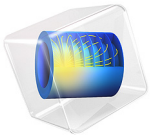

Copper Deposition in a Through-Hole Via

Introduction

Copper electrodeposition in a Through-Hole (TH) via is prevalent in electronic industry, particularly for the Printed Circuit Boards (PCBs). This model demonstrates the "butterfly" filling mechanism of the TH via during copper electrodeposition. Due to the presence of halide-suppressor additives in the electrolyte, electrodeposition occurs selectively at the center of the via, thus avoiding the formation of electrolyte enclosures. The example is based on a scientific paper (Ref. 1).

The purpose of the model is to demonstrate the use of deforming geometries for plating processes and the use of the Adsorbing-Desorbing Species functionlaity to model the influence of a suppressor on the plating result.

Model Definition

The model is defined by the material balances for the involved species (copper, Cu^{2+}, chloride, Cl^- and suppressor additive polyether, P) in the electrolyte solution and the adsorbed species (chloride, Cl and suppressor additive polyether, P) on the electrode surface, as well as an electrolyte charge balance assuming the presence of a supporting electrolyte.

The model geometry is shown in Figure 1. A 2D axi-symmetric space dimension is considered in the model. The upper horizontal boundary represents the anode and the cathode is placed at the bottom. The rightmost and leftmost vertical walls correspond to

insulation (axial symmetry). The bottommost horizontal boundary corresponds to symmetry.

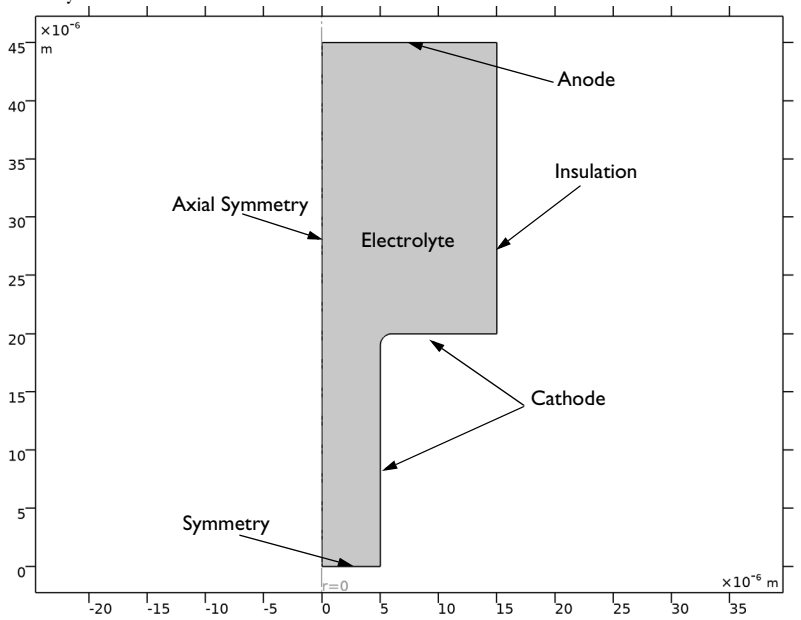

Figure 1: Model domain with boundaries corresponding to the anode, cathode, and symmetry walls.

The flux for each of the species in the electrolyte is given by the Nernst–Planck equation

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi_l$$

where $\mathbf{N}_i$ denotes the transport vector (mol/(m^2·s)), c_i the concentration in the electrolyte (mol/m^3), z_i the charge for the ionic species, u_i the mobility of the charged species (m^2/(s·J·mole)), F Faraday's constant (As/mole), and ϕ_l the potential in the electrolyte (V). The material balances are expressed through

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0$$

one for each species, that is $i = 1, 2$ and 3.

