vias and footed vias that resemble the experimental features with an imposed inlet velocity  $U_x$  of 40 cm·s<sup>-1</sup>. Aspect ratios of the vias in the simulations, drawn to scale, make clear that the experimental radii are larger than the target value.

experiments and thus being modeled herein. In contrast, annular microscale TSV readily exhibited localized bottom-up filling at rotation rates lower than 100 rpm (in fact, down to 0 rpm).<sup>12-14</sup> To gain more insight, simulations exploring the influence of forced convection and buoyancy driven flow on the growth front evolution for the 1.5 h potential-step waveform detailed above are presented in Fig. 5. The transition of the Peclet number (Pe), representing the locally defined ratio of forced convection to diffusive transport (for  $Cu^{2+}$ ), across the value of unity is mapped at 5 min into the deposition process. The value of Pe = 1 marks the transition from dominance of chemical transport by convection to dominance by diffusion. For the  $0 \text{ cm} \cdot \text{s}^{-1}$  flow condition the buoyancy driven velocity in the z-direction is represented in the color map with velocity vectors in the xz plane at 5 min. For inlet velocities of  $1 \text{ cm} \cdot \text{s}^{-1}$ , 40 cm $\cdot \text{s}^{-1}$ , 80 cm $\cdot \text{s}^{-1}$ , and 200 cm $\cdot \text{s}^{-1}$  the position of the Pe = 1 contour for Cu<sup>2+</sup> at the center of the via moves progressively farther from the via opening: 207  $\mu$ m, 323  $\mu$ m, 345  $\mu$ m, and 366  $\mu$ m, respectively. Note that, when plotted for chloride, the distance of Pe = 1 from the opening at the via middle is shallower: 175  $\mu m$ , 280  $\mu$ m, and 310  $\mu$ m, and 342  $\mu$ m with increasing velocity. Streamlines in the flow fields from 2 h to 12.5 h reveal the eddy

location within the vias without regard to the magnitude of the local flow velocity. A prior simulation of convective flow in mm-TSV also predicts two counter-rotating vortices near the via opening with diffusive only or buoyancy driven flow lower in the via.<sup>28</sup> The pink line in each image represents an isocontour of flow velocity equal to 0.1% of the inlet flow rate (i.e.,  $0.2 \text{ cm} \cdot \text{s}^{-1}$  for the simulations in the top row), providing a qualitative indicator of the effective reach of significant convection within the via. The position of the fractional iso-velocity line is similar for all four flowrates. As a result, flow velocities at a given depth scale with the inlet flow rate. The growth front profiles following metal deposition at 80 cm s<sup>-1</sup> and 40 cm s<sup>-1</sup> inlet velocities are nearly identical. At 8 h the  $80 \text{ cm} \cdot \text{s}^{-1}$  condition yields a slightly higher and more symmetric final deposit profile although the additional convection does not significantly alter cupric ion depletion toward the via bottom. The minimum copper concentration in the volume throughout the filling evolution in these two simulations is  $0.43 \text{ mol} \cdot \text{L}^{-1}$  for  $40 \text{ cm} \cdot \text{s}^{-1}$  and  $0.55 \text{ mol} \cdot \text{L}^{-1}$  for  $80 \text{ cm} \cdot \text{s}^{-1}$ , both occurring during the earliest potential step. The lower natural convection eddies at 2 h disappear by 4 h as Cu fills the bottom of the via and cupric ion depletion lessens. In both cases, the flux of the suppressing additives is sufficient to passivate the via



**Figure 5.** Simulations of the 1.5 h waveform shown in Fig. 4 at the indicated inlet velocities and deposition times. The magenta contour line represents 0.1% of the imposed velocity  $U_x$ . The ratio of convective flux to diffusive flux (i.e., Peclet number, Pe) is represented in a colorized plot at 5 min into each deposition process. The color scale saturates beyond 0.9 and 1.1 to emphasize the boundary at which transport transitions from convective-dominant to diffusive-dominant, corresponding to a value of 1.0. Streamlines are normalized to highlight eddy locations within the via. The 5 min image for the 0 cm·s<sup>-1</sup> condition shows the z-direction velocity in the color map and velocity vectors in the xz plane.

