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Finite Element Technique for Electrochemical Copper Deposition

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Abstract: Electrochemical systems are devices or processes in which an ionic conductor mediates the interconversion of chemical and electrical energy. This paper presents a model to simulate the electroplating of copper in a microcavity typically found in the plating of copper onto circuit boards. We successfully demonstrate the use of moving meshes for plating processes and we 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.

Keywords: Electrochemical energy; Copper deposition; Moving meshes; Simulation.

1. Introduction

Today, copper films have draw great interest to fabricate the printed circuit boards, electronic devices such as sensors, wearable electronics, batteries, and Radio Frequency Identification (RFID) tags, and electric lead in narrow bezel touch screen owing to their high electrical conductivity in the electronic industry [1-3].

A two-chamber galvanic cell enabled the simultaneous study of both oxidation and reduction processes involved in electroless copper deposition presented in [4]. Electrochemical impedance spectroscopy (EIS) results interpreted with regard to other recent experimental studies for copper deposition in the presence of polyethylene glycol and CI^- in [5]. Futhermore, Galvanostatic studies of the kinetics of deposition and dissolution in the copper + copper sulphate system presented in [6]. In this work, we design the electroplating of copper in a microcavity typically found in the plating of copper onto circuit boards. In addition, we investigate the influence of the cavity on the plating result using the finite element method (FEM) with COMSOL multiphysics package. COMSOL modeling is performed by following a procedural flow as in Figure 1 [7].

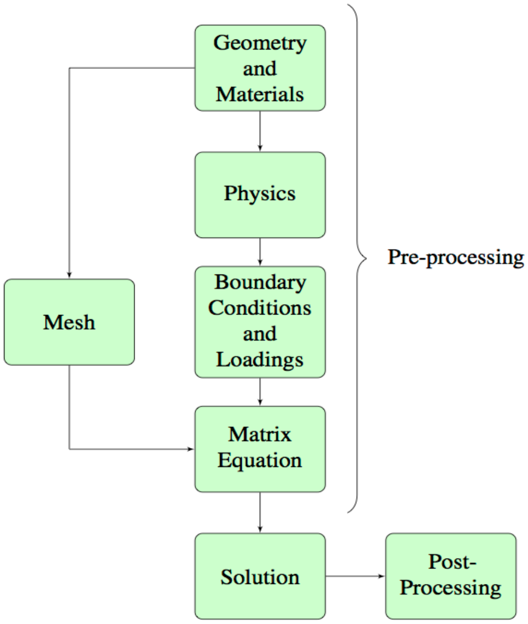


Figure 1: The steps in COMSOL modeling [7]

2. Results and Discussion

The model simulates the deposition process at pH4, which implies that the proton concentration is very low compared to the copper and sulfate ion concentrations. The deposition at the cathode and the dissolution at the anode are assumed to take place with one hundred present current yields. During the process, differences in electrolyte density arise in the enclosed cell, giving higher density at the anode compared to the cathode.

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 2. The upper horizontal boundary corresponds to the anode, while the cathode is placed at the bottom. The vertical walls represents the pattern on the master electrode with the assumption is to be insulating.

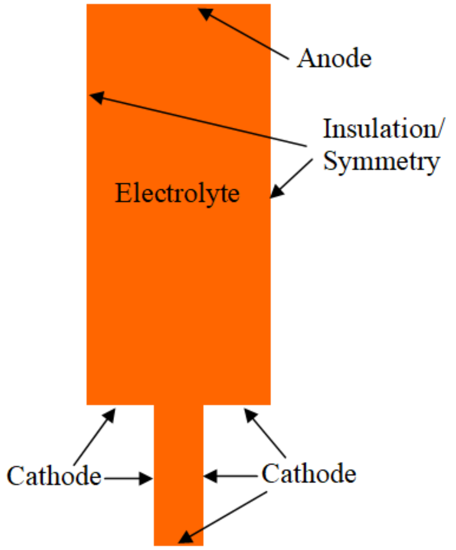


Figure 2. Cross section of the Model with boundaries corresponding to the anode, cathode, and vertical symmetry walls

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

$$\vec{N}_\mathrm{i} = -\left(D_i \nabla c_i + z_i u_i F c_i \nabla \phi_i\right) \qquad (1)$$

where

$\vec{N}_\mathrm{i}$: the transport vector (mol/(m^2·s)),

D_i : is the diffusion coefficient (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 given by:

$$\frac{\partial c_i}{\partial t} = -\nabla \bullet \vec{N}_\mathrm{i} \qquad (2)$$