The electrolyte charge transport is solved assuming a supporting electrolyte charge conservation model according to

$$\nabla \cdot (-\sigma \nabla \phi_l) = 0$$

At the cathode surface, copper electrodeposition reaction occurs according to

$$Cu^{2+} + 2e^{-} = Cu$$

The boundary condition for the cathode is given by the Butler-Volmer equation for copper deposition. This gives the following relation for the local current density as a function of potential and copper concentration

$$i_{Cu} = i_0\left(\exp\left(\frac{1.5F\eta}{RT}\right) - \exp\left(-\frac{0.5F\eta}{RT}\right)\right)$$

where η denotes the overpotential defined as

$$\eta = \phi_{s,0} - \phi_l - E_{eq,Cu}$$

where $\phi_{s,0}$ denotes the electronic potential of the respective electrode. The equilibrium potentials for the copper reduction reaction is calculated using the Nernst Equation

$$E_{eq,Cu} = E^0_{eq,Cu} + \frac{RT}{nF}\ln\frac{c_{Cu}}{c_{Cu,ref}}$$

The exchange current density, i_0 , is defined is defined in terms of surface coverage of the suppressor additive polyether, P, and the cupric ion concentration according to

$$i_0 = (i_{0,unsuppr}(1-\theta_P) + i_{0,suppr}\theta_P) \times \frac{c_{Cu}}{c_{Cu,ref}}^{0.75} \quad (1)$$

where $i_{0,unsuppr}$ is the unsuppressed reference exchange current density, $i_{0,suppr}$ is the suppressed reference exchange current density and θ_P is the surface coverage of the suppressor additive polyether, P.

The flux condition for the copper ions at the cathode boundary is defined as

$$-\mathbf{n}\cdot\mathbf{N}_{Cu} = -\frac{\nu_{Cu}i_{Cu}}{2F}$$

where $\mathbf{n}$ denotes the normal vector to the boundary.

For the chloride ions, flux condition is defined as

$$-\mathbf{n}\cdot\mathbf{N}_{Cl} = -\Gamma_{Cl}k^{plus}_{Cl}c_{Cl}(1-\theta_{Cl})$$

For the suppressor additive polyether, P, flux condition is defined as

$$-\mathbf{n}\cdot\mathbf{N}_P = -\Gamma_P k_P^{plus} c_P(\theta_{Cl}-\theta_P)$$

Using the Electrode Surface boundary node, with an added Dissolving-Depositing species, the ion fluxes and the boundary mesh velocity are based on the reaction currents, the number of electrons, and the specified stoichiometric coefficients of the electrode reactions. The sign of the stoichiometric coefficient for a species depends on whether the species is getting oxidized (positive) or reduced (negative) in the reaction. The stoichiometric coefficient is $\nu_{Cu} = -1$ for the copper ions in the electrolyte, whereas that for the copper atoms in the electrode is $\nu_{d,Cu} = 1$.

Using the Electrode Surface boundary node, with an added Adsorbing-Desorbing species, surface coverage is evaluated according to

$$\frac{d\theta_{Cl}}{dt} = k_{Cl}^{plus} c_{Cl}(1-\theta_{Cl}) - k_{Cl}^{minus}\theta_{Cl} v$$

$$\frac{d\theta_P}{dt} = k_P^{plus} c_P(\theta_{Cl}-\theta_P) - k_P^{minus}\theta_P v$$

where k_{Cl}^{plus} and k_P^{plus} are adsorption kinetics, k_{Cl}^{minus} and k_P^{minus} are deactivation kinetics for chloride and suppressor, respectively, and deposition velocity, v (m/s), is calculated according to

$$v = \frac{-\nu_{d,Cu} i_{Cu}}{nF}\frac{M}{\rho}$$

where M is the mean molar mass (63.55 g/mol) and ρ is the density (8960 kg/m^3) of the nickel atoms and n is number of participating electrons.

At the anode surface, the electrolyte potential is set to 0 and concentration of all involved species is set to their initial concentrations.

All other boundaries are insulating.

The initial conditions set the composition of the electrolyte according to

$$c_{Cu} = c_{0,\,Cu}$$

$$c_{Cl} = c_{0,\,Cl}$$

$$c_P = c_{0,\,P}$$

You set up the above equations using the Tertiary Current Distribution, Nernst–Planck Equations interface. The Deformed Geometry node keeps track of the deformation of the mesh.