shortly after 8 h (essentially identical deposit height at 12.5 h). Increasing the velocity to 200 cm·s<sup>-1</sup> results in the appearance of a third eddy at 6 h and slightly earlier passivation of the deposition process. The higher rate of convection produces a smaller fractional increase in cupric ion flux relative to chloride flux, driving passivation deeper into the via by  $\approx 60 \ \mu m$ .

Reducing the inlet velocity to  $1 \text{ cm} \cdot \text{s}^{-1}$  significantly changes the predicted growth profile and also removes the second counterrotating eddy. Greater depletion of copper at early times (as low as  $0.28 \text{ mol} \cdot \text{L}^{-1}$  during the first potential step) produces natural convection eddies (clear in these unscaled maps) at the via bottom at 2 h and leads to reduced deposition by 4 h. As the potential is

stepped more negative, metal ion depletion prevents deposition on the bottom and lower sidewall surfaces from keeping up with the advance of the active-passive transition up the sidewall. The result is void formation by 7 h. Simulation in the absence of forced convection also shows localization of deposition to the bottom of the via at 2 h. However, metal ion depletion has already placed the location of maximum thickness high up in the active sidewall region. The minimum copper concentration in the via (at the bottom) is below  $0.26 \text{ mol} \cdot \text{L}^{-1}$  for the entire first potential step at -0.51 V, and as before leads to counter-rotating eddies due to natural convection. As potential is stepped further negative, the active-passive transition shifts upward, with deposition primarily occurring along the sidewall as the developing reentrant thickness gradient ever more clearly manifests the underlying metal ion gradient. By the final potential step (-0.56 V at 7.5 h) the active-passive transition is three-quarters of the way up the via sidewall, and preferential thickening of the sidewall deposits results in a large void being formed by 9.4 h.

The predicted profiles in Fig. 5 provide insight into experimental conditions for feature filling and wafer-level pattern plating in general. The selection of a  $40 \text{ cm} \cdot \text{s}^{-1}$  inlet velocity corresponds, approximately, to workpiece locations 1 cm from the center of rotation at 400 rpm through the otherwise stagnant electrolyte. Accepting this simplification, the nearly identical deposit profiles at  $80 \text{ cm} \cdot \text{s}^{-1}$  and  $40 \text{ cm} \cdot \text{s}^{-1}$  are consistent with observed uniformity of experimental mm-TSV filling for centimeter size fragments of the patterned substrates, and the prediction of only incremental change at 200 cm·s<sup>-1</sup> suggests the feasibility of filling across significantly larger substrates. This indicates that reasonable processing windows should be available for electroplating cells that generate uniform flow fields such as rotating disk electrodes, fountain cells, and even for time average uniform plating environments such as paddle cells. In the present simulations the inlet velocity had to be reduced to 1 cm s<sup>-1</sup> before cupric ion supply was insufficient to permit bottomup fill, while simulations for  $4 \text{ cm} \cdot \text{s}^{-1}$ , not shown, still exhibit bottom-up fill. Increasing the rotation from zero serves to decrease the effective aspect ratio of the feature to be filled, as convection enhances metal ion transport farther down the via, when the deposition process is limited by the available Cu<sup>2+</sup> flux. On the other hand, the enhanced flux of suppressing additives at higher flow rates favors earlier termination of the filling process by passivation. Optimization of the influence of forced convection on feature filling involves balancing these trends against the effects of additive concentration and applied potential.

