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Tertiary Current Distributions on the Wafer in a Plating Cell

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2. Modeling for calculating the current distributions with shear-plate agitating fluid flows
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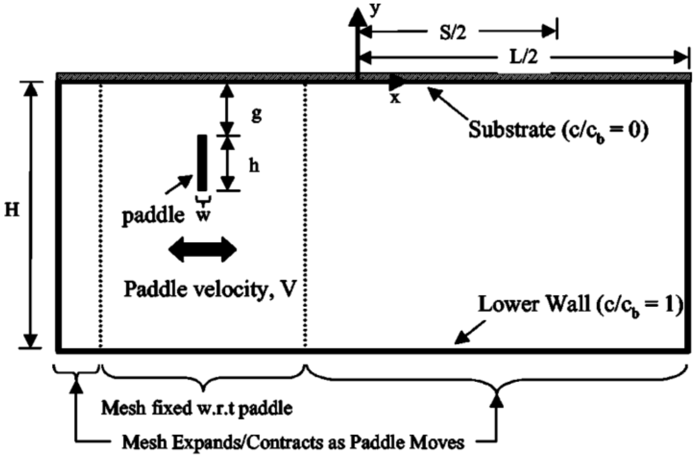
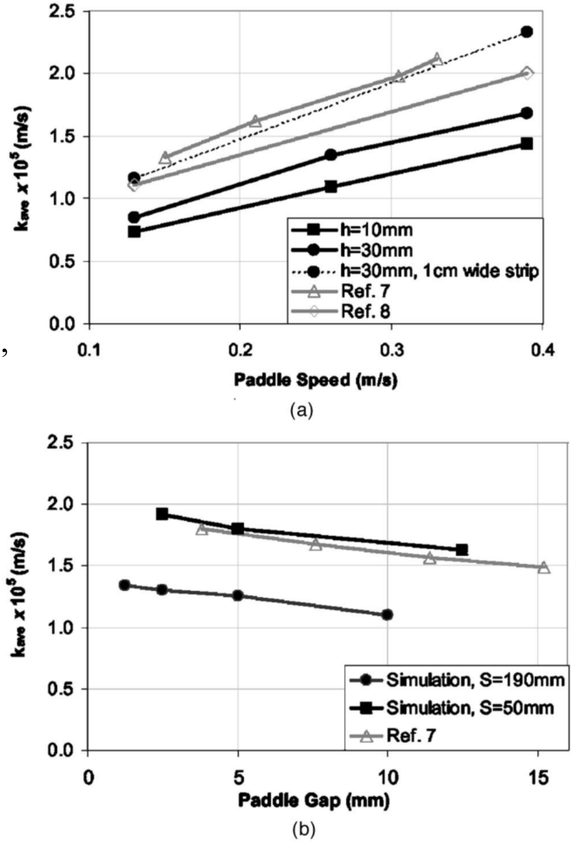
   - Tertiary current distributions
   - Effect of the distance between wafer and shear plate
5. Conclusions

Plating cell and tertiary current distributions (1)

The reciprocating paddle cell is a known practical method for depositing alloy films on wafer substrates.



G.J. Wilson, P.R. McHugh", *J. Electrochem. Soc.*, **152** (6), C357 (2005)



(a)

(b)

Figure 12. (a) Sensitivity of mass-transfer coefficient (k_{ave}) to paddle speed and substrate open area (Simulation: $h = 10$ and 30 mm, $g = 10$ mm, $S = 190$ mm, and $H = 150$ mm), and (b) sensitivity of mass-transfer coefficient (k) to paddle gap (g) (Simulation: $h = 10$ mm, $S = 50$ and 190 mm, $H = 150$ mm, and $V = 0.26$ m/s; Ref. 7 data: 12.7 mm tall dual-stacked triangle paddle, $S \sim 253.7$ mm, $V = 0.255$ m/s, and 0.863 cm^2 open area).