Results and Discussion

Figure 2 shows the surface plot for concentration distribution of chloride ions along with contour plot and the displacement of the cathode surface after 14.5 minutes of operation. The figure clearly shows that copper electrodeposition occurs selectively at the center of the TH and grows radially inwards, leading to sidewall impingement at the TH via center and resulting in "butterfly" filling of copper in the TH via. The selective copper electrodeposition, avoiding the formation of undesirable electrolyte entrapment, is attributed to chloride-polyether additives adsorption-desorption at the cathode surface. The chloride ion concentration depletion can also be seen in Figure 2 towards the center of the TH via.

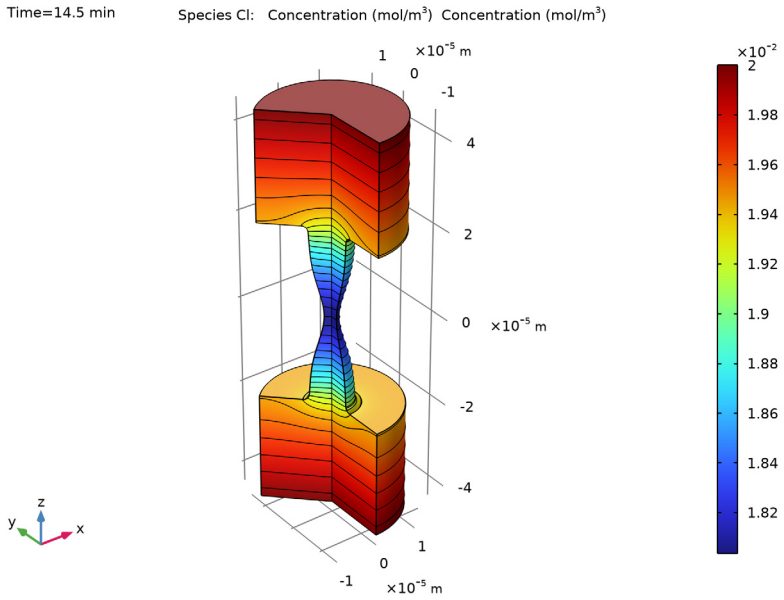

Figure 2: Chloride ion concentration (mol/m^3) along with contour plot and electrode displacement in the cell after 14.5 minutes of operation.

Figure 3 shows the thickness of the deposition from the center along the vertical cathodic surface of the TH via. The lines reveal the development of the nonuniform deposition

which is found to be more towards the center of via when compared to the mouth of the via.

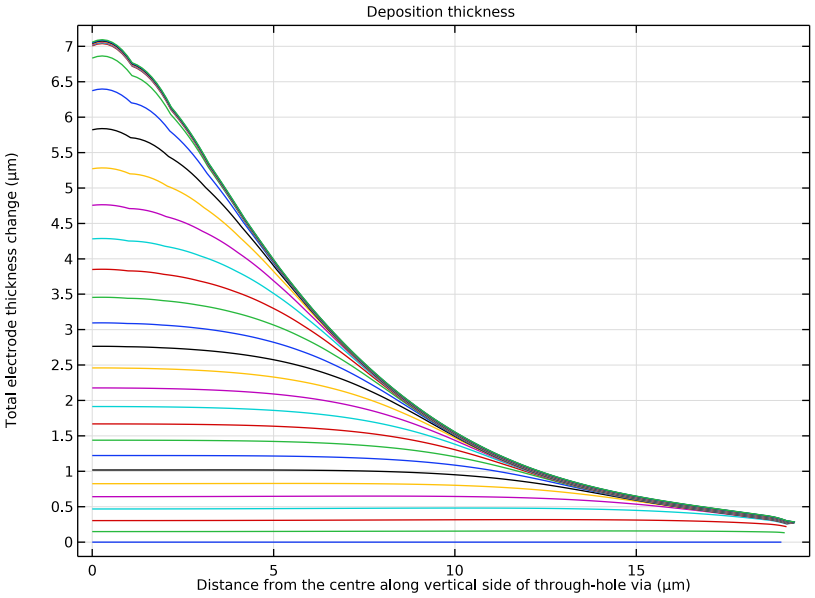

Figure 3: Thickness of the deposition from the center along the vertical cathode boundary of TH via.

