

Copper Deposition in a Trench

Introduction

This model simulates the electroplating of copper in a microcavity typically found in the plating of copper onto circuit boards. The plating cell is a laboratory cell under potentiostatic control where the anode is placed in close vicinity of the cathode. 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 to investigate the influence of the cavity on the plating result. The deforming geometry makes it possible to simulate the growth of the cathode boundary as the process proceeds.

For a detailed description of how to build this model, including screenshots, see the *Introduction to the Electrodeposition Module* book.

Model Definition

The model simulates the deposition process at pH 4, which implies that the proton concentration is very low compared to the copper and sulfate ion concentrations. For this reason, the material balance of the protons does not need to be modeled. Sulfate is also treated as a fully dissociated ion. The deposition at the cathode and the dissolution at the anode are assumed to take place with 100% current yield, which means that the model does not include possible side reactions. During the process, differences in electrolyte density arise in the enclosed cell, giving higher density at the anode compared to the cathode. This can induce free convection in the cell. Under the modeled conditions, however, the variations in composition are small and it is therefore possible to neglect free convection.

The process is inherently time-dependent because the cathode boundary moves as the deposition process takes place. The model is defined by the material balances for the involved ions (copper, Cu^{2+} , and sulfate, SO_4^{2-}) and the electroneutrality condition. This gives three unknowns and three model equations. The dependent variables are the copper ion concentration, sulfate ion concentration, and ionic potentials. Additional variables keep track of the deformation of the mesh.

The model geometry is shown in Figure 1. The upper horizontal boundary represents the anode, while the cathode is placed at the bottom. The vertical walls correspond to the pattern on the master electrode and are assumed to be insulating.



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

The flux for each of the ions 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/(m²·s)), c_i the concentration in the electrolyte (mol/m³), z_i the charge for the ionic species, u_i the mobility of the charged species (m²/(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. The electroneutrality condition is given by the following expression:

$$\sum_{i} z_i c_i = 0$$

The boundary conditions for the anode and cathode are given by the Butler-Volmer equation for copper deposition. The deposition process is assumed to take place through the following simplified mechanism:

$$Cu2+ + e- = Cu+$$
$$Cu+ + e- = Cu$$

where the first step is rate determining step, RDS, and the second step is assumed to be at equilibrium (Ref. 1). This gives the following relation for the local current density as a function of potential and copper concentration:

$$i_{\rm ct} = i_0 \left(\exp\left(\frac{1.5F\eta}{RT}\right) - \frac{c_{\rm Cu^{2+}}}{c_{\rm Cu^{2+}}, {\rm ref}} \exp\left(-\frac{0.5F\eta}{RT}\right) \right)$$

where η denotes the overpotential defined as

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

where $\phi_{s,0}$ denotes the electronic potential of the respective electrode. This gives the following condition for the cathode:

$$\begin{split} \mathbf{N}_{\mathrm{Cu}^{2*}} \cdot \mathbf{n} &= -\frac{i_0}{2F} \Big(\exp \Big(\frac{1.5F(\phi_{\mathrm{s,\,cat}} - \phi_{\mathrm{l}} - \Delta \phi_{\mathrm{eq}})}{RT} \Big) \\ &- \frac{c_{\mathrm{Cu}^{2*}}}{c_{\mathrm{Cu}^{2*},\mathrm{ref}}} \exp \Big(-\frac{0.5F(\phi_{\mathrm{s,\,cat}} - \phi_{\mathrm{l}} - \Delta \phi_{\mathrm{eq}})}{RT} \Big) \Big) \end{split}$$

where \mathbf{n} denotes the normal vector to the boundary. The condition at the anode is

$$\mathbf{N}_{\mathrm{Cu}^{2*}} \cdot \mathbf{n} = -\frac{i_0}{2F} \left(\exp\left(\frac{1.5F(\phi_{\mathrm{s,an}} - \phi_{\mathrm{l}} - \Delta\phi_{\mathrm{eq}})}{RT}\right) - \frac{c_{\mathrm{Cu}^{2*}}}{c_{\mathrm{Cu}^{2*},\mathrm{ref}}} \exp\left(-\frac{0.5F(\phi_{\mathrm{s,an}} - \phi_{\mathrm{l}} - \Delta\phi_{\mathrm{eq}})}{RT}\right) \right)$$

