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Modeling Electrochemical Deposition of Aluminum from Ionic Liquids for PCB Applications

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Abstract
The present paper describes the development of simulation models for the electrochemical deposition of aluminum on a metallized PCB substrate containing through holes. During the deposition process, the Al-species is reduced from a non-aqueous electrolyte based on $AlCl_3$ and [EMIm]Cl – an ionic liquid. In order to represent physical phenomena over three orders of magnitude, a two stage modeling approach was utilized. In the first stage, fluid dynamics within the process chamber were characterized using a macroscale model based on CAD data. In the second stage, obtained results were implemented in a microscale model for calculating the electrolyte flow and resulting ion transport in the vicinity of the via to be coated. Local aluminum deposition rates were calculated and layer geometries were qualitatively compared to experimental data.

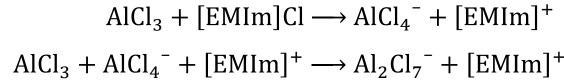
Keywords: Multiphysics Simulation, Electroplating, Aluminum, Ionic Liquid Electrolytes.

Introduction
While copper remains the dominant material for conduction paths in printed circuit board (PCB) applications, both technological and economic reasons have been motivating research on substituting copper with aluminum (Al) [1]. Despite its 60 % higher specific electrical resistance, aluminum features twice the conductivity of copper per weight, enabling lighter weight applications where volume is no major constraint such as in aerospace technology. Additionally, it excels at superconductivity in low-temperature quantum computing environments [2].
Electroplating is an established method for producing metallic layers and patterns on circuit board substrates. Here, an electric current is applied between the cathodic substrate and an anode, thus reducing the metal ions electrochemically and forming a metallic layer at the substrate surface. One major obstacle for wide spread usage of Al for PCB applications arises from its highly negative standard electrode potential, preventing electrochemical deposition from aqueous electrolytes. To address this limitation, ionic liquids (IL) – organic salts in liquid state at process temperature – mixed with Al salts can be utilized. One of the most investigated IL for the deposition of Al is the eutectic mixture of 1-ethyl-3-methyl-imidazolium ([EMIm]Cl) and $AlCl_3$. In this configuration, the deposition of metallic Al is only possible from Lewis acidic melts containing the easily reduceable $Al_2Cl_7^-$ anion [3]. The underlying reaction kinetics have been studied and described in great detail by Böttcher *et al* [4].
While enabling electrochemical deposition of Al, these IL-based electrolytes bring another challenge regarding the coating of vertical interconnect accesses (vias), which electrically connect both sides of the PCB substrate. In order to supply these through holes with fresh electrolyte, an additional convective flow can be integrated into the electroplating process. Due to the physical properties of ILs, the dynamic viscosity of these electrolytes is one order of magnitude higher than that of aqueous electrolyte solutions, which results in unfavorable flow conditions. In this study, a method to increase electrolyte replacement within these vias by means of a controlled substrate movement between two opposing electrode plates inside the electrolyte bath setup is modeled and characterized.

Theory
During electrochemical metal deposition, physical phenomena from the fields of electrodynamics, fluid dynamics, thermodynamics, resulting ion transport and reaction kinetics as well as the substrate geometry are interacting with each other. Depending on the specific system, their relevance on the resulting geometry of the deposited layer may vary. While fluid and thermodynamic processes might have a decisive influence on a deposition process, a representation of electrochemical mechanisms is fundamentally necessary, as these determine both the migration of charge carriers in the IL and the kinetics of chemical reactions at the electrode surfaces. Only by knowing about the cathode-side charge exchange, the local rate of material deposition and thus the layer geometry can be calculated via Faraday's law. During the process to be modeled, the process chamber is actively kept at a constant temperature.