Figure 4 shows the surface coverage of chloride ions along the vertical cathodic surface of the TH via. The lines reveal that adsorption of additive (chloride) begins at the mouth of the TH via and then gradually covers the entire surface of the TH via. The surface coverage

of additives is found to be the lowest at the center of the TH via leading the highest copper electrodepsosition in that region.

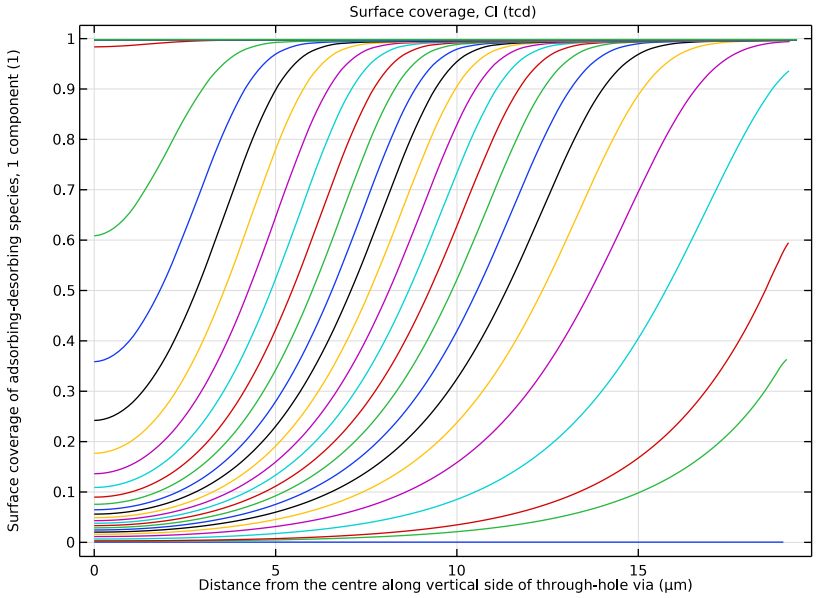

Figure 4: Surface coverage of chloride ions from the center along the vertical cathode boundary of TH via.

Reference

1. T. M. Braun, D. Josell, J. John and T. P. Moffat, "Simulation of Copper Electrodeposition in Though-Hole Vias," *Journal of The Electrochemical Society*, vol. 167, 013510, 2020.

Application Library path: `Electrodeposition_Module/Tutorials/cu_deposition_suppressor`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **2D Axisymmetric**.

2 In the **Select Physics** tree, select **Electrochemistry>Electrodeposition, Deformed Geometry> Electrodeposition, Tertiary with Supporting Electrolyte**.

3 Click **Add**.

4 In the **Number of species** text field, type 3.

5 In the **Concentrations** table, enter the following settings:

cCu
cCl
cP

6 Click **Study**.

7 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Time Dependent with Initialization**.

8 Click **Done**.

GEOMETRY 1

Draw the geometry by making a union of two rectangles. Round off the corner of the hole using a fillet.

Rectangle 1 (r1)

1 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `15e-6`.

4 In the **Height** text field, type `25e-6`.

5 Locate the **Position** section. In the **z** text field, type `20e-6`.

Rectangle 2 (r2)

1 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `5e-6`.

4 In the **Height** text field, type `20e-6`.

5 Click **Build Selected**.

6 Click the **Zoom Extents** button in the **Graphics** toolbar.

Union 1 (uni1)

1 In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Union**.

2 In the **Settings** window for **Union**, locate the **Union** section.

3 Clear the **Keep interior boundaries** check box.

4 Click in the **Graphics** window and then press Ctrl+A to select both objects.

Fillet 1 (fil1)

1 In the **Geometry** toolbar, click **Fillet**.

2 On the object **uni1**, select Point 5 only.

3 In the **Settings** window for **Fillet**, locate the **Radius** section.

4 In the **Radius** text field, type `1e-6`.

Form Union (fin)

1 In the **Model Builder** window, click **Form Union (fin)**.

2 In the **Settings** window for **Form Union/Assembly**, click **Build Selected**.

GLOBAL DEFINITIONS

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cu_deposition_suppressor_parameters.txt`.