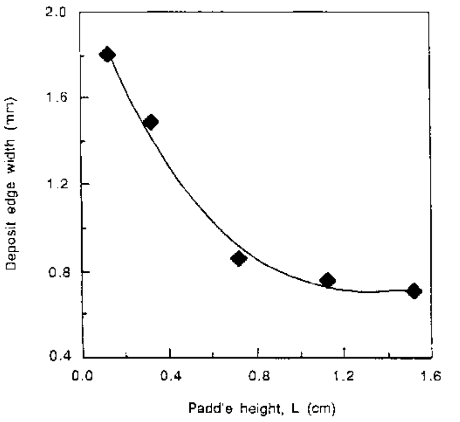
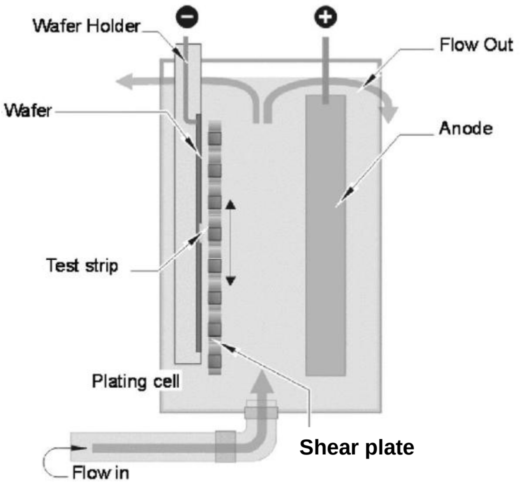


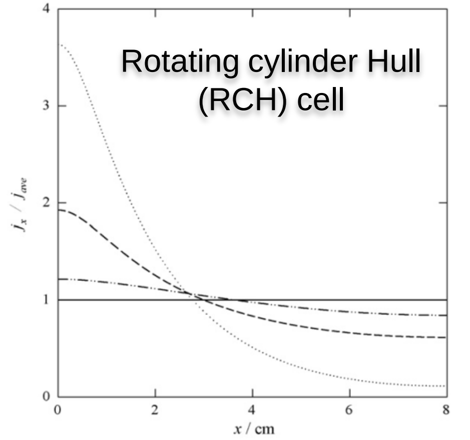
Fig. 3. Variation of copper deposit edge width with paddle height above the cathode for a plating solution of 0.05M $CuSO_4$ and 9 mM H_2SO_4.

D.E. Rice, D. Sundstrom, M.F. McEachern, L.A. Klumb, J.B. Talbot, *J. Electrochem. Soc.*, **135** (11), 2779 (1988)

Plating cell and tertiary current distributions (2)



B.Q. Wu, Z. Liu, A. Keigler, J. Harrell, *J. Electrochem. Soc.* **152** (5), C272 (2005).



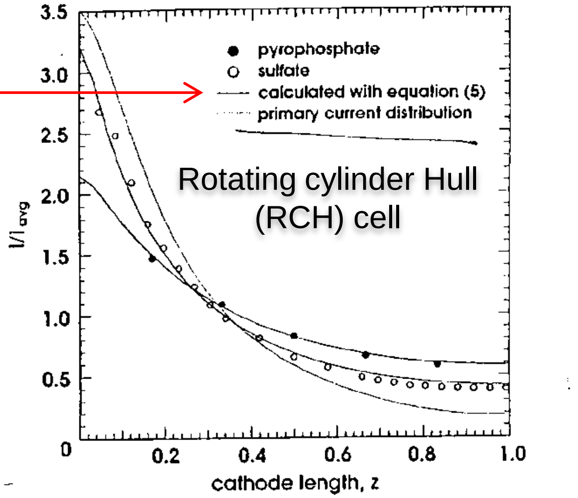
Rotating cylinder Hull (RCH) cell

C.T.J. Low, E.P.L. Roberts, F.C. Walsh, *Electrochim. Acta*, **52**, 3839 (2007).

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.

Tertiary current distribution (limited current)

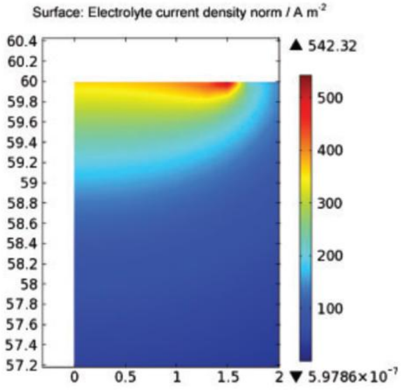
C. Madore, D. Landolt, C. Haβenpflug, and J.A. Hermann, *Plating & Surface Finishing* **82**, 38 (1995)



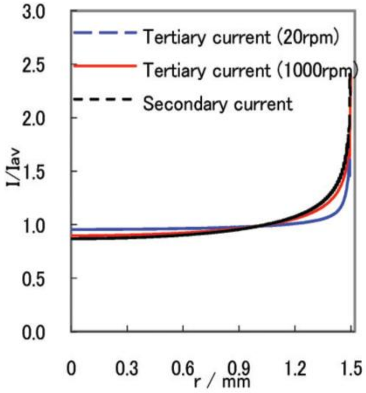
Rotating cylinder Hull (RCH) cell

Fig. 4—Measured and calculated current distributions along the cylindrical cathode for pyrophosphate and sulfate electrolytes.