Chemical Reactions
The deposition of aluminum from ILs, due to the limited cathodic stability of the organic cation, is only possible from Lewis acidic electrolytes, in

which $Al_2Cl_7^-$ is formed by a molar excess of $AlCl_3$ [3]:



$$\mathrm{AlCl_3 + [EMIm]Cl \longrightarrow AlCl_4^- + [EMIm]^+}$$

$$\mathrm{AlCl_3 + AlCl_4^- + [EMIm]^+ \longrightarrow Al_2Cl_7^- + [EMIm]^+}$$

The overall reduction of Al consists of several chemical and electrochemical steps, which can be summarized to a net equation involving the transfer of three electrons [4]:

$$\mathrm{4\ Al_2Cl_7^- + 3\ e^- \longrightarrow Al + 7\ AlCl_4^-} \quad (1)$$

This deposition process is already possible at room temperature and does not require strong complexing agents. The reaction rate can be transposed into a local electric current density j according to the Butler-Volmer equation for mass transfer-influenced conditions:

$$j = j_0 \underbrace{\left\{C_{\mathrm{ox}} \exp\left[\frac{\alpha_{\mathrm{a}} z e \eta}{k_B T}\right]\right.}_{\text{Oxidation at anode}} - \underbrace{\left.C_{\mathrm{red}} \exp\left[-\frac{\alpha_{\mathrm{c}} z e \eta}{k_B T}\right]\right\}}_{\text{Reduction at cathode}} \quad (2)$$

In this general form, indices ox / a and red / c correspond to the oxidation at the anode and the reduction at the cathode, respectively. The expressions $C = c(0,t)/c_{\mathrm{init}}$ can be calculated from the time-dependent ion concentration $c(0,t)$ at the respective electrode surface in relation to the initial concentration c_{init}. There are two rates which determine the current-voltage relationship for an electrode: (i) the reaction rate and (ii) the mass-transfer rate. The slowest of these rates determines the overall rate of the process. If (ii) is much greater than (i), the concentration ratios C can be set to 1. Local reaction kinetics are determined by temperature T, charge exchange ze and the Boltzmann constant k_B. The deposition process of Al is characterized by its exchange current density j_0, charge transfer coefficients α and the activation overpotential $\eta = E - E_{\mathrm{eq}}$ which is defined as the difference between the electrode potential E and the equilibrium potential E_{eq}.

Ion Transport

It is assumed that the total ion flux $\mathbf{N}$ of a species i is composed of three elements according to the Nernst-Planck equation:

$$\mathbf{N}_{\mathrm{i}} = \underbrace{-D_{\mathrm{i}} \nabla c_{\mathrm{i}}}_{\text{Diffusion}} - \underbrace{\mu_{\mathrm{i}} c_{\mathrm{i}} \nabla \phi}_{\text{Electromigration}} + \underbrace{c_{\mathrm{i}} \mathbf{u}}_{\text{Advection}} \quad (3)$$

The diffusive flux is governed by the diffusion coefficient D and against the gradient of the respective concentration c of ion i. Similarly, electromigration can be calculated from its electrical mobility μ and the gradient of the electric potential ϕ. Both D and μ are temperature-dependent properties of the moving chemical species. The third component contributing to the ion transport is the advection according to the flow field $\mathbf{u}$ of the electrolyte.

For the considered electrodeposition process of Al from the $[EMIm]Cl–AlCl_3$ mixture, the ion transport equation (3) can be simplified. Since the Imidazolium ion of the IL is 15 to 40 times more mobile than the $Al_2Cl_7^-$ complex, the latter is only minimally contributing to electrical conductivity of the electrolyte [5]. Therefore, only ion transport by diffusion and advection is of major relevance for the transport of the electroactive Al species. The charge transfer within the electrolyte thus can be described by a constant electric conductivity σ.

Layer Deposition

The deposition rate v_{d} of a metallic layer can be derived using Faraday's law:

$$v_{\mathrm{d}} = \frac{V_{\mathrm{m}} j}{zF} \quad (4)$$

Molar volume V_{m} and valence z, which amounts to the net number of electrons transferred according to the net deposition reaction (1), and Faraday's constant F are invariant parameters. The local electric current density j is calculated from equation (2) and inserted into this relation.

Fluid Dynamics

The electrolyte flow within the process chamber was modeled according to the Navier-Stokes equations and the continuity equation. Preliminary calculations under consideration of the physical properties of the incompressible electrolyte as well as geometric and dynamic conditions yielded Reynolds numbers below 100, indicating laminar flow conditions. The resulting system of equations simplifies to

$$\nabla \cdot \mathbf{u} = 0 \quad (5)$$

and

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = \nu \nabla^2 \mathbf{u} - \frac{\nabla p}{\rho} \quad (6)$$

describing conservation of mass and momentum in a liquid with kinematic viscosity ν and mass density ρ subjected to a pressure gradient ∇p.