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

$$\sum_{i=0}^{n} z_i c_i = 0 \qquad (3)$$

The boundary conditions for the anode and cathode are given by the *Butler-Volmer equation* for copper deposition. The deposition process is expressed through:

$$Cu^+ = Cu^{2+} + e^- \qquad (4)$$

$$Cu = Cu^+ + e^- \qquad (5)$$

The first step (4) is rate determining step (RDS), and the second step (5) is assumed to be at equilibrium. This provides the following relation for the local current density as a function of potential and copper concentration as given by:

$$i_{ct} = i_0 \left\{ e^{\left(\frac{1.5F\gamma}{RT}\right)} - \left(\frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\right) e^{\left(-\frac{0.5F\gamma}{RT}\right)} \right\} \qquad (6)$$

where

γ : the overpotential

The overpotential is expressed through:

$$\eta = \phi_{S,0} - \phi_1 - \Delta\phi_{eq} \qquad (7)$$

where

$\phi_{S,0}$: the electronic potential of the respective electrode.

This provides the following condition for the cathode:

$$\vec{N}_{Cu^{2+}} \bullet \vec{a}_n = \frac{i_0}{2F} \left\{ \begin{array}{l} -e^{\left(\frac{-1.5F\left(-\phi_{s,cat} + \phi_l + \Delta\phi_{eq}\right)}{RT} \right)} \\ + \left(\frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}} \right) e^{\left(\frac{0.5F\left(-\phi_{s,cat} + \phi_l + \Delta\phi_{eq}\right)}{RT} \right)} \end{array} \right\} \quad (7)$$

Where

$\vec{a}_n$: the normal vector to the boundary.

The condition at the anode is given by

$$\vec{N}_{Cu^{2+}} \bullet \vec{a}_n = \frac{i_0}{2F} \left\{ \begin{array}{l} -e^{\left(\frac{-1.5F\left(-\phi_{s,an} + \phi_l + \Delta\phi_{eq}\right)}{RT} \right)} \\ + \left(\frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}} \right) e^{\left(\frac{0.5F\left(-\phi_{s,an} + \phi_l + \Delta\phi_{eq}\right)}{RT} \right)} \end{array} \right\} \quad (8)$$

All other boundaries are insulating which expressed through:

$$\vec{N}_{Cu^{2+}} \bullet \vec{a}_n = 0 \quad (9)$$

For the sulfate ions ($SO_4^{\ 2-}$), *insulating conditions* apply everywhere as given by:

$$\vec{N}_{SO_4^{\ 2-}} \bullet \vec{a}_n = 0 \quad (10)$$

The *initial conditions* set the composition of the electrolyte by:

$$c_{Cu^{2+}} = c_0 \quad (11)$$

$$c_{SO_4^{\ 2-}} = c_0 \quad (12)$$

The total reaction of this model is given by

$$Cu = Cu^{2+} + 2e^{-} \quad (13)$$

Figure 3 shows Mesh of the model consists of 6117 elements with minimum quality 0.6088 and average quality 0.9357, while Figure 4 illustrate the Surface concentration of the copper ion.

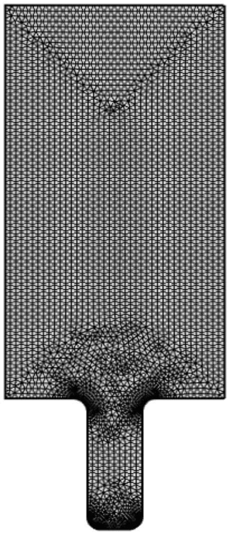


Figure 3. Mesh of the model consists of 6117 elements

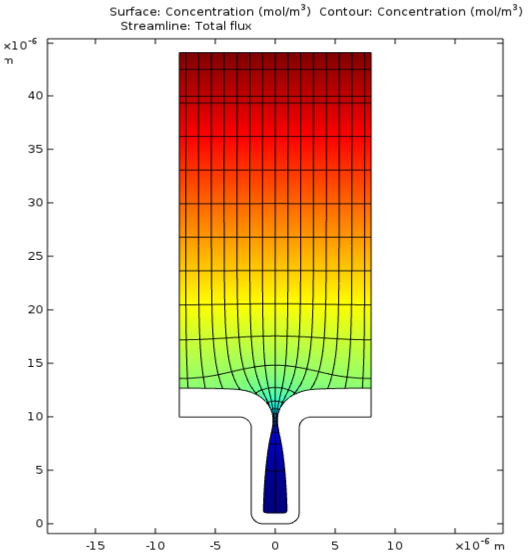


Figure 4. Surface concentration of the copper ion

Figure 5 presents the stream line, while Figure 6 the arrow surface of the model.