DEFINITIONS

Load the model variables from a text file.

Variables 1

1 In the **Home** toolbar, click **Variables** and choose **Local Variables**.

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cu_deposition_suppressor_variables.txt`.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now set up the electrochemical model, starting with the Electrolyte node.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.

3 In the D_{cCu} text field, type `D_Cu`.

4 In the D_{cCl} text field, type `D_Cl`.

5 In the D_{cP} text field, type `D_P`.

6 Locate the **Migration in Electric Field** section. In the z_{cCu} text field, type `z_Cu`.

7 In the z_{cCl} text field, type `z_Cl`.

8 Locate the **Electrolyte Current Conduction** section. From the σ_{l} list, choose **User defined**. In the associated text field, type `sigmal`.

Electrode Surface 1

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

2 Select Boundaries 5, 6, and 8 only.

Create a selection of the boundaries to facilitate choosing this electrode surface later on when post processing the problem.

3 In the **Settings** window for **Electrode Surface**, locate the **Boundary Selection** section.

4 Click **Create Selection**.

5 In the **Create Selection** dialog box, type `Cathode` in the **Selection name** text field.

6 Click **OK**.

7 In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.

8 Click **Add**.

9 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Cu	rho_Cu	Mw_Cu

The dissolving-depositing species `Cu` contributes to the deposition velocity.

10 Click to expand the **Adsorbing-Desorbing Species** section. In the Γ_{s} text field, type `Gamma_Cl`.

11 Click **Add**.

12 Click + **Add**.

13 In the table, enter the following settings:

Species	Site occupancy number (1)
Cl	1
P	Gamma_Cl/Gamma_P

14 Locate the **Electrode Phase Potential Condition** section. In the $\phi_{s,ext}$ text field, type `phis_cathode`.

Electrode Reaction 1

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type `2`.

4 In the ν_{cCu} text field, type `-1`.

5 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
Cu	1

6 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Erev`.

7 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0ref`.

8 In the α_a text field, type `alpha_a`.

Electrode Surface 1

Next, set the flux for species `cCl` and `cP` and reaction rates for adsorbing-desorbing species `Cl` and `P` using the Non-Faradaic Reactions node.

1 In the **Model Builder** window, click **Electrode Surface 1**.

Non-Faradaic Reactions 1

1 In the **Physics** toolbar, click **Attributes** and choose **Non-Faradaic Reactions**.

2 In the **Settings** window for **Non-Faradaic Reactions**, locate the **Reaction Rate** section.

3 Select the **Species cCl** check box.

4 In the $R_{0,cCl}$ text field, type `R_Cl`.

5 Select the **Species cP** check box.

6 In the $R_{0,cP}$ text field, type `R_P`.

7 In the **Reaction rate for adsorbing-desorbing species** table, enter the following settings:

Species	Reaction rate (mol/(m^2*s))
Cl	Rad_Cl
P	Rad_P

Electrolyte Potential 1

Next, set the electrolyte potential at the top boundary.

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrolyte Potential**.

2 Select Boundary 4 only.

Concentration 1

Next, also set the concentration of all spcies at the top boundary.

1 In the **Physics** toolbar, click **Boundaries** and choose **Concentration**.

2 Select Boundary 4 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 Select the **Species cCu** check box.

5 In the $c_{0,\mathrm{cCu}}$ text field, type `c0_Cu`.

6 Select the **Species cCl** check box.

7 In the $c_{0,\mathrm{cCl}}$ text field, type `c0_Cl`.

8 Select the **Species cP** check box.

9 In the $c_{0,\mathrm{cP}}$ text field, type `c0_P`.

Symmetry 1

Finally, define the symmetry boundaries.

1 In the **Physics** toolbar, click **Boundaries** and choose **Symmetry**.

2 Select Boundary 2 only.

Initial Values 1

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the cCu text field, type `c0_Cu`.

4 In the cCl text field, type `c0_Cl`.

5 In the cP text field, type `c0_P`.

MULTIPHYSICS

Nondeforming Boundary 1 (ndbdg1)

1 In the **Model Builder** window, under **Component 1 (comp1)>Multiphysics** click **Nondeforming Boundary 1 (ndbdg1)**.

