A 2D Axisymmetric Electrodeposition Model

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Abstract: Electroplating is a vital technology widely employed for many technological applications ranging from decorative or anti-corrosion coatings to high precision nanotechnology passive electromagnetic cloaking devices. This 2D Axisymmetric Electroplating Model demonstrates one of the modeling methodologies that can be used to calculate the transient generation of a coating thickness of a deposited metal layer on the cathode electrode well in a copper-electroplating bath. This model computes the mass transport and deposition on the electrode of copper ions through the fluid medium, thus resulting in the transient calculation of the electrodeposition (electroplating) of a new copper layer.

Keywords: electroplating, nanotechnology, cloaking, electrodeposition, coating thickness.

1. Introduction

Electrodeposition is a critical technology that is widely employed for many diverse technological applications ranging from decorative or anti-corrosion coatings to high precision nanotechnology passive electromagnetic cloaking devices.

This 2D Axisymmetric Electroplating Model demonstrates one of the transient modeling methodologies that can be used to calculate the coating thickness of the deposited metal layer on the cathode electrode for a well structure immersed in a copper-electroplating bath (Figure 1).
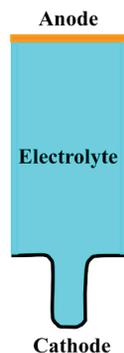
Figure 1. Cathode electrode well structure.

This model computes the mass transport and deposition on the well structure electrode of copper ions through the fluid medium, thus resulting in the transient calculation of the electrodeposition (electroplating) of a new copper layer.

2. The COMSOL Multiphysics Model

There is a very large literature of specific, experimentally detailed electroplating processes just for copper and copper alloys {1}. Many of those highly detailed books have been written such that they include specific solution process chemistry and time/power process details.

The object of this 2D Axisymmetric model is to demonstrate specifically, on a first approximation basis, the modeling of an example of the copper sulfate electroplating process, where the bath acidity (pH 4) is in the moderate range. Many of the more common electroplating processes utilize consumable anodes (copper) as the source of copper ion replenishment for the electroplating bath.

Since in this case the model is for a first approximation to the copper electroplating process, trace additives that are typically included in the bath to improve the second order properties of the deposited copper (brightness, porosity, adhesion, etc.) are not included within this model.

The inclusion of additional trace additives and the related ions will significantly increase the difficulty of building and solving the model. That inclusion of process detail will not necessarily expand or clarify the desired fundamental understanding sought by building a model of the electroplating process.

This model is set up as a two-dimensional axisymmetric time-dependent model. It employs the Nernst-Planck Equation (chnp) found in the Chemical Species Transport physics interface in conjunction with the Moving Mesh (ale) technique found in the Mathematics Interface. The Nernst-Planck Equation governs the ionic mass transport process that occurs in the fluid electro-

lyte. The Nernst-Planck Equation is a conservation of mass equation and is an extension of Fick's Law of diffusion to include electrostatic forces. The Moving Mesh tracks the growth of the copper layer.

3. Governing Process

The Nernst-Planck Equation {2} specifies the ionic mass transport process that occurs in the fluid electrolyte. The Nernst-Planck Equation is a conservation of mass equation and is an extension of Fick's Law of diffusion {3} to include electrostatic forces.

The flux of each of the ions in the electrolyte is given by the Nernst-Planck equation as follows:

$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla V$$

(1)

Where: N_i = mass transport vector [mol/(m^2*s)]
D_i = Diffusivity of the ith species in the electrolyte [m^2/s]
c_i = Concentration of the ith species in the electrolyte [mol/m^3]
z_i = Charge of the ith species in the electrolyte [1] (unitless)
u_i = Mobility of the ith species in the electrolyte [(mol*m^2)/(J*s)]
F = Faraday's constant [A*s/mol]
V = Potential in the fluid [V]

And the mobility u_i can be expressed as:

$$u_i = \frac{D_i}{RT}$$

(2)

Where: D_i = Diffusivity of the ith species in the electrolyte [m^2/s]
R = Universal gas constant 8.31447[J/mol*K]
T = Temperature [K]

The material balances for each species are expressed as:

$$\frac{\partial c_i}{\partial t} = -\nabla \bullet N_i$$

(3)

Where: c_i = Concentration of the ith species in the electrolyte [mol/m^3]
N_i = mass transport vector [mol/(m^2*s)]
t = time [t]

The electroneutrality condition is given as follows:

$$\sum_i -z_i c_i = 0$$

(4)

Where: z_i = Charge of the ith species in the electrolyte [1] (unitless)
c_i = Concentration of the ith species in the electrolyte [mol/m^3]

The boundary conditions at the anode and the cathode are determined by the assumed electrochemical reaction and the Butler-Volmer equation {4}.