Simulations reveal the detailed coupling between mass transport and deposition kinetics as the overpotential is increased for full feature filling. This approach requires tuning of the applied potential waveform to optimize filling. The rapid variation in the local deposition rate with each potential step will also impact the deposit microstructure, another opportunity for optimization. An alternative approach is galvanostatic, or galvanodynamic deposition that is well-aligned with conventional industrial electroplating practice based on a 2-electrode configuration with a power supply that provides both operational simplicity and cost advantages in process control. Consequently, simulations of galvanostatic copper electrodeposition in mm-TSV were explored. Figure 6 shows via filling simulations for an applied current density (the imposed current divided by the projected area  $W_{cell}^2$  of  $-4.4 \text{ mA} \cdot \text{cm}^{-2}$  and inlet velocity of 40 cm $\cdot$ s<sup>-1</sup>. If all surfaces, i.e., including the via sidewalls, were actively subject to conformal growth then the actual initial applied current density would correspond to only  $-0.92 \text{ mA} \cdot \text{cm}^{-2}$ . However, with the suppressor additives accumulating on the freesurface and via sidewalls, the applied current can quickly be concentrated on small active regions giving rise to significantly higher local current densities. In the case of perfectly uniform deposition on the flat via bottoms alone this would correspond to a local current density of -22 mA·cm<sup>-</sup>

Simulation of galvanostatic deposition begins with idling the workpiece for 2 min at 1% of the target applied current to allow mixing between the ethanol-wetted vias and the electrolyte.

Following application of the target current, copper deposition quickly localizes to the bottom of the via with conformal growth on all surface segments below the sidewall active-passive transition; the result is analogous to the initial deposit evolution observed for the potential-stepped waveform in Fig. 4. After 4 h, deposition propagates with the bottom surface and sidewalls merging to form a v-shaped notch that flattens by 8 h. At this juncture the growth front position is close to where Pe = 1, and convection becomes increasingly important in providing the needed Cu<sup>2+</sup> flux. This is evident in the decreased thickness of the Cu<sup>2+</sup> depletion gradient at the growth front between 6 h and 8 h. By 10 h an instability develops with further localization of Cu deposition to a smaller region within the via. Both the time increment and the concentration range in the color map are reduced to highlight these changes. With further deposition the smaller active zone migrates across the available growth front (image is a 2D slice of a 3D geometry, thus, not a complete rendering) breaking its cylindrical symmetry. However, as the more advanced surface receives a higher suppressor flux the region passivates and deposition shifts to the slightly more recessed surface segments that were "left behind." Over the next two hours this process averages out such that at 12.5 h the recessed growth front in the via is almost symmetric again. However, closer inspection reveals that the onset of fluctuations at 10 h is coincident with an expansion of the electroactive area as the growth front begins to extend up the side walls and onto the free surface. The build-up on the sidewalls is asymmetric, with a larger thickness on the "downstream" side. The expansion of electroactive area leads to a decrease in the local current density within the via as larger segments of the free surface become active. Unlike the potentiodynamic approach where the deposit ultimately passivates due to increased suppressor flux, galvanostatic control necessarily continues to drive deposition. The increasing suppressor flux is accompanied by increasing driving force to maintain deposition (i.e., increased overpotential). The active region moves to where transport constraints provide the least suppression, until localization disappears entirely and deposition occurs uniformly over the entire electrode. As with potential control, current control also requires thoughtful selection of operating conditions. For example, simulations for a current density only  $2 \times$  higher than the value used for the simulations in Fig. 6 ( $-8.8 \text{ mA} \cdot \text{cm}^{-2}$  as estimated by projected area) predict formation of a large void as shown in Fig. 7. The larger applied current produces a higher active-passive transition point, the taller region of active deposition beneath yielding more significant Cu<sup>2+</sup> depletion, resulting in the maximum deposition rate occurring more than a third of the way up the via.