All other boundaries are insulating:

4 | COPPER DEPOSITION IN A TRENCH

$$\mathbf{N}_{\mathbf{C}\mathbf{u}^{2+}}\cdot\mathbf{n} = \mathbf{0}$$

For the sulfate ions, insulating conditions apply everywhere:

$$\mathbf{N}_{\mathbf{SO}_4^{2-}} \cdot \mathbf{n} = \mathbf{0}$$

The initial conditions set the composition of the electrolyte according to

$$c_{\mathrm{Cu}^{2+}} = c_0$$
$$c_{\mathrm{SO}_4^{2-}} = c_0$$

You set up Equation 1 through Equation 11 using the Tertiary Current Distribution, Nernst-Planck Equations interface. The Deformed Geometry node keeps track of the deformation of the mesh.

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. In the case for the total reaction in this model

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

the stoichiometric coefficient is $v_{Cu^{2+}} = -1$ for the copper ions in the electrolyte, and $v_{Cu} = 1$ for the copper atoms in the electrodes.

Results and Discussion

Figure 2 shows the concentration distribution of copper ions, the isopotential lines, the current density lines, and the displacement of the cathode and anode surfaces after 14 seconds of operation. The figure clearly shows that the mouth of the cavity is starting to narrow due to the nonuniform thickness of the deposition. This effect can be detrimental to the quality of the deposition because a trapped electrolyte can later cause corrosion of components in the circuit board. In addition, the simulation shows substantial variations in copper ion concentration in the cell. Such variations eventually

cause free convection in the cell. The model is symmetric along a vertical line in the middle of the cell. An asymmetric result would be a sign of poor mesh resolution.



Figure 2: Copper ion concentration (mol/m^3) , isopotential lines, current density streamlines, and electrode displacement in the cell after 14 seconds of operation.

Figure 3 shows the thickness of the deposition along one of the vertical cathodic surfaces. The lines reveal the development of the nonuniform deposition due to nonuniform

current density distribution. This effect is accentuated by the depletion of copper ions along the depth of the cavity.



Figure 3: Thickness of the deposition along the vertical cathode boundaries. The lines are generated for increments of 0.4 seconds from 0 to 4.4 seconds.

Despite the simplicity of this model, it can easily be expanded to more complicated geometries or to include the influence of other ions on the process.

Reference

1. E. Mattsson and J.O'M. Bockris, "Galvanostatic Studies of the Kinetics of Deposition and Dissolution in the Copper + Copper Sulphate System," *Trans. Far. Soc.*, vol. 55, p. 1586, 1959.

Application Library path: Electrodeposition_Module/Tutorials/ cu_trench_deposition

Modeling Instructions

From the File menu, choose New.

NEW

In the New window, click 🔗 Model Wizard.

MODEL WIZARD

- I In the Model Wizard window, click 🤏 2D.
- 2 In the Select Physics tree, select Electrochemistry>Electrodeposition, Deformed Geometry> Electrodeposition, Tertiary with Electroneutrality.
- 3 Click Add.
- 4 In the **Concentrations** table, enter the following settings:

cCu cS04

- 5 Click 🔿 Study.
- 6 In the Select Study tree, select Preset Studies for Selected Physics Interfaces> Time Dependent with Initialization.
- 7 Click **M** Done.

GLOBAL DEFINITIONS

Parameters 1

- I In the Model Builder window, under Global Definitions click Parameters I.
- 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_trench_deposition_parameters.txt.

GEOMETRY I

Draw the geometry by making a union of two rectangles. Round off the corners of the trench using fillets.

Rectangle 1 (r1)

- I 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 1.6e-5.
- 4 In the **Height** text field, type 3e-5.
- 5 Locate the Position section. In the x text field, type -0.8e-5.
- 6 In the y text field, type 1e-5.