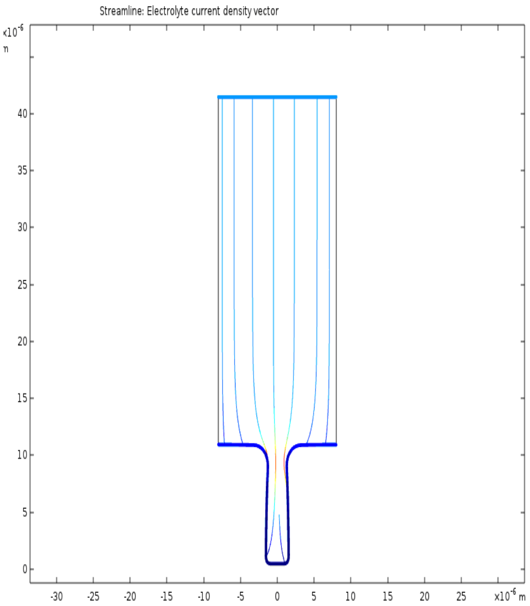


Figure 5. Stream Line of the model

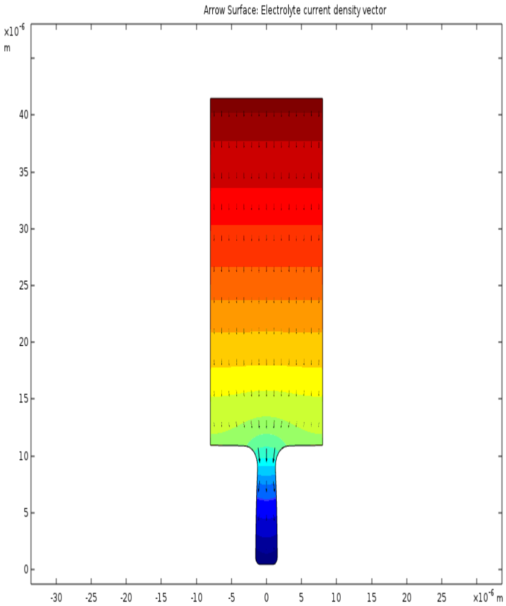


Figure 6. Arrow surface of the model

Figure 7 shows the thickness of the deposition along one of the vertical cathodic surfaces.

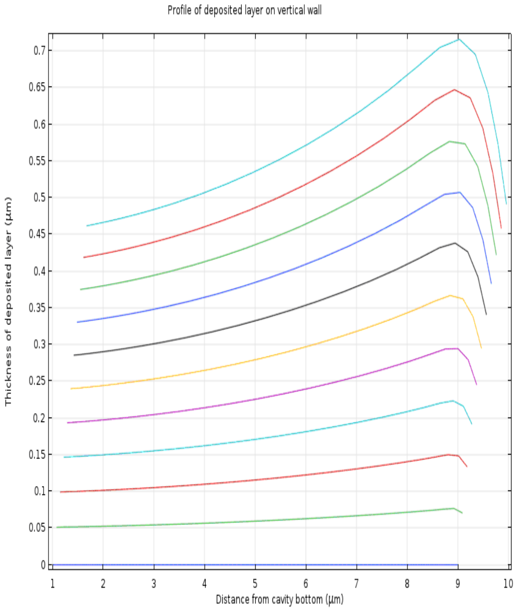
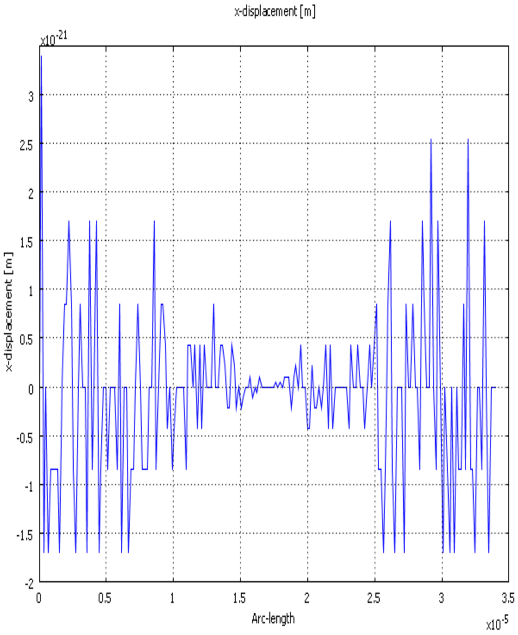
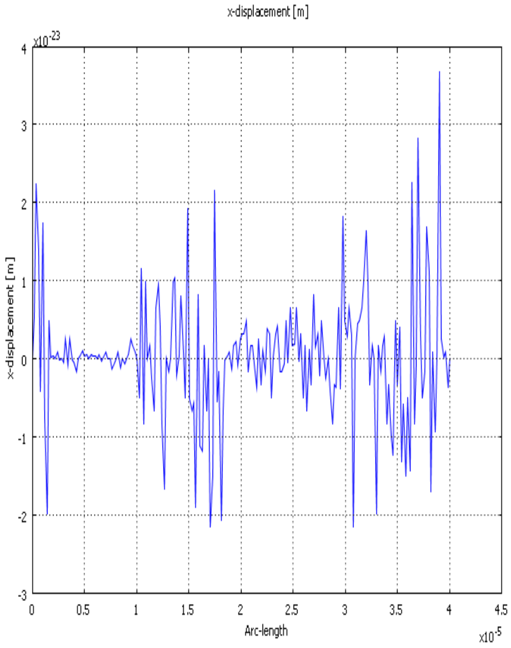