Simulation of feature arrays.—The competition between transport of suppressor species and potential driven activation of the passivating adlayer dictates the distribution of active deposition within the via. For both potential and current controlled techniques rapid transport of suppressing additives passivates the field and upper walls of the via, while transport-limited additive depletion linked primarily to chloride consumption within the via maintains active deposition toward the bottom. The critical behavior in S-NDR systems naturally tends to activate the electrode where charge transfer resistance or inhibition is smallest. This can lead to a dynamic shift of deposit localization due to small variations in local conditions, as noted in the predictions shown in Fig. 6. Thus far, all simulations of the S-NDR model have been for individual features. This contrasts with the multi-feature arrays used in the experiments. As captured in the experimental results shown in Figs. 3 and 4, little variation in the deposit profile is observed across a range of vias on an individual wafer fragment in the low chloride (0  $\mu$ mol·L<sup>-1</sup> to 100  $\mu$ mol·L<sup>-1</sup>) electrolyte.<sup>14,19–22,26,27</sup> However, this likely reflects averaging due to the macroscopically turbulent flow associated with the asymmetric specimen shape and atypical "helicopter blade" rotational geometry. Indeed, in other experiments, both potentiostatic and galvanostatic, significant variation in via filling within a given array has been reported for various stages of the



**Figure 6.** Simulations of galvanostatic deposition at  $-4.4 \text{ mA} \cdot \text{cm}^{-2}$  (based on projected area of the cell geometry) for the indicated deposition times with an imposed lateral inlet velocity  $U_x$  of 40 cm·s<sup>-1</sup>. Isocontours of chloride concentration are overlaid on color maps of copper concentration, both scaled by their respective bulk quantities. Images between 10.5 h and 12.5 h show a smaller range for copper concentration to emphasize the radial movement of localization of deposition within the via.

process.<sup>13,26-28</sup> The global coupling between the imposed control condition and the non-uniform patterned workpiece combined with the critical nature of local bifurcation reactions suggest that such variations in filling might not be uncommon, especially given additional variations of the electrical response and mass transport conditions typical of many electroplating cells. Accordingly, filling of a  $4 \times 1$  array (x-direction) of mm-TSV were examined using the same conditions as the 1.5 h potentiodynamic waveform in Fig. 4. For the simulations shown in Fig. 8 the cyan line represents the final growth position for a single run with forced convection imposed in the y-direction (into the page). It is seen that through the first 5 h all four vias grow at the same rate, with equivalent deposit profiles predicted for both flow directions. After 6 h, the vias begin to individually, and dynamically, passivate and reactivate (the absence or presence, respectively, of cupric depletion for flow in the x-direction being a clear indicator of each state): the 3rd via passivates by 6 h, the 2nd passivates by 7 h, and the 1st and 4th passivate while the 3rd reactivates by 8 h. By 10 h all four vias are fully passivated, similar to the individual via simulation presented in Fig. 4 but with a

range of final fill heights. Experimentally, local variation in chemical and electrical gradients may be expected due to the difficulty of producing a fully symmetric system. Computationally, the variation in deposit uniformity in the  $4 \times 1$  array reflects a shift in the active region similar to what is observed in Fig. 6; non-uniformity in individual vias appears when slight variations in the flux of inhibitor begins to overpower the potential-driven consumption and activation. It is noteworthy that variation between vias becomes evident as convection plays an increasingly larger role in transport of all species into the vias and, in the present case, fluctuations arise that are related to numerical noise or computational perturbations. In fact, a simulation of the same  $4 \times 1$  array but without additives and in a through-mask configuration (i.e., sidewalls and top of features are insulating) results in a comparatively minor variation of the fill height for each hole; via heights from left to right are 96.56  $\mu$ m, 96.55  $\mu$ m, 96.45  $\mu$ m, and 96.59  $\mu$ m after 5 h of deposition. That the minimum value (albeit barely so) occurs on the 3rd via while the 3rd via also passivates first in Fig. 8, may indicate a subtle systemic asymmetry, possibly related to meshing. If so, the initially small



**Figure 7.** Simulations of galvanostatic deposition at  $-8.8 \text{ mA} \cdot \text{cm}^{-2}$  (based on projected area of the cell geometry) for the indicated deposition times with an imposed inlet velocity of 40 cm s<sup>-1</sup>. Isocontours of chloride concentration are overlaid on color maps of copper concentration, both scaled by their respective bulk quantities.