Rectangle 2 (r2)

- I 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 0.4e-5.
- 4 In the **Height** text field, type 1e-5.
- 5 Locate the **Position** section. In the **x** text field, type -0.2e-5.
- 6 Click 틤 Build Selected.
- 7 Click the 🕂 Zoom Extents button in the Graphics toolbar.

Union I (unil)

- I In the Geometry toolbar, click P 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 I (fill)

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



- 3 In the Settings window for Fillet, locate the Radius section.
- 4 In the Radius text field, type 1e-6.

Form Union (fin)

- I In the Model Builder window, click Form Union (fin).
- 2 In the Settings window for Form Union/Assembly, click 🔚 Build Selected.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now set up the electrochemical model, consisting of a species properties and an electrolyte domains and two electrode boundaries.

Species Charges 1

- In the Model Builder window, under Component I (compl)>Tertiary Current Distribution, Nernst-Planck (tcd) click Species Charges I.
- 2 In the Settings window for Species Charges, locate the Charge section.
- **3** In the z_{cCu} text field, type z_Cu.
- **4** In the z_{cSO4} text field, type z_SO4.

Electrolyte I

- I In the Model Builder window, click Electrolyte I.
- 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_{cSO4} text field, type D_SO4.

Electrode Surface I

- I In the Physics toolbar, click Boundaries and choose Electrode Surface.
- **2** Select Boundary **3** only.

Create a selection of the boundary to facilitate choosing this electrode surface later on when postprocessing the problem.

- 3 In the Settings window for Electrode Surface, locate the Boundary Selection section.
- 4 Click har Create Selection.
- 5 In the Create Selection dialog box, type Anode in the Selection name text field.
- 6 Click OK.
- 7 In the Settings window for Electrode Surface, locate the Electrode Phase Potential Condition section.
- **8** In the $\phi_{s.ext}$ text field, type phis_anode.
- 9 Click to expand the Dissolving-Depositing Species section. Click + Add.
- **IO** In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
cdep_anode	8960	0.06355

Electrode Reaction 1

- I In the Model Builder window, click Electrode Reaction I.
- **2** In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.
- **3** In the *n* text field, type **2**.
- **4** In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (I)
cdep_anode	1

- **5** Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type i0_ref.
- **6** In the α_a text field, type alpha_a.

Electrode Surface 2

 In the Model Builder window, under Component I (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd) right-click Electrode Surface I and choose Duplicate.

The easiest way to select the curved cathode boundaries is to first select all boundaries, and then to deselect the top and side boundaries.

- 2 In the Settings window for Electrode Surface, locate the Boundary Selection section.
- **3** From the **Selection** list, choose **Manual**.
- 4 Select Boundaries 2, 4–7, and 9–12 only.



- 5 Click here a Create Selection.
- 6 In the Create Selection dialog box, type Cathode in the Selection name text field.
- 7 Click OK.
- 8 In the Settings window for Electrode Surface, locate the Electrode Phase Potential Condition section.
- **9** In the $\phi_{s,ext}$ text field, type phis_cathode.

Electrode Reaction I

- I In the Model Builder window, expand the Electrode Surface 2 node, then click Electrode Reaction I.
- **2** In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

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

Species	Stoichiometric coefficient (I)
cdep_anode	1

Initial Values 1

- I In the Model Builder window, under Component I (compl)>Tertiary Current Distribution, Nernst-Planck (tcd) click Initial Values I.
- 2 In the Settings window for Initial Values, locate the Initial Values section.
- 3 In the *cSO*4 text field, type Cinit.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

- I 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 I

Now make the settings for the mesh.

Size

- I In the Model Builder window, under Component I (comp1) right-click Mesh I and choose Edit Physics-Induced Sequence.
- 2 In the Settings window for Size, locate the Element Size section.
- 3 From the Predefined list, choose Extra fine.
- 4 Click the **Custom** button.
- 5 Locate the Element Size Parameters section. In the Maximum element size text field, type 5e-7.
- 6 In the Curvature factor text field, type 1.
- 7 In the Resolution of narrow regions text field, type 10.
- 8 Click 📗 Build All.

