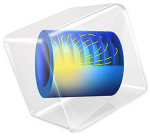


Copper Deposition in a Trench

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.

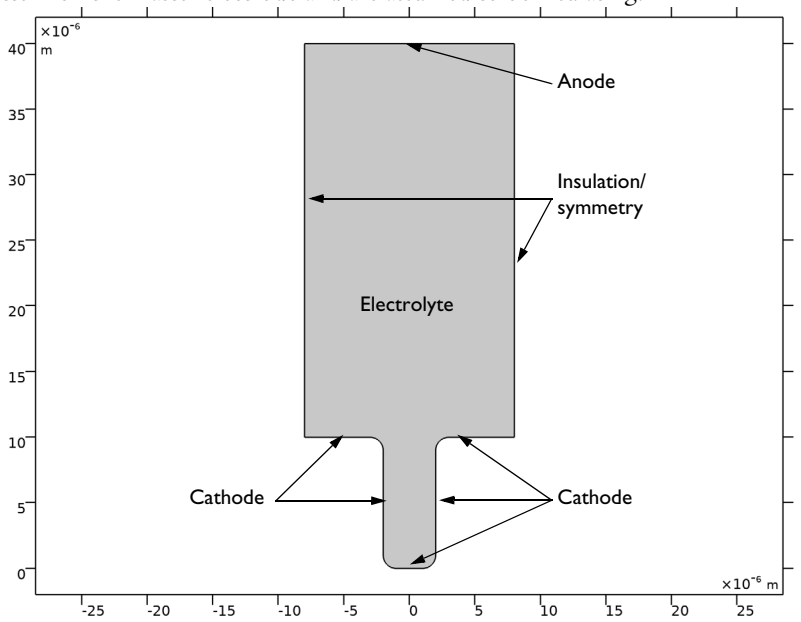


Figure 1: Model domain with boundaries corresponding to the anode, cathode, and vertical symmetry walls.

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/(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 $i = 1, 2$. 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:

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

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:

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

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:

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

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

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

All other boundaries are insulating:

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

For the sulfate ions, insulating conditions apply everywhere:

$$\mathbf{N}_{SO_4^{2-}} \cdot \mathbf{n} = 0$$

The initial conditions set the composition of the electrolyte according to

$$c_{Cu^{2+}} = c_0$$
$$c_{SO_4^{2-}} = c_0$$

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

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

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

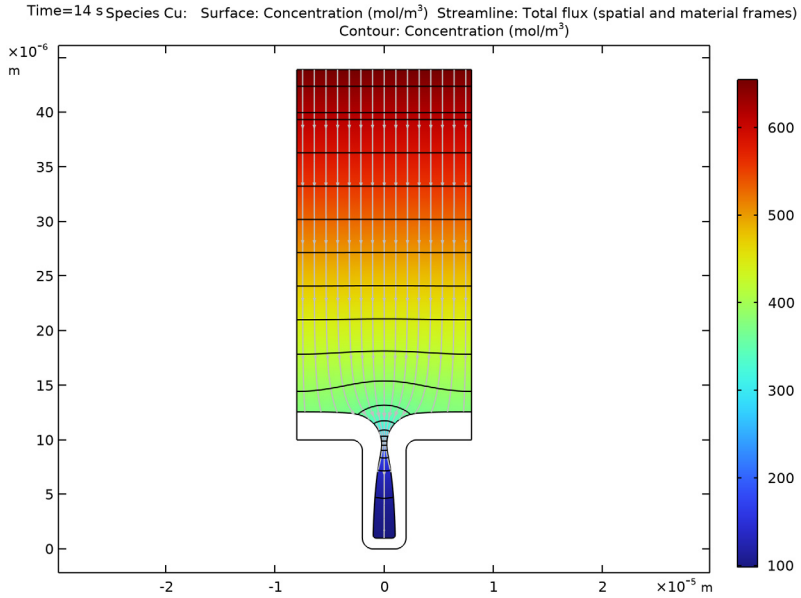


Figure 2: Copper ion concentration (mol/m^3), isopotential lines, current density streamlines, and electrode displacement in the cell after 14 seconds of operation.

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.

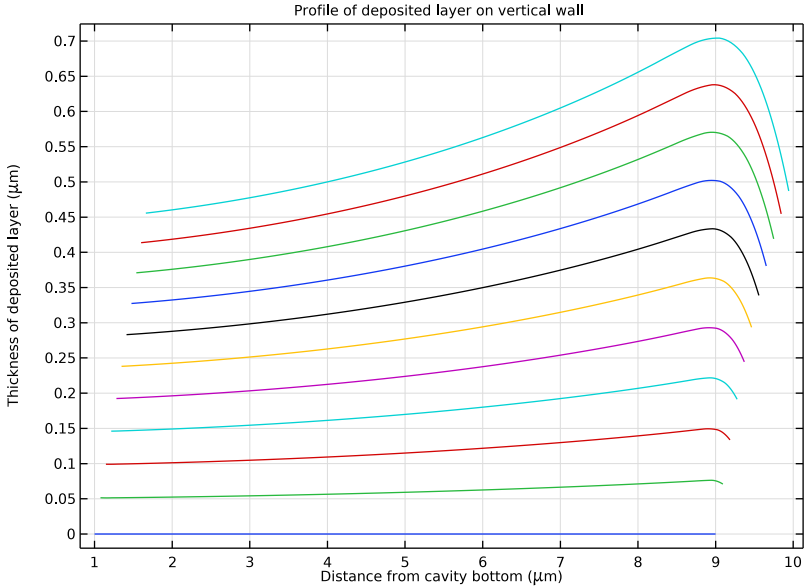


Figure 3: Thickness of the deposition along the vertical cathode boundaries. The lines are generated for increments of 0.4 seconds from 0 to 4.4 seconds.