**Figure 8.** Simulations of the filling of a linear array  $(4 \times 1)$  of mm-TSV using the 1.5 h potential waveform shown in Fig. 4 for the indicated deposition times with an imposed inlet velocity in the x-direction,  $U_x$ , of 40 cm·s<sup>-1</sup>. Isocontours of chloride are overlaid on color maps of copper concentration (except for the 10 h image), both scaled by their respective bulk values. Growth fronts for a simulation with inlet velocity imposed in the y-direction,  $U_y$ , (cyan) are superimposed on each of the images.

difference of  $\approx 0.1 \ \mu m$  that leads to dynamic passivation and reactivation of individual vias speaks to the critical nature of the system.

Simulations of galvanodynamic deposition at  $-4.4 \text{ mA} \cdot \text{cm}^{-2}$  in the same  $4 \times 1$  array with inlet velocity imposed in the x-direction are presented in Fig. 9. Computations were repeated with flow in the

y-direction (cyan line). As with the potentiodynamic waveform, galvanostatic deposition is uniform across the array until 5 h, and by 7 h the 2nd via has passivated. For fluid flow in the y-direction the 3rd via has passivated instead. As with the potentiodynamic case, numerical noise or perturbations associated with the computational solver are the most likely trigger for these variations. By 9 h, the 2nd



**Figure 9.** Simulations of galvanostatic deposition at  $-4.4 \text{ mA} \cdot \text{cm}^{-2}$  (based on projected area of the cell geometry) for a linear  $4 \times 1$  array of mm-TSV at the indicated deposition times with an imposed inlet x-direction velocity of  $40 \text{ cm} \cdot \text{s}^{-1}$ . Color maps of normalized copper concentration are shown in the unfilled volume of the TSV. Growth fronts for a simulation where the inlet velocity is instead imposed in the y-direction (cyan) are superimposed on each image.

via has re-activated while the other three vias now appear fully passivated; thus, essentially all of the applied current is localized to the 2nd via, evident by the more substantial  $Cu^{2+}$  depletion in the color map. A similar incident, except occurring in the 3rd via, is apparent for the y-velocity simulation.

Instabilities and variations in experimental S-NDR systems can arise from inhomogeneities related to transport (i.e., convection, electromigration, etc) or charge transfer and crystallization (i.e., morphology and microstructure, etc). The simulations presented here, however, represent a nominally homogeneous metal interface and symmetric transport conditions, particularly for flow orthogonal to the via array (y-direction). The instabilities that arise in Figs. 8 and 9 are triggered by computational noise or perturbations associated with the computational software. Figure 10 shows an example of a perturbation caused by the automatic remeshing algorithm that ultimately results in passivation of the 3rd via for the simulation presented in Fig. 8 where the velocity is imposed in the y-direction and the depletion profiles between features are not expected to overlap. The solver automatically re-meshes the geometry when the square root of the maximum element distortion (see COMSOL documentation for additional details) exceeds a value of 1.2. After re-mesh at approximately t = 6.5 h the deposition velocity at the bottom of via 3 increases faster than the others until t  $\approx 6.85$  h when it sharply quenches. The growth profiles immediately before and after re-mesh in Fig. 10b clearly display the different adjustment of interface position that occurs during re-meshing of the two vias. This difference, approximately 5  $\mu$ m along the midline, accelerates deposition in via 3 so that filling in it advances well ahead of that in the other vias. Eventually, the increased additive flux at via 3 due to its higher position quenches deposition. The associated relaxation of the ohmic drop sustains deposition in the other vias past that in via 3. The coupling between individual via passivation and iR relaxation continues until each individual via passivates at a different height. This phenomenon is accentuated by the fact that the simulation has only 4 features. In a practical plating application, the corresponding fractional drop in iR due to passivation of a single via will be less significant for substrates having 100 s or 1000 s of features.

