COMSOL MULTIPHYSICS®

Electrochemical Copper Deposition

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Electrochemical Copper Deposition

Introduction

This model simulates the electroplating of copper in a microcavity typically found in the plating of copper onto circuit boards. The purpose of the model is to demonstrate the use of moving meshes for plating processes and to investigate the influence of the cavity on the plating result. The moving mesh makes it possible to simulate the growth of the cathode boundary as the process is carried out.

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. However, under the modeled conditions, 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, sulfate ion, and ionic potentials. Additional variables keep track of the deformation of the mesh.

The model geometry is depicted 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.

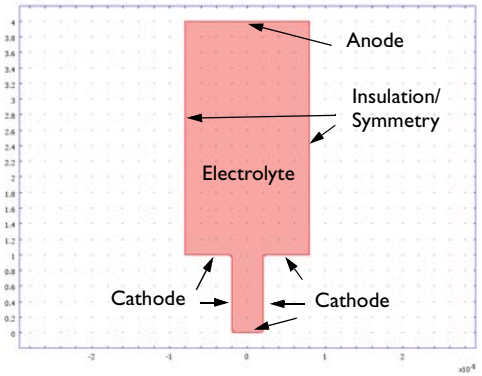

Figure 1: Model domain with boundaries corresponding to the anode, cathode, and vertical symmetry walls.

The flux for each of the ions in the electrolyte is given by the Nernst-Planck equation

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

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_i the potential in the electrolyte (V). The material balances are expressed through

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0 \qquad (1)$$

one for each species, that is $i = 1, 2$. The electroneutrality condition is given by the following expression:

$$\sum_i -z_i c_i = 0\,. \qquad (2)$$

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 first 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:

$$i_{ct} = i_0\left(\exp\left(\left(\frac{1{,}5F\eta}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(-\frac{0{,}5F\eta}{RT}\right)\right)\right)$$

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:

$$\mathbf{N}_{Cu^{2+}} \cdot \mathbf{n} = -\frac{i_0}{2F}\left(\exp\left(\frac{1{,}5F(\phi_{s,cat} - \phi_l - \Delta\phi_{eq})}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(-\frac{0{,}5F(\phi_{s,cat} - \phi_l - \Delta\phi_{eq})}{RT}\right)\right) \quad (3)$$

where **n** denotes the normal vector to the boundary. The condition at the anode is

$$\mathbf{N}_{Cu^{2+}} \cdot \mathbf{n} = -\frac{i_0}{2F}\left(\exp\left(\frac{1{,}5F(\phi_{s,an} - \phi_l - \Delta\phi_{eq})}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(-\frac{0{,}5F(\phi_{s,an} - \phi_l - \Delta\phi_{eq})}{RT}\right)\right) \quad (4)$$

All other boundaries are insulating:

$$\mathbf{N}_{Cu^{2+}} \cdot \mathbf{n} = 0\,. \quad (5)$$

For the sulfate ions, insulating conditions apply everywhere:

$$\mathbf{N}_{SO_4^{2-}} \cdot \mathbf{n} = 0\,. \quad (6)$$

The initial conditions set the composition of the electrolyte according to

$$c_{Cu^{2+}} = c_0$$
$$c_{SO_4^{2-}} = c_0 \tag{7}$$

You set up Equation 1 through Equation 7 using the Nernst-Planck application mode in the Chemical Engineering Module. The Moving Mesh (ALE) application mode keeps track of the deformation of the mesh. You find the input data in the model by choosing **Constants** and **Expressions** on the **Options** menu in COMSOL Multiphysics.

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 4.4 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 for the quality of the deposition because 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. Note that the model is symmetric along a vertical line

in the middle of the cell. A nonsymmetric result would have been a sign of poor mesh resolution.

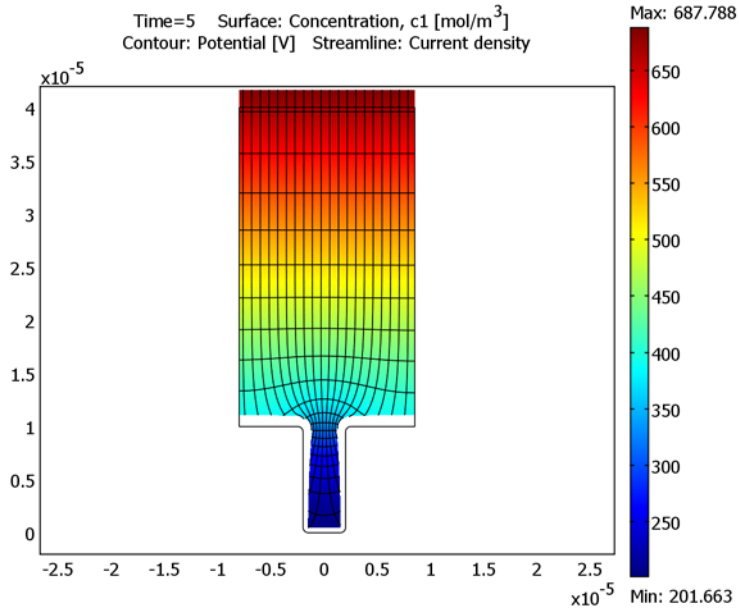

Figure 2: Copper ion concentration (mol/m^3), isopotential lines, current density streamlines, and electrode displacement in the cell after 4.4 seconds of operation.

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.

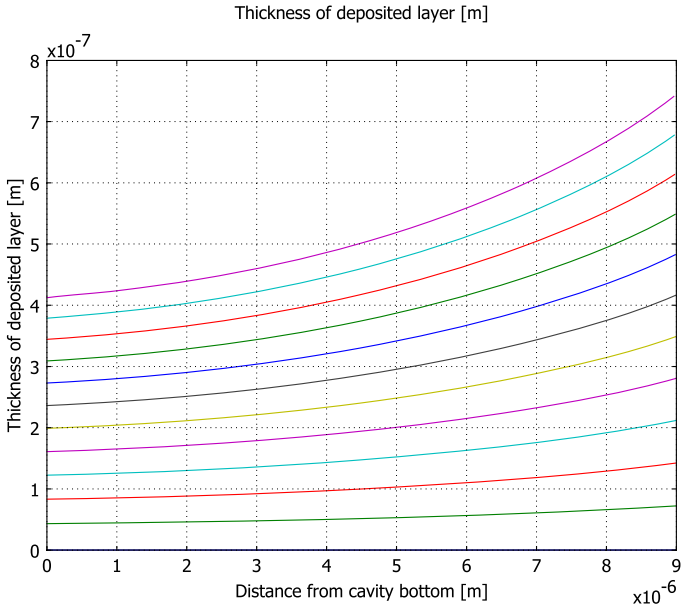

Figure 3: Thickness of the deposition along the vertical cathode boundaries. The lines are generated for increments of 0.4 seconds from 0 to 4.4 seconds.

Despite the simplicity of this model, it can easily be expanded to more complicated geometries, and it is also possible to expand it 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.