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`

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

NEW

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

MODEL WIZARD

1 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
cSO4

5 Click **Study**.

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

7 Click **Done**.

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_trench_deposition_parameters.txt`.

GEOMETRY 1

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

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 `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)

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 `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 **Build Selected**.

7 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.

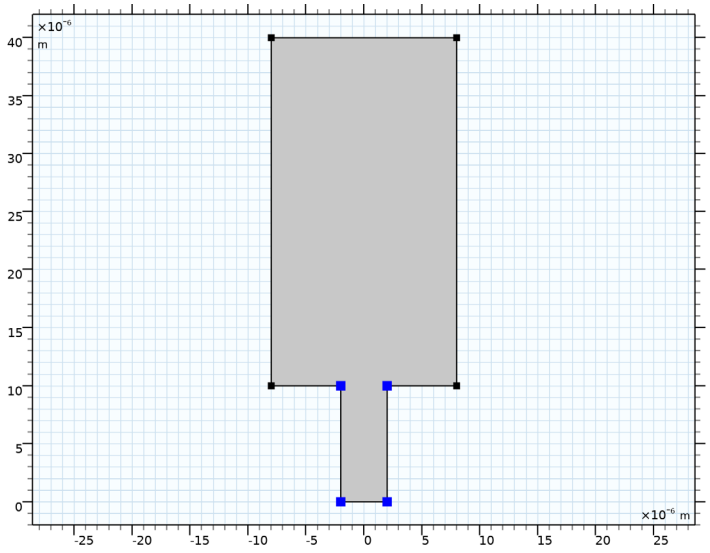
3 Clear the **Keep interior boundaries** check box.

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 Points 3–6 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**.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now set up the electrochemical model, consisting of an electrolyte domain and two electrode boundaries.

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_{cSO4} text field, type `D_SO4`.

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

6 In the z_{cSO4} text field, type `z_SO4`.

Electrode Surface 1

1 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 **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**.

10 In the table, enter the following settings:

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

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

Species	Stoichiometric coefficient (1)
cdep_anode	1

5 Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0_ref`.

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

Electrode Surface 2

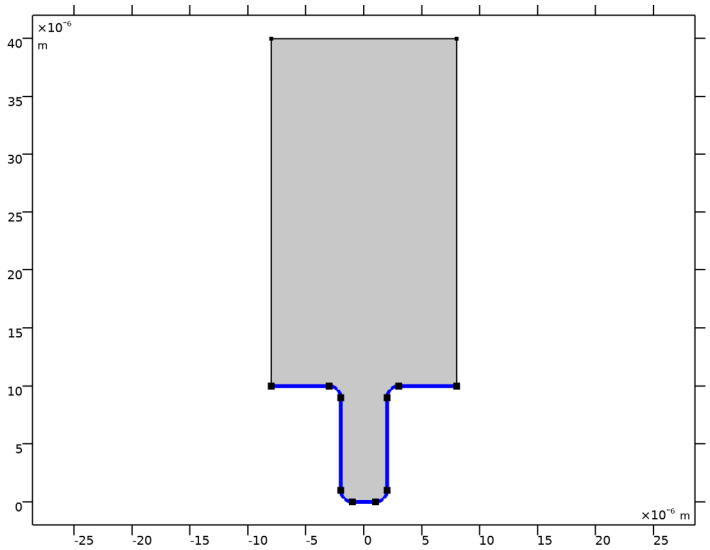
1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** right-click **Electrode Surface 1** and choose **Duplicate**.

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 **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 1

1 In the **Model Builder** window, expand the **Electrode Surface 2** node, then click **Electrode Reaction 1**.

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 (1)
cdep_anode	1

Initial Values 1

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

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

3 In the $cSO4$ text field, type `Cinit`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value 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

Now make the settings for the mesh.

Size

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

Step 2: Time Dependent

1 In the **Model Builder** window, under **Study 1** 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 1

1 In the **Model Builder** window, right-click **Concentration, Cu (tcd)** and choose **Contour**.

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 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

1 In the **Model Builder** window, click **Streamline 1**.

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 **Activate Selection** toggle button.

5 From the **Selection** list, choose **Anode**.

6 Locate the **Streamline Positioning** section. In the **Number** text field, type 15.

Line 1

1 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 1/Solution 1 (sol1)**.

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

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 **Manual**.

4 In the **Title** text area, type `Profile of deposited layer on vertical wall`.

5 Locate the **Plot Settings** section. Select the **x-axis label** check box.

6 In the associated text field, type `Distance from cavity bottom (\mu m)`.

7 Select the **y-axis label** check box.

8 In the associated text field, type `Thickness of deposited layer (\mu m)`.

Line Graph 1

1 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 **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

1 In the **Home** toolbar, click **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 **Add Study** to close the **Add Study** window.

STUDY 2

Step 2: Time Dependent

1 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)

1 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 1 (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 **Zoom Extents** button in the **Graphics** toolbar.