Tertiary Current Distributions on the Wafer in a Plating Cell

Lizhu Tong

Keisoku Engineering System Co., Ltd.

October 4, 2012

Excerpt from the Proceedings of the 2012 COMSOL Conference in Boston
1. Plating cell and tertiary current distributions
2. Modeling for calculating the current distributions with shear-plate agitating fluid flows
3. COMSOL Electrodeposition module
4. Results
   - Shear-plate agitating fluid flows
   - Tertiary current distributions
   - Effect of the distance between wafer and shear plate
5. Conclusions
The reciprocating paddle cell is a known practical method for depositing alloy films on wafer substrates.


Plating cell and tertiary current distributions (2)


Fig. 8. Dimensionless current density vs. distance profiles. (---) Uniform current distribution; (−−−) primary current distribution; (⋯⋯) secondary current distribution; (−−−−) tertiary current distribution. Average current density is 10 mA cm\(^{-2}\) and working electrode rotation speed is 750 rpm.

Electrode (Cathodic) Reactions

\[ M^{n+} + ne \rightarrow M \]

Deposition of metal M

Faradaic current \( I \)

Plating time \( t \)

\[ w = -M \cdot I \cdot t/(nF) \]

Atomic weight of metal M

Current distribution - Butler-Volmer equation

\[ i_{loc} = i_0\left[\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta}{RT}\right)\right] \]

Concentration diffusion and mass transfer are included

\[ i_{loc} = i_0\left(\prod \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{\gamma_{i,a}} \exp\left(\frac{\alpha_a F\eta}{RT}\right) - \prod \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{\gamma_{i,c}} \exp\left(-\frac{\alpha_c F\eta}{RT}\right)\right) \]
The plating cell

Meshing

$t = \frac{1}{4}T$

$t = \frac{3}{4}T$

$T$ is the reciprocating period of shear plate

$m = m_1 + m_2$
Electrolyte Transport of Charged and Neutral Species

- The Nernst-Planck Equation
- Flux = diffusion + convection + migration

\[ \mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_i \]
Electrolyte Current Density

- Current density
  \[ j = F \sum_i z_i N_i \]

- Electroneutrality, charge conservation
  \[ j = F \left( \sum_i -z_i D_i \nabla c_i + u \sum_i z_i c_i - \nabla \phi \sum_i (z_i)^2 m_i F c_i \right) \]

- Perfectly mixed
  \[ j = - \left( F \sum_i (z_i)^2 m_i F c_i \right) \nabla \phi \]

\( \kappa = \text{conductivity} \)
Basic equations used in this work (1)

- **Continuity equation**
  \[ \nabla \cdot (\rho \mathbf{u}) = 0 \]

- **Momentum equation**
  \[
  \rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot \left( \mu \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right) + \mathbf{F}
  \]

- **Material balance equation for the species i**
  \[
  \frac{\partial c_i}{\partial t} + \nabla \cdot \left( -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i + c_i \mathbf{u} \right) = R_{i,tot}
  \]

- **Current density \( i_l \) in the electrolyte**
  \[ i_l = F \sum_{i=1}^{n} z_i \left( -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i \right) \]

- **Charge balance in the electrolyte**
  \[ \nabla \cdot i_l = Q_l \]

- **Electroneutrality**
  \[ \sum z_i c_i = 0 \]
Basic equations used in this work (2)

It is known that the local current density on the electrode is related to the local overvoltage, $\eta$, on the electrode, i.e.,

$$\eta = V - \phi_0$$

- Overvoltage at low current density

$$\eta = \frac{i}{i_0} \left( \frac{RT}{(\partial a + \partial c)2F} \right)$$

- Exchange current density

$$i_0 = \left( \frac{c_w}{c_b} \right)^\gamma i_0(c_b)$$
Physics interfaces in Electrodeposition Module

- Current and potential distribution based on:
  - Charge and current balances
  - Material transport
  - Fluid flow
  - Heat transfer