Model Descriptions

To represent the electroplating process of Al on a PCB substrate containing vias by simulation, a two-stage modeling approach was developed and implemented in COMSOL Multiphysics. In the first stage, fluid dynamics within the process chamber geometry (~10^{-1} m) imported from CAD data were modeled in 3D. Here an unperforated PCB substrate is fully immersed into the IL and performing an oscillating motion between two electrode plates. This motion was implemented into the model using the Moving Mesh interface. As the IL is comparatively viscous, the resulting electrolyte convection was computed using the Laminar Flow interface. The resulting pressure difference between the opposing surfaces of the substrate was integrated into the second stage of the modeling approach. In this stage, a 2D representation of a via (~10^{-4} m) through the substrate was modeled utilizing rotational symmetry. Based on the pressure data of

the macroscopic CFD model and a given current characteristic, this microscopic model was used to compute ion transport, Al deposition and the resulting layer geometry in the vicinity of the via.

Macroscale Model

In this first model, the electrolyte flow and pressure distribution, resulting from a controlled substrate movement within the process chamber, was calculated. The 3D geometry of process chamber was built from CAD data and is shown in Figure 1.

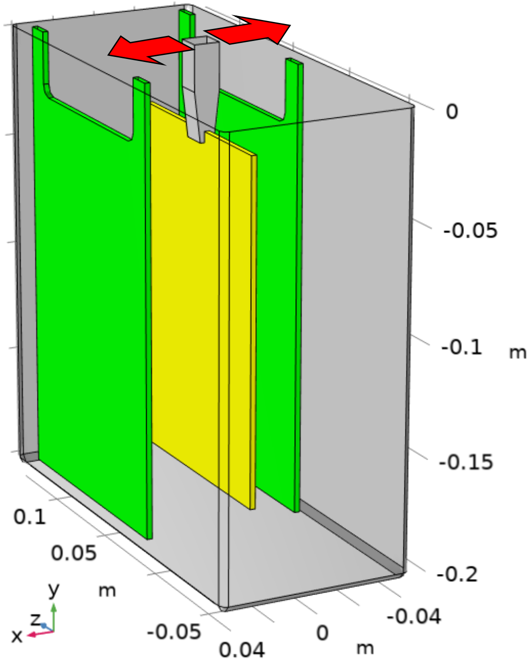


Figure 1: Geometry of the process chamber including a PCB substrate (yellow) which is swayed between two electrode plates (green) arranged on both sides.

In this setup, a container houses two parallelly aligned fixed electrode plates (green) distanced 70 mm from each other. Between them, a 100×160 mm² PCB substrate (yellow) is swayed periodically (red arrows), resulting in a varying distance to an electrode plate from 17.5 mm to 52.5 mm. In Figure 2, this motion is visualized over the course of 1.5 periods T starting from the initial center position. The small gaps between the substrate and the container walls measure 5 mm to the bottom and 14 mm to the closer, left-hand side.

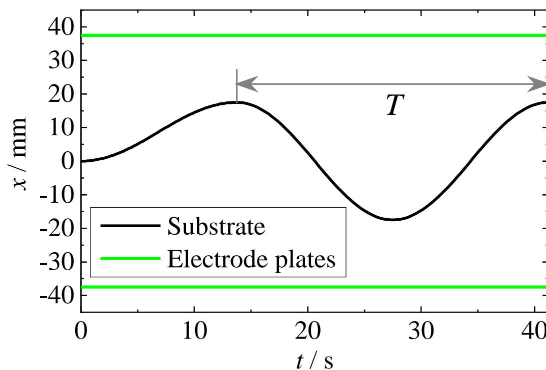


Figure 2: Position of the swaying substrate between the fixed electrode plates.

In order to calculate the resulting isothermal electrolyte flow conditions, only the negative of the process chamber, i. e. the volume filled with electrolyte, was modeled. All relevant process parameters are summarized in Table 1. The physical properties of the IL based electrolyte were obtained experimentally.

