# Copper Electroless Deposition

## Introduction

In the electroless deposition, partial oxidation and reduction reactions occur simultaneously at the same position at the electrode surface. The difference between the equilibrium potentials for the two reactions is hence the driving force for the deposition process. The potential at the electrode surface is estimated from the mixed potential theory so that the total anode current density is equal and opposite to the total cathode current density (Ref. 1 and Ref. 2).

This model simulates copper electroless deposition wherein copper reduction is a cathodic reaction and formaldehyde oxidation is an anodic reaction. The model accounts for mass transport by diffusion and electrochemical reactions at the electrode surface. The equilibrium potentials of partial electrochemical reactions are considered to be concentration dependent. The model estimates the change in current density, deposition thickness and concentration of ionic species during the electroless deposition.

## Model Definition

The model is solved over a 1D computational domain comprised of diffusion layer with electrode surface at one end and bulk electrolyte at the other end, as shown in Figure 1. The diffusion layer thickness is set to 2 mm.

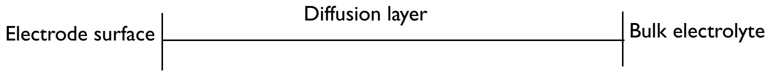

*Figure 1: Description of the boundary layer adjacent to the steel surface.*

Mass transport by diffusion for five ionic species is solved using the **Electroanalysis** physics interface:

$$\begin{aligned} \mathbf{N}_i &= -D_i \nabla c_i \\ \frac{\partial c_i}{\partial t} &+ \nabla \cdot \mathbf{N} = 0 \end{aligned} \qquad (1)$$

where $c_i$ (mol/m$^3$) is the concentration, $\mathbf{N}_i$ (mol/(m$^2$·s)) is the flux vector, $D_i$ (m$^2$/s) is the diffusion coefficient and subscript $i$ indicates $i^{th}$ species. All species are assumed to be diluted in water. The species along with their diffusion coefficients and initial concentrations are tabulated in Table 1.

TABLE 1: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS (Ref. 1).

| SPECIES | D $(m^2/s)\cdot 10^9$ | $c_{ref}$ $(mol/m^3)\cdot 10^{-3}$ |
|---|---|---|
| $Cu(OH)_2L_2^{-4}$ | 0.7 | 0.06 |
| HCHO | 1.2 | 0.22 |
| $HCOO^-$ | 1.454 | 0 |
| $OH^-$ | 5.273 | 0.016 |
| $L^{-2}$ | 0.794 | 0.39 |

Concentration at the bulk electrolyte boundary is set to the reference concentration as tabulated in Table 1.

$$c = c_{\mathrm{ref}} \tag{2}$$

At the electrode surface boundary, **Electrode Surface** boundary condition is used wherein the total current is set to 0. This boundary condition yields a constant potential, $\phi_{s,\mathrm{ext}}$, at the electrode surface boundary that satisfies the condition:

$$\int(\mathbf{n}\cdot\mathbf{i}_l)dl = 0 \tag{3}$$

where

$$\mathbf{n}\cdot\mathbf{i}_l = \sum_m i_{\mathrm{loc},\,m} \tag{4}$$

The initial value for boundary electric potentials is set to -0.85 V.

### ELECTROCHEMICAL REACTIONS

The following electrochemical reactions occur at the electrode surface:

Copper reduction

$$\mathrm{Cu(OH)_2L_2^{-4} + 2e^- \rightarrow Cu + 2OH^- + 2L^{-2}} \qquad E^0_{\mathrm{eq,\,Cu}} = -0.52\,V \tag{5}$$

Formaldehyde oxidation

$$\mathrm{2HCHO{+}4OH^- \rightarrow 2HCOO^- + H_2 + 2H_2O + 2e^-} \qquad E^0_{\mathrm{eq,\,HCHO}} = -1.04\,V \tag{6}$$

**Concentration dependent kinetics** is used to model copper reduction and formaldehyde oxidation reactions, which will set the local current density according to

$$i_{\mathrm{loc,\,m}} = i_{0,\,\mathrm{m}}\left(C_{\mathrm{R,m}}\exp\left(\frac{0.5F\eta_{\mathrm{m}}}{RT}\right) - C_{\mathrm{O,m}}\exp\left(-\frac{0.5F\eta_{\mathrm{m}}}{RT}\right)\right) \tag{7}$$

where $i_{0,\mathrm{m}}$ is the exchange current density, $C_{\mathrm{R,m}}$ is the reduced species expression, $C_{\mathrm{O,m}}$ is the oxidized species expression and $\eta_{,\mathrm{m}}$ is the overpotential for species m (Cu and HCHO, respectively).