Figure 7. Thickness of the deposition along the vertical cathode boundaries

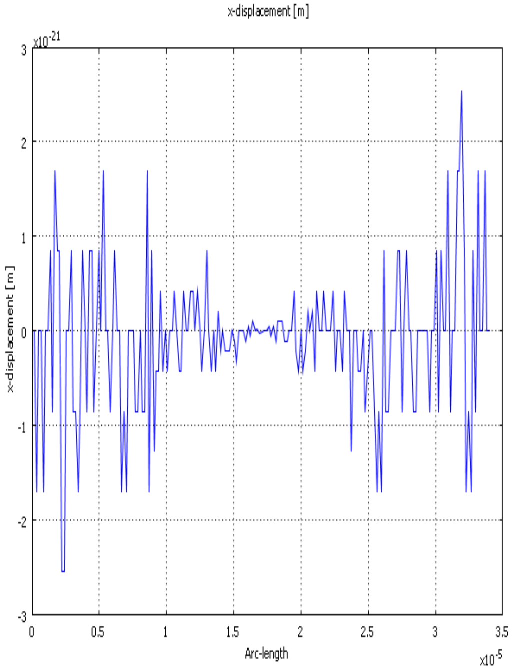
From our model, Figure 8 (a-d) shows the potential distribution analysis in different location.



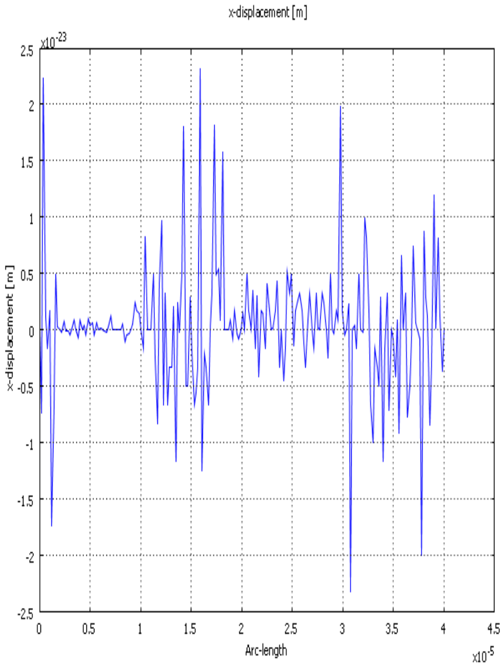
(a)



(b)



(c)



(d)

Figure 8. Analysis of potential distribution of the model (a – d)

3. Conclusions

This paper has demonstrated the use of the FEM method COMSOL multiphysics to 2-D model of the electroplating of copper in a microcavity typically found in the plating of copper onto circuit boards. We successfully illustrated the use of moving meshes for plating processes and the influence of the cavity on the plating result. The results obtained in this research are encouraging and motivating for further study.

4. References

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