Table 1: Definition of process parameters relevant to the macroscale model

Parameter	**Value**
Molar $AlCl_3$ to [EMIm]Cl ratio	1.5:1
Mass density ρ	1.32 kg/l
Dynamic viscosity μ	13.36 mPa s
Oscillation amplitude A	17.5 mm
Oscillation period T	27.49 s
Maximum substrate velocity	4 mm/s

All boundaries enclosing the electrolyte domain were modeled as walls with a no-slip condition. The substrate movement was implemented by deforming the respective boundaries of the electrolyte domain according to Figure 2. The corresponding mesh displacement equation is:

$$\Delta x = \begin{cases} A/2\left[1 - \cos\left(\frac{2\pi}{T}t\right)\right], & 0 \leq t \leq \frac{T}{2} \\ -A\cos\left(\frac{2\pi}{T}t\right), & \frac{T}{2} < t \leq \frac{3}{2}T \end{cases}$$

Due to the continuous mesh deformation, automatic remeshing is initiated when the resulting distortion exceeds a certain threshold. The initial discretized electrolyte domain is shown in Figure 3.

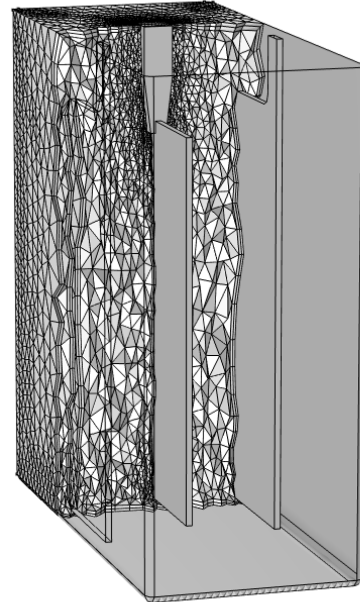


Figure 3: Partial representation of the discretized electrolyte domain.

The mesh consists of tetrahedral elements, connected by pyramids to prismatic elements near walls, totaling approximately 370,000 volume elements. The size of these elements ranges from 0.5 mm to 17 mm.

Microscale Model

The second model was developed to calculate the Al deposition on the PCB substrate within a range of 1 mm around a through hole. In order to accurately implement the convection of the electrolyte caused by the motion of the substrate, pressure boundary conditions based on results of the macroscale model were integrated. The 2D geometry utilizing rotational symmetry is shown in Figure 4.

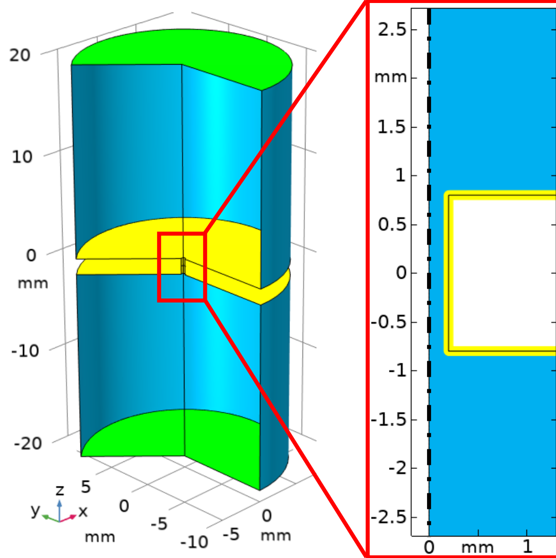


Figure 4: Rotationally symmetric geometry of a PCB substrate (yellow) in the vicinty of a through hole, positioned between two electrodes (green).

The electrolyte domain (blue) is connected through the substrate (yellow) of 1.6 mm thickness by a through hole with a diameter of 0.4 mm. As the deposition process is current-controlled, the distance of the substrate to the electrodes (green) is of minor relevance and was set to 19.2 mm. Supplementary to Table 1, all parameters relevant to the deposition process according to equations (2) and (3) are defined as listed in Table 2.

Table 2: Additional process parameters relevant to the deposition process in the microscale model.