Rotating disc electrode (RDE)



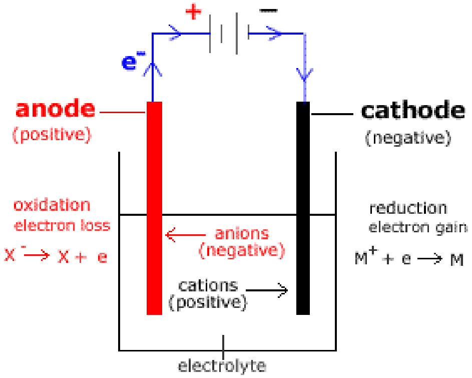
7 Tertiary current distribution around working electrode at ω=300 rev min^{-1}



8 Tertiary current distribution at working electrode in comparison with secondary current distribution: I_{av} is average current density over working electrode

L.Z. Tong, *Trans. Inst. Met. Fin.*, **90** (3), 122-123 (2012)

Plating cell and tertiary current distributions (3)



Electrode (Cathodic) Reactions

$$M^{n+} + ne => M$$

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

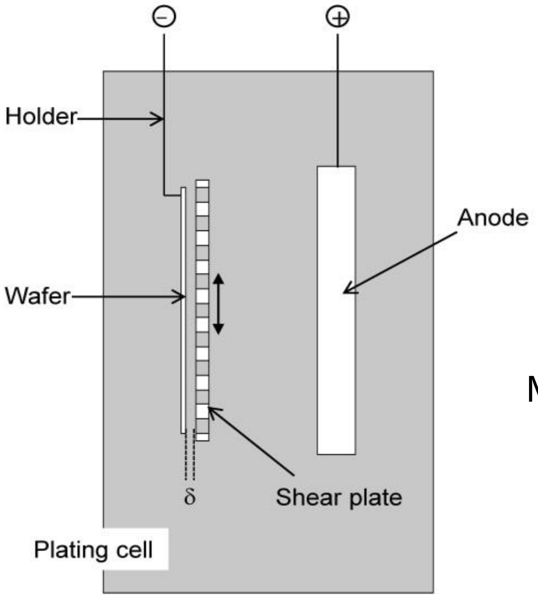
$$i_{\mathrm{loc}} = i_0 [\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp(-\frac{\alpha_c F \eta}{RT})]$$

Concentration diffusion and mass transfer are included

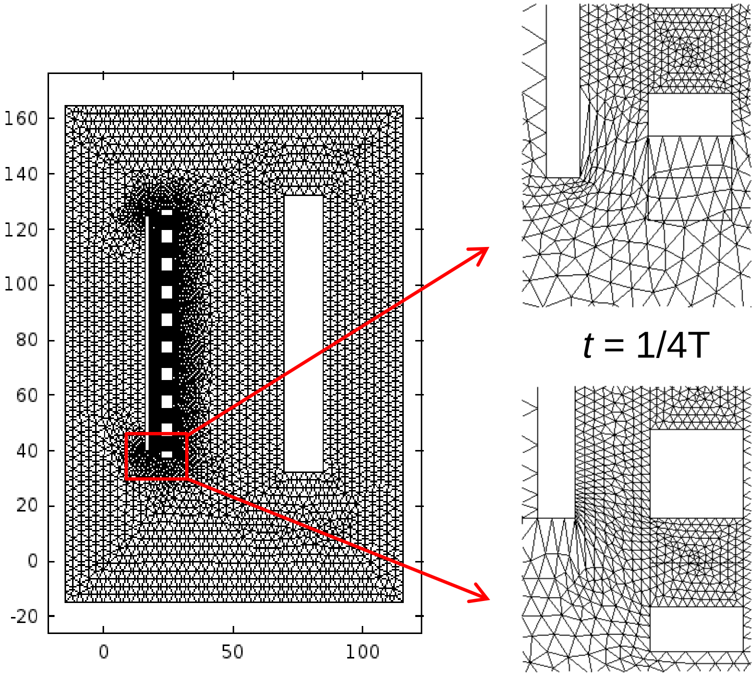
$$i_{\mathrm{loc}} = i_0 \left(\prod \left(\frac{c_i}{c_{i,\mathrm{ref}}} \right)^{\gamma_{i,a}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \prod \left(\frac{c_i}{c_{i,\mathrm{ref}}} \right)^{\gamma_{i,c}} \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right)$$

Modeling (1)