In the case of building this model, the assumed electrochemical reaction by which copper is deposited on the cathode is as follows. There are two reactions that occur. They are: $Cu^{2+}+e^- = Cu^+$ and $Cu^+ +e^- = Cu$. Typically, since not all things are equal and it is known that the Rate Determining Step (RDS) (slowest) is the $Cu^{2+}+e^- = Cu^+$, by about a factor of 1000 {5}, it is herein assumed that the $Cu^{2+}+e^- = Cu^+$ step is in equilibrium.

That being the case, then the cathode mass transport is:

$$N_{Cu^{2+}} \cdot n = \frac{i_0}{2F}\left(\exp\left(\frac{1.5F\eta_{cat}}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(-\frac{0.5F\eta_{cat}}{RT}\right)\right)$$

(5)

Where: N_i = mass transport vector [mol/(m^2*s)]
n = normal vector
i_0 = Exchange current density [A/m^2]
R = Universal gas constant [J/(mol*K)]
$c_{Cu^{2+}}$ = Concentration of the Cu^{2+} species in the electrolyte [mol/m^3]
$c_{Cu^{2+},ref}$ = Reference concentration of the Cu^{2+} species in the electrolyte [mol/m^3]
η_{cat} = Cathode overpotential [V]
F = Faraday's constant [A*s/mol]
T = Temperature [K]

It also follows from the above then that, the anode mass transport is:

$$N_{Cu^{2+}} \cdot n = \frac{i_0}{2F}\left(\exp\left(\frac{1.5F\eta_{an}}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(-\frac{0.5F\eta_{an}}{RT}\right)\right)$$

(6)

Where: N_i = mass transport vector [mol/(m^2*s)]
   n = normal vector
   i_0 = Exchange current density [A/m^2]
   R = Universal gas constant [J/(mol*K)]
   $c_{Cu^{2+}}$ = Concentration of the Cu^{2+} species in the electrolyte [mol/m^3]
   $c_{Cu^{2+},ref}$ = Reference concentration of the Cu^{2+} species in the electrolyte [mol/m^3]
   η_{an} = Anode overpotential [V]
   F = Faraday's constant [A*s/mol]
   T = Temperature [K]

For the insulating boundaries, where the mass transport is zero,

$$N_{Cu^{2+}} \cdot n = 0$$

(7)

Where: N_{Cu}^{2+} = mass transport vector [mol/(m^2*s)]
   n = normal vector

And for sulfate ions, the insulating applies everywhere, thus,

$$N_{SO_4^{2+}} \cdot n = 0$$

(8)

Where: N_{SO4}^{2+} = Mass Transport Vector [mol/(m^2*s)]
   n = normal vector

4. Building the Model

Figure 2 shows the Model Builder flow chart from the completed 2D Axisymmetric Electrodeposition Model. The Model Builder flowchart shows that this model is set up as a two-dimensional axisymmetric time-dependent model. It employs the physics of the Nernst-Planck Equation (chnp) found in the Chemical Species Transport physics interface in conjunction with the Moving Mesh (ale) technique found in the Mathematics Interface.
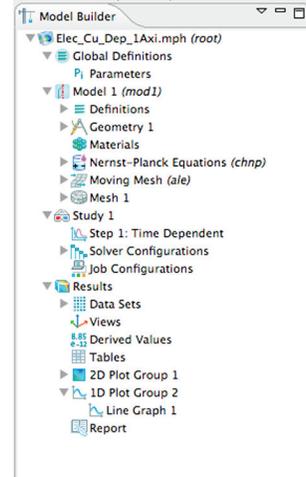

Figure 2. 2D Axisymmetric Electrodeposition Model.

Once the model platform has been established, the Global Parameters are entered in the Parameters table. The Global Parameters are as follows in Table 1:

Table 1: Global Parameters

Name	Expression	Description
Cinit	500 [mol/(m^3)]	Initial concentration
T0	298[K]	System temperature
i0	150[A/m^2]	Exchange current density
phi_eq	0[V]	Relative equilibrium potential
alpha	0.75[1]	Symmetry factor
phi_s_anode	0.0859[V]	Anode potential
phi_s_cathode	-0.0859[V]	Cathode potential
z_net	2[1]	Net species charge
z_c1	z_net[1]	Charge, species c1
z_c2	-z_net[1]	Charge, species c2
um_c1	D_c1/R_const/T0	Mobility, species c1
um_c2	um_c1	Mobility, species c2

Name	Expression	Description
MCu	63.546e-3[kg/mol]	Cu molar mass
rhoCu	7.7264e3[kg/m^3]	Cu density
D_c1	2e-9[m^2/s]	Diffusivity
alpha1	0.5[1]	Symmetry factor
alpha2	1.5[1]	Diffusivity
D_c2	D_c1	Symmetry factor