Parameter	Value
Electrolyte conductivity σ	14.49 mS/cm
Spatially averaged current density j_{avg}	13 mA/cm²
Current pulse duration t_{p}	9 s
Current pulse frequency f	1/10 Hz
Bulk/initial concentration of Al species c_{init}	4.8 mol/l
Diffusion coefficient D [5]	5×10^{-8} cm²/s
Exchange current density j_0 [4]	0.87 mA/cm²
Anodic transfer coeff. α_a [4]	0.17
Cathodic transfer coeff. α_c [4]	0.33
Net electron transfer z [4]	3
Equilibrium potential E_{eq} [4]	-1.66 V vs NHE

Figure 5 and Table 3 summarize electrochemical and fluid dynamic boundary conditions.

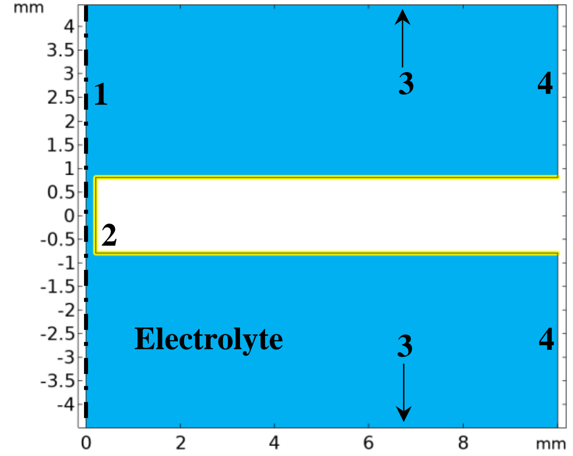


Figure 5: Boundaries of the electrolyte domain

Table 3: Boundary conditions of the microscale model

Boundary	Condition
1	Axial symmetry
2	No-slip wall Current characteristic (j_{avg}, t_{p}, f) Geometry deformation (Eq. (4))
3	Outlet ($\Delta p(t)$) El. potential ($\phi = E_{\mathrm{eq}}$) Concentration ($c = c_{\mathrm{init}}$)
4	Outlet ($\Delta p(t)$)

Boundary 1 represents the symmetry axis of the electrolyte domain. The Al deposition reactions and resulting geometry deformation are defined on boundary 2. The deposition process is controlled by setting a spatially averaged current density applied according to its pulse characteristics. While the electrolyte potential on boundary 3 was set to the standard reduction potential vs NHE of Al E_{eq}, the concentration of the Al species was kept constant at c_{init}, representing its bulk concentration in the electrolyte. The pressure conditions obtained from the macroscale model were applied to boundaries 3 and 4.

Figure 6 shows the mesh of the deposition model.

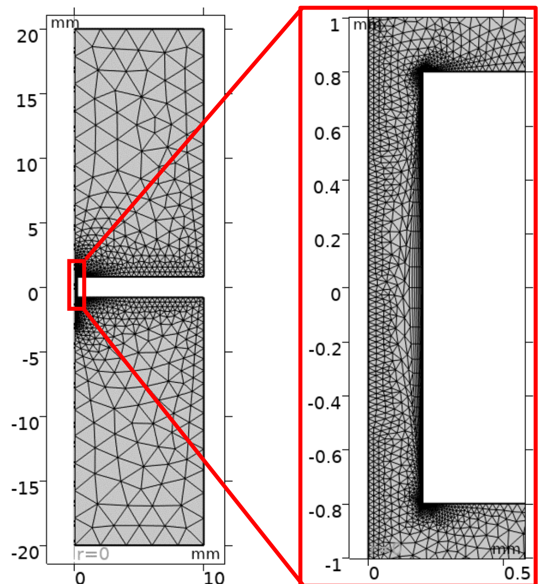


Figure 6: Mesh of the microscale deposition model.

The 2D model was discretized in approx. 5,700 volume elements with a size between 1 µm and 2.3 mm. The majority of the mesh consists of triangular elements. An additional boundary layer consisting of thin quadrilateral elements was used in the area of the via wall.