STUDY I

Step 2: Time Dependent

- I In the Model Builder window, under Study I click Step 2: Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.
- 3 In the **Output times** text field, type range(0,0.5,5).

Modify the times for the solver to simulate the deposition process during 5 s, storing the solution every 0.1 s. Then start the computation.

4 In the **Home** toolbar, click **= Compute**.

RESULTS

Contour I

- I In the Model Builder window, right-click Concentration, Cu (tcd) and choose Contour.
- In the Settings window for Contour, click Replace Expression in the upper-right corner of the Expression section. From the menu, choose Component I (comp1)>
 Tertiary Current Distribution, Nernst-Planck>Species cCu>cCu 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.

Streamline 1

- I In the Model Builder window, click Streamline I.
- 2 In the Settings window for Streamline, locate the Streamline Positioning section.
- **3** From the **Positioning** list, choose **On selected boundaries**.
- **4** Locate the **Selection** section. Click to select the **Delivered Selection** toggle button.
- 5 From the Selection list, choose Anode.
- 6 Locate the Streamline Positioning section. In the Number text field, type 15.

Line I

- I In the Model Builder window, right-click Concentration, Cu (tcd) and choose Line.
- 2 In the Settings window for Line, locate the Data section.
- 3 From the Dataset list, choose Study I/Solution I (soll).
- 4 From the Time (s) list, choose 0.
- 5 Locate the Coloring and Style section. From the Coloring list, choose Uniform.
- 6 From the Color list, choose Black.

- 7 Click to expand the Title section. From the Title type list, choose None.
- 8 In the Concentration, Cu (tcd) toolbar, click 💿 Plot.

Deposition Thickness

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, type Deposition Thickness in the Label text field.
- 3 Click to expand the Title section. From the Title type list, choose Manual.
- 4 In the Title text area, type Profile of deposited layer on vertical wall.
- 5 Locate the Plot Settings section.
- 6 Select the x-axis label check box. In the associated text field, type Distance from cavity bottom (\mu m).
- 7 Select the y-axis label check box. In the associated text field, type Thickness of deposited layer (\mu m).

Line Graph I

- I Right-click Deposition Thickness and choose Line Graph.
- **2** Select Boundary 4 only.
- 3 In the Settings window for Line Graph, locate the y-Axis Data section.
- **4** In the **Expression** text field, type x-Xg.

(Xg is the original geometry coordinate variable.)

- 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 y.
- 8 From the **Unit** list, choose µm.
- **9** In the **Deposition Thickness** toolbar, click **OM Plot**.

ROOT

Now create a new study and extend the simulation time to 14 s. Enable automatic remeshing in order to remesh the geometry if the mesh quality gets too low. First, add a new Study node.

ADD STUDY

- I In the Home toolbar, click ~ 2 Add Study to open the Add Study window.
- 2 Go to the Add Study window.

- 3 Find the Studies subsection. In the Select Study tree, select Preset Studies for Selected Physics Interfaces>Time Dependent with Initialization.
- 4 Click Add Study in the window toolbar.
- 5 In the Home toolbar, click $\stackrel{\text{res}}{\longrightarrow}$ Add Study to close the Add Study window.

STUDY 2

Step 2: Time Dependent

- I In the Model Builder window, under Study 2 click Step 2: Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.
- 3 In the **Output times** text field, type range(0,1,14).
- 4 Click to expand the **Study Extensions** section. Select the **Automatic remeshing** check box.
- 5 In the Model Builder window, click Study 2.
- 6 In the Settings window for Study, locate the Study Settings section.
- 7 Clear the Generate default plots check box.
- 8 In the **Home** toolbar, click **= Compute**.

RESULTS

Concentration, Cu (tcd)

- I In the Model Builder window, under Results click Concentration, Cu (tcd).
- 2 In the Settings window for 2D Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study 2/Remeshed Solution I (sol5).
- 4 From the Time (s) list, choose Interpolation.
- 5 In the Time text field, type 14.
- 6 In the Concentration, Cu (tcd) toolbar, click 💽 Plot.
- **7** Click the $4 \rightarrow$ **Zoom Extents** button in the **Graphics** toolbar.