Now that the Parameters have been entered, the model geometry can be built as shown in Figure 3.
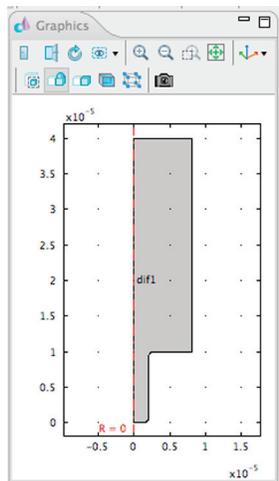
Figure 3. 2D Axisymmetric Electrodeposition Model Geometry

Once the geometry has been completed, the local variables are added to the model by entry in the Variables 1 edit field, as indicated in Figure 4.
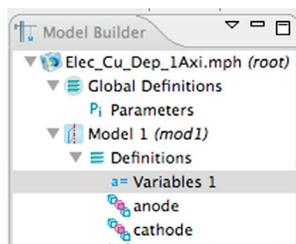
Figure 4. Local Variables, Variable 1.

The expressions are indicated in Table 2.

The anode and cathode selections shown in Figure 4 are created for convenience in boundary selection, when establishing the interface boundary conditions.

Table 2: Local Variables

Name	Expression	Description
i_anode	i0*(exp(alpha*z_net*F_const/R_const/T0*(phi_s_anode-V-phi_eq))-c1/Cinit*exp(-alpha1*z_net*F_const/R_const/T0*(phi_s_anode-V-phi_eq)))	Anode current density
i_cathode	i0*(exp(alpha2*z_net*F_const/R_const/T0*(phi_s_cathode-V-phi_eq))-c1/Cinit*exp(-alpha1*z_net*F_const/R_const/T0*(phi_s_cathode-V-phi_eq)))	Cathode current density
growth	i_cathode*MCu/rhoCu/z_net/F_const	Deposition rate, cathode
n_growth	i_anode*MCu/rhoCu/z_net/F_const	Deposition rate, anode
displ_r	abs(r-R)	Absolute displacement in r direction

5. Specifying the Modeling Conditions

One of the most important parts of any model is the definition and specification of the condition within the domains and at the boundaries of the model. Each physics interface requires a set of conditions that define the behavior of the media within and at each boundary.

As discussed in section 3 of this paper, the appropriate parameters and variable expressions need to be entered in subsections of the Nernst-Planck Equations Interface (chnp) and the Moving Mesh Interface (ale) as shown in Figure 5.
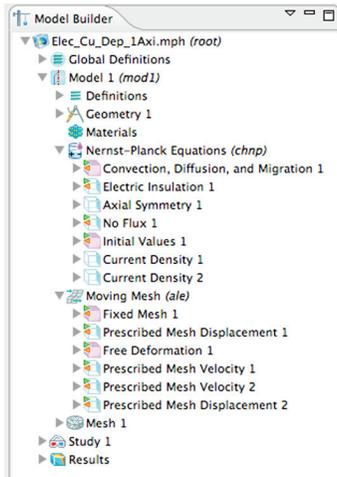
Figure 5. Model Builder, Domain and Boundary
Condition Specification.

6. Results

The model, once configured, runs to convergence quickly. The converged result is shown in Figure 6.
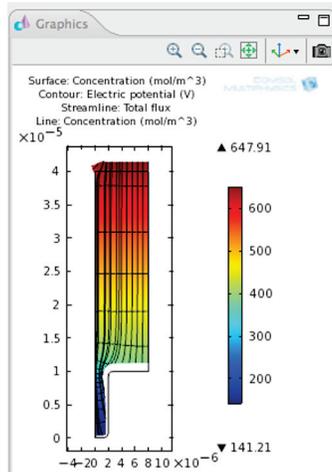

Figure 6. 2D Axisymmetric Electrodeposition Model.

Figure 7 shows the thickness of the copper coating as a function of distance from the bottom of the cavity.
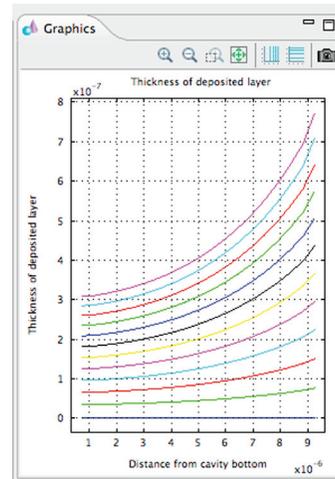
Figure 7. Copper coating thickness as a function
of the distance from the bottom of the cavity.

7. Conclusions

COMSOL Multiphysics 4.x works well for the solution of electrodeposition and many other types of multiphysics problems.

8. References

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