Results

Macroscale Model

The macroscale CFD model was solved for a process time of 1.5 oscillation periods T which equals about 41.2 s (see Figure 2). The electrolyte flow in the process chamber at $t = 1.25\,T$ is depicted in Figure 7.

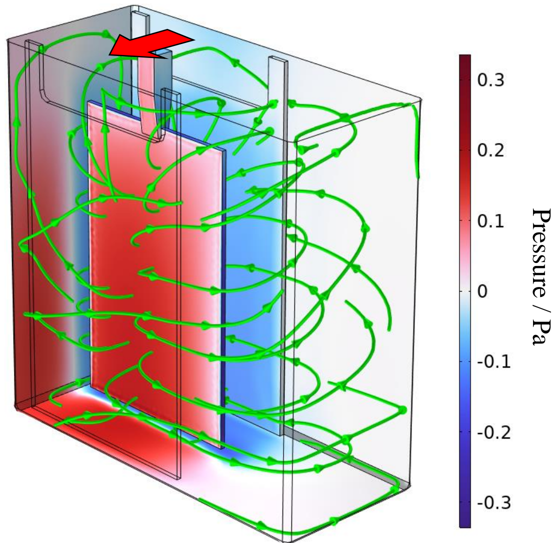


Figure 7: Electrolyte flow characteristics (green) and pressure distribution caused by substrate movement (red arrow) in the process chamber $t = 1.25 \times T = 34.4\ s$.

Over the course of the simulated time period, flow velocities do not exceed 10 mm/s, confirming laminar flow conditions. While electrolyte in front and behind the substrate is following its movement, a balancing counterflow is induced around its edges. This characteristic is caused by the pressure difference between both sides of the substrate. The spatially averaged variation in pressure over the course of the process $\Delta p(t)$ is shown in Figure 8. It can be described by a wave function slightly shifted to the left compared to the substrate movement shown in Figure 2. The pressure data during the last oscillation (black dots) were used to calculate a sine curve fit with an amplitude of approximately 0.32 Pa. This pressure curve was used as boundary condition to model the fluid dynamics in the microscale model of the Al deposition process in the vicinity of a through hole.

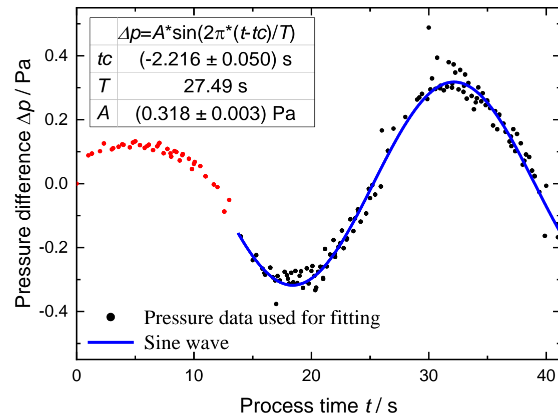


Figure 8: Pressure difference between both sides of the moving substrate: Pressure data represented by black dots was used to calculate a wave fitting function (blue line).

Microscale Model

After integrating in the obtained pressure conditions, the Al deposition process was modeled over the course of 60 min. Figure 9 shows the concentration of the Al species and electrolyte flow near the beginning (t = 5 s) and the end (t = 3590 s) of the process.

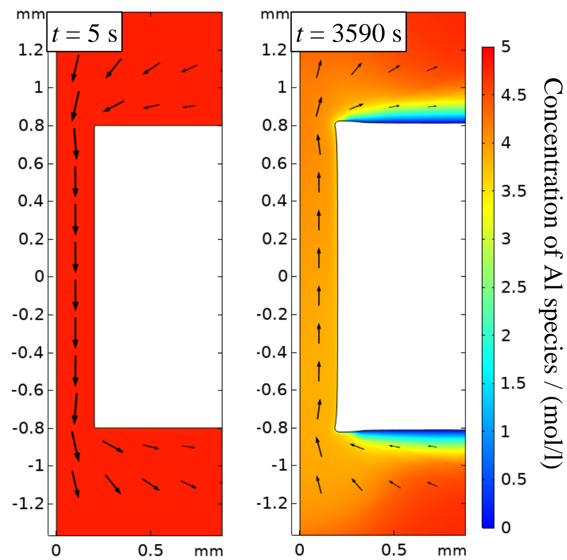


Figure 9: Concentration of Al species and electrolyte flow at t = 5 s and t = 3590 s.