#### Conclusions

A Cu electrodeposition suppression model based on the formation and breakdown of a poloxamine-chloride inhibition adlayer is compared to experimental feature filling of millimeter-scale through-siliconvias. Coupling of additive transport and potential-dependent activation of the passivated interface directs localization of copper deposition within the via; operating conditions such as applied potential and flowrate dictate the height of the active-passive transition for a given electrolyte composition. Simulations capture the upward shift in the active-passive position at more negative potentials as well as the transition from sidewall deposition to bottom-up filling that are observed experimentally. Potential-stepped waveforms take advantage of the upward shift in active-passive position and, with some optimization, enable millimeter TSV to be filled in 12.5 h. Simulations, however, predict passivation near the middle in the via, below where it is observed experimentally. Accurate prediction of chemical transport in these 125  $\mu$ m diameter and 600  $\mu$ m deep vias requires calculation of convective flow fields. Simulation using the Navier–Stokes equation indicates a  $40 \text{ cm} \cdot \text{s}^{-1}$  flowrate (400 rpm equivalent rotation rate) shifts the effective diffusive boundary layer down 200  $\mu$ m into the via. Operationally, this effectively decreases the aspect ratio of the feature to be filled. At lower convection rates,  $1 \text{ cm} \cdot \text{s}^{-1}$  or less,  $\text{Cu}^{2+}$  flux is insufficient for deposition to fill from the bottom of the via before the applied potential is stepped more negative, and thereby results in prediction of void formation. The simulations make clear that the derived increase of metal ion transport underlies the experimental need for enhanced flow to observe localized, bottom-up filling in these very large features under the present conditions.

Simulations of current-controlled deposition predict that the millimeter TSV can be filled using a single applied current to similar height as was obtained using the potentiodynamic waveforms. The filling profiles in the earlier stages are like those seen for the potentiodynamic case, but significant differences become evident as the growth front becomes sufficiently high in the vias. With the increased flux of chloride and minimal cupric ion depletion the galvanostatic simulations predict further area reduction and localized migration of the active deposition region within the via. Coincident with this, new active zones begin to develop on the remaining sidewalls and free surface where the convolution of area change,



**Figure 10.** Evidence of a computationally induced perturbation that triggers further instability during simulation of potentiodynamic deposition in a linear  $4 \times 1$  array of mm-TSV with inlet velocity imposed in the y-direction (cyan line from Fig. 8). (a) Plot of deposition velocity at the bottom of each individual via and the re-mesh condition imposed by the automatic re-meshing algorithm. (b) Deposit profile immediately before and after re-mesh for the middle two vias.

local current density, and additive flux lead to complex and oscillatory shape evolution.

Simulations of both potentiodynamic and galvanostatic deposition in  $4 \times 1$  arrays of mm-TSV predict non-uniformity in the deposit profile across the array in agreement with that seen in experiments.<sup>27,28</sup> In both cases, deposition is initially uniform across all four vias. However, individual vias begin to passivate and reactivate dynamically as filling advances and the flux of suppressor additive can vary significantly. For potentiodynamic deposition eventually all four vias spontaneously passivate, although at different heights. In contrast, under galvanostatic control the growth process can not terminate but rather can be redistributed, with the cumulative deposition being determined by the duration and magnitude of the applied current. For the conditions examined, the competition between deposition and passivation leads to localization of deposition to a single via within the array that corresponds to a nominal  $4 \times$  increase in the local current density. The mismatch with the available flux leads to the activepassive sidewall transition point advancing rapidly resulting in incipient formation of a small void. While modeling of individual

vias captures a range of experimental observations, the critical nature of the S-NDR model yields variability when extended to simulations of via arrays that has been alluded to although not widely discussed in experimental work.<sup>12,13,27,28</sup>

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