The overpotential $\eta_{,\mathrm{m}}$ (V) is calculated from

$$\eta_{\mathrm{m}} = \phi_{s,\,\mathrm{ext}} - \phi_l - E_{\mathrm{eq,\,m}} \tag{8}$$

The equilibrium potentials for copper reduction and formaldehyde oxidation reactions are considered to be concentration dependent and are estimated from a Nernst Equation as,

$$E_{\mathrm{eq,Cu}} = E^0_{\mathrm{eq,\,Cu}} + \frac{RT}{nF}\ln\frac{[\mathrm{Cu(OH)_2L_2^{-4}}]^2}{[\mathrm{OH^-}]^2[\mathrm{L^{-2}}]^2} \tag{9}$$

$$E_{\mathrm{eq,HCHO}} = E^0_{\mathrm{eq,\,HCHO}} + \frac{RT}{nF}\ln\frac{[\mathrm{HCOO^-}]^2}{[\mathrm{OH^-}]^4[\mathrm{HCHO}]^2} \tag{10}$$

At the electrode surface boundary, fluxes of ionic species are defined in terms of the electrochemical reactions as,

$$\mathbf{n}\cdot\mathbf{N}_j = \frac{\nu_j i_j}{n_j F} \tag{11}$$

where, $\nu_j$ is stoichiometric coefficient, $i_j$ is the local current density, $n_j$ is the number of electrons involved in $j^{th}$ number of electrochemical reactions and $F$ is Faraday's constant (96485 C/mol). This will set the flux to be proportional to the electrode current density according to Faraday's law. The electrode kinetics parameters: $i_{0,\mathrm{Cu}}$=1 A/m$^2$ and $i_{0,\mathrm{HCHO}}$=1 A/m$^2$are taken from the current-potential curves reported in Ref. 2.

## *Results and Discussion*

Figure 2 shows the change in the mixed potential at the electrode surface during electroless deposition. It can be seen that the change is significant during the initial stages of deposition, which is attributed to the equilibrium potentials of copper reduction and formaldehyde oxidation reactions and a constraint of equal and opposite anode and cathode current densities. At about 400 s the potential reaches a maximum.

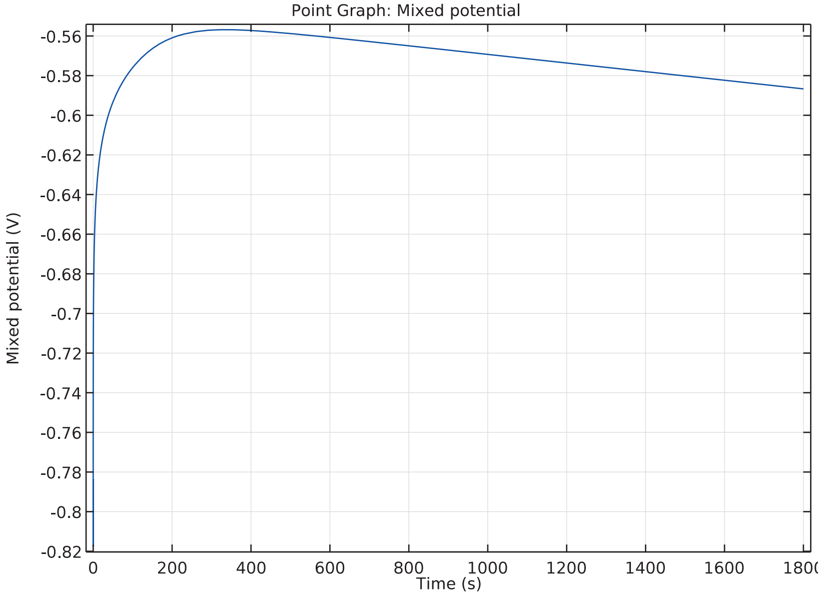

*Figure 2: The change in the mixed potential at the electrode surface against time during electroless deposition.*

Figure 3 shows the change in the local current density at the electrode surface during electroless deposition. It can be seen that the current density is considerably high in the initial stages of electroless deposition, corresponding to the trend observed for the mixed potential in Figure 2.

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