- Deposited layer thickness and composition through:
  - Electrode reactions coupled to surface species balances
  - Fixed and moving boundaries coupled to surface species balances
The Electrodeposition Module is able to model arbitrary reaction mechanisms:

- Electrode kinetics using Butler-Volmer or by just typing in arbitrary expressions
- Multiple competing reactions
- Adsorption reactions including diffusion of adsorbed species at the electrode surface

Stoichiometric Coefficients

- Positive for reduced species, i.e. the species getting oxidized in the reaction
- Negative for oxidized species, i.e. the species getting reduced (same side as the electron)

\[
\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e^- \\
\nu_{\text{Cu}(s)} = 1 \\
\nu_{\text{Cu}^{2+}} = -1
\]

Equilibrium potential:

\[
E_{\text{eq}} = \text{User defined}
\]

Equilibrium potential at reference temperature:

\[
E_{\text{eq}, \text{ref}} = E_{\text{eq}}
\]

Temperature derivative of equilibrium potential:

\[
dE_{\text{eq}}/dT = 0
\]

Reference temperature:

\[
T_{\text{ref}} = 298.15 \text{[K]}
\]

\[
E_{\text{eq}} = E_{\text{eq}, \text{ref}} + dE_{\text{eq}}/dT (T - T_{\text{ref}})
\]

Electrode Kinetics

Kinetics expression type:

- User defined
- Butler-Volmer
- Linearized Butler-Volmer
- Anodic Tafel equation
- Cathodic Tafel equation

Concentration dependent kinetics

Number of participating electrons:

\[
n_m = 2
\]

Stoichiometric coefficient:

\[
\nu_{c1} = -1 \\
\nu_{c2} = 0
\]

\[
R_{i,m} = \frac{\nu_{i,m} n_{i,m}}{n_m F}
\]

\[
R_{i,m} = \frac{\nu_{i,m} n_{i,m}}{n_m F}
\]
Computational conditions

Shear plate
- Dimension: 5 mm thickness and 90 mm height
- Stroke length, $S$: 5 mm
- Reciprocating frequency: 5 Hz
- Distance between wafer and shear plate, $\delta$: 2-6 mm

Electrolyte properties
- Density: 1000 kg/m$^3$
- Kinematic viscosity: $1 \times 10^{-6}$ m$^2$/s
- Bulk concentration of cupric ions: 9.6 mol/m$^3$
- Diffusion coefficient of cupric ions: $5.37 \times 10^{-10}$ m$^2$/s

Electrode characteristics
- Factor for the effect of concentration, $\gamma$: 0.6
- Exchange current density, $i_0(c_p)$: 10 A/m$^2$
- Average current density on the wafer: 10 A/m$^2$

Boundary conditions
- The solved domain is limited up to the interface between air and solution.
- The boundary for the interface is regarded as free-slip wall.
- The bottom and side boundaries as well as the surfaces of electrodes are stationary no-slip walls.
The copper electrodeposition from an acid sulfate electrolyte composed of CuSO₄·5H₂O of 2.4 g/L and H₂SO₄ of 90 g/L was considered in this work.

Reference:
Results (2)

Flow velocity

Pressure

Current density
Results (3)

Distributions of tertiary current densities and concentrations on the wafer

Reduced current density

Reduced concentrations
Tertiary current distributions on the wafer for $\delta = 2$, $3$, $4$ mm

at the different phases of the reciprocating cycle
This paper presented the study of tertiary current distributions on the wafer in an industrial plating cell. The coupled solution of fluid equations and mass-transport equations were performed.

The simulation results included the velocity and pressure of fluid flows, ion concentrations, potential, and current densities in a plating cell.

The obtained distributions of tertiary current densities and ion concentrations on the wafer present an oscillating wave form, indicating the strong effect of shear-plate agitation on the current distributions.

The study of the distance between the wafer and shear plate allows us to control the current distributions on the wafer so as to further improve the quality of the deposited film in the plating cell in future.
Thank you for your attention!

Questions & Comments?