While the concentration is diminished in the vicinity of the through hole, the alternating electrolyte flow keeps the concentration levels above 3.5 mol/l in its center. On the open surface of the substrate, the concentration drops to 0 mol/l. It can be concluded, that the deposition process is current-limited within the via and diffusion-limited on the outer surface of the PCB substrate.

The deposition rates along the substrate surface starting from the center of the via are shown in Figure 10. On the open surface, deposition rates of 0.244 µm/min were observed, which is in good agreement with the theoretical average value of 0.242 µm/min according to equation (4), taking the duty cycle of 0.9 into account. At the via, deposition rates are deviating from 0.01 µm/min near its center,

increasing to a maximum of 0.38 µm/min near its edge. This variation is caused by a significant increase in local current density during current-limited deposition conditions.

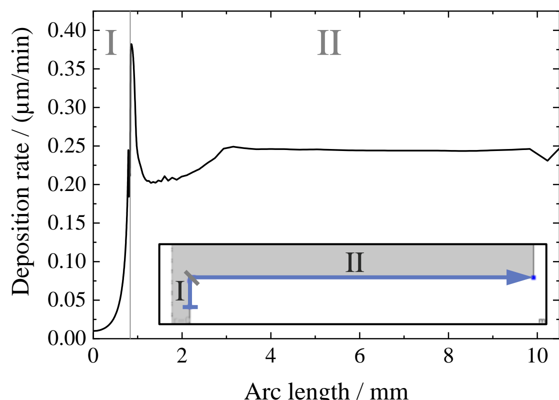


Figure 10: Al deposition rate in the via (I) and on the open surface (II) along the substrate boundary as illustrated in the inset.

The final geometry of the deposited Al layer after a process time of 60 min is depicted in Figure 11 and compared to experimental results after a process time of 133 min. The bottom image has been scaled accordingly to reflect this difference and allow qualitative comparison.

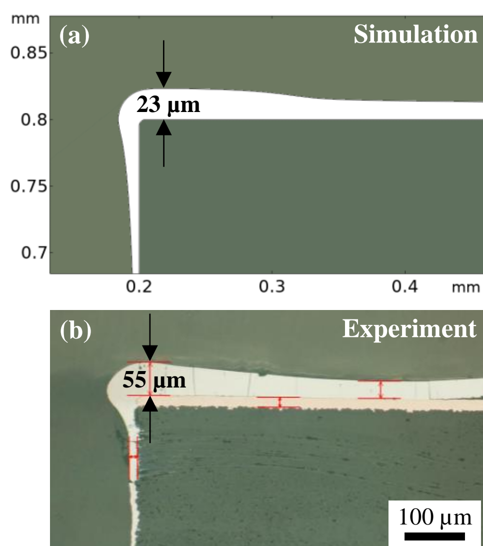


Figure 11: Deposited aluminum layer near the edge of the via: (a) simulation result after 60 min and (b) micrograph of an experimental result after 133 min. The images have been scaled to reflect differences in process time.

Both simulation and experiment show a maximum layer thickness near the edge of the via, thus forming a protrusion which is less pronounced in the simulation result. Within the via, decreasing deposition rates result in a quick decline in layer thickness. The experimentally obtained deposition rate of 0.23 µm/min on the open surface is in good accordance with both simulated and theoretical values, confirming a current efficiency close to 100 %.

Conclusions

In this simulation work the electrochemical deposition of aluminum from an ionic liquid electrolyte on a PCB substrate with vias was modeled. By linking macroscale and microscale models, fluid dynamic conditions within a process chamber based on CAD data were considered. Based on that the deposition process in the vicinity of a 400 µm via was modeled. Resulting electrolyte flow, ion concentrations and deposition rates were described and characterized. The obtained deposition rates averaging 0.24 µm/min were in good agreement with theoretical values. It was shown that both current-limited and diffusion-limited deposition occurs within the via and on the substrate's open surface, respectively. The resulting layer geometry was qualitatively compared to experimental results.

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