2 In the **Settings** window for **Nondeforming Boundary**, locate the **Nondeforming Boundary** section.

3 From the **Boundary condition** list, choose **Zero normal displacement**.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value to be used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General>Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T0`.

MESH 1

Define a physics-controlled extra fine mesh.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.

2 In the **Settings** window for **Mesh**, locate the **Physics-Controlled Mesh** section.

3 From the **Element size** list, choose **Extra fine**.

4 Click **Build All**.

STUDY 1

Select only **Tertiary Current Distribution, Nernst Planck (tcd)** interface to be solved for in the first study step.

Step 1: Current Distribution Initialization

1 In the **Model Builder** window, under **Study 1** click **Step 1: Current Distribution Initialization**.

2 In the **Settings** window for **Current Distribution Initialization**, locate the **Physics and Variables Selection** section.

3 In the table, clear the **Solve for** check box for **Deformed geometry (Component 1)**.

4 In the table, clear the **Solve for** check boxes for **Nondeforming Boundary 1 (ndbdg1)** and **Deforming Electrode Surface 1 (desdg1)**.

Step 2: Time Dependent

1 In the **Model Builder** window, click **Step 2: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 From the **Time unit** list, choose **min**.

4 In the **Output times** text field, type `range(0,0.5,14.5)`.

5 In the **Home** toolbar, click **Compute**.

RESULTS

Several plots are added by default. Now, to reproduce the plots from the Results and Discussion section, follow the below steps.

Mirror 3D 1

1 In the **Results** toolbar, click **More Datasets** and choose **Mirror 3D**.

2 In the **Settings** window for **Mirror 3D**, locate the **Plane Data** section.

3 From the **Plane** list, choose **XY-planes**.

Concentration, Cl, 3D (tcd)

Next, plot the chloride concentration using the mirror dataset.

1 In the **Model Builder** window, under **Results** click **Concentration, Cl, 3D (tcd)**.

2 In the **Settings** window for **3D Plot Group**, locate the **Data** section.

3 From the **Dataset** list, choose **Mirror 3D 1**.

Contour 1

Right-click **Concentration, Cl, 3D (tcd)** and choose **Contour**.

Contour 1

1 In the **Model Builder** window, expand the **Results>Concentration, Cl, 3D (tcd)** node, then click **Contour 1**.

2 In the **Settings** window for **Contour**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck>Species cCl>cCl - Concentration - mol/m³**.

3 Locate the **Coloring and Style** section. From the **Coloring** list, choose **Uniform**.

4 From the **Color** list, choose **Black**.

5 Clear the **Color legend** check box.

6 In the **Concentration, Cl, 3D (tcd)** toolbar, click **Plot**.

The plot should look like Figure 2.

Deposition thickness

Next, plot the deposition thickness along the vertical side of through-hole via.

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Deposition thickness` in the **Label** text field.

3 Click to expand the **Title** section. From the **Title type** list, choose **Label**.

Line Graph 1

1 In the **Deposition thickness** toolbar, click **Line Graph**.

2 Select Boundary 5 only.

3 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

4 In the **Expression** text field, type `tcd.sbtot`.

5 From the **Unit** list, choose **µm**.

6 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

7 In the **Expression** text field, type `z`.

8 From the **Unit** list, choose **µm**.

9 Select the **Description** check box.

10 In the associated text field, type `Distance from the centre along vertical side of through-hole via`.

11 In the **Deposition thickness** toolbar, click **Plot**.

The plot should look like Figure 3.

Deposition thickness

Next, plot the surface coverage of chloride.

Surface coverage, Cl (tcd)

1 In the **Model Builder** window, right-click **Deposition thickness** and choose **Duplicate**.

2 In the **Model Builder** window, click **Deposition thickness 1**.

3 In the **Settings** window for **1D Plot Group**, type `Surface coverage, Cl (tcd)` in the **Label** text field.

Line Graph 1

1 In the **Model Builder** window, click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `tcd.theta_es1_Cl`.

4 In the **Surface coverage, Cl (tcd)** toolbar, click  **Plot**.

The plot should look like Figure 4.