The plating cell



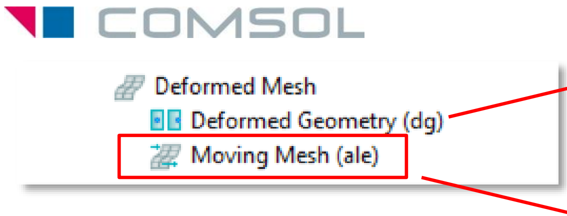
Meshing

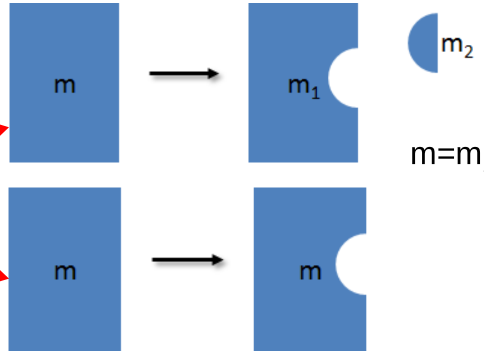


t = T

t = 1/4T

t = 3/4T





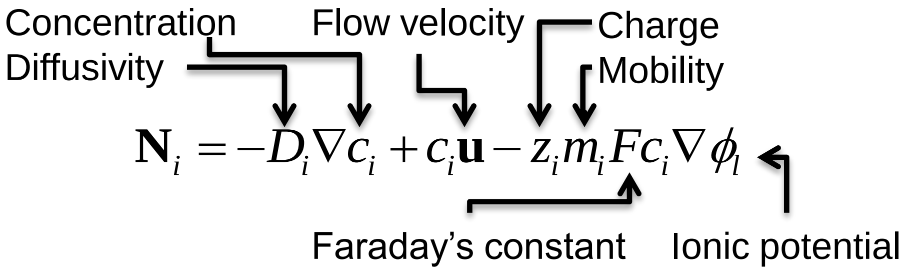
$m=m_1+m_2$

***T* is the reciprocating period of shear plate**

Modeling (2)

Electrolyte Transport of Charged and Neutral Species

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



Concentration

Diffusivity

Flow velocity

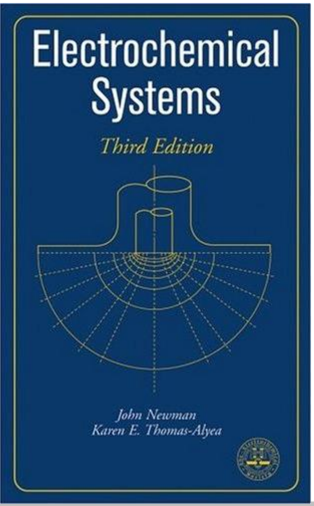
Charge

Mobility

$$\mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_l$$

Faraday’s constant

Ionic potential



Electrochemical Systems

Third Edition

John Newman

Karen E. Thomas-Alyea

Modeling (3)

Electrolyte Current Density

- Current density

$$\mathbf{j} = F\sum_i z_i \mathbf{N}_i$$

⇨

$$\mathbf{j} = F\left(\sum_i -z_i D_i \nabla c_i + \mathbf{u}\overbrace{\sum_i z_i c_i}^{\text{sum of charges}} - \nabla\phi_l \sum_i \left(z_i\right)^2 m_i F c_i\right)$$

- Electroneutrality, charge conservation sum of charges = 0

$$\mathbf{j} = F\left(\sum_i -z_i D_i \nabla c_i - \nabla\phi_l \sum_i \left(z_i\right)^2 m_i F c_i\right)$$

- Perfectly mixed (*primary* and *secondary current distribution*)

$$\mathbf{j} = -\underbrace{\left(F\sum_i \left(z_i\right)^2 m_i F c_i\right)}_{\kappa = conductivity}\nabla\phi_l$$

Modeling (4)

Basic equations used in this work (1)

- Continuity equation

$$\nabla \cdot (\rho \mathbf{u}) = 0$$

- Momentum equation

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

- Material balance equation for the species *i*

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + c_i \mathbf{u} \right) = R_{i,tot}$$

- Current density $\mathbf{i}_l$ in the electrolyte

$$\mathbf{i}_l = F \sum_{i=1}^{n} z_i \left(-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l \right)$$

- Charge balance in the electrolyte

$$\nabla \cdot \mathbf{i}_l = Q_l$$

- Electroneutrality

$$\sum z_i c_i = 0$$

Modeling (5)

Basic equations used in this work (2)

It is known that the local current density on the electrode is related to the local overvoltage, η on the electrode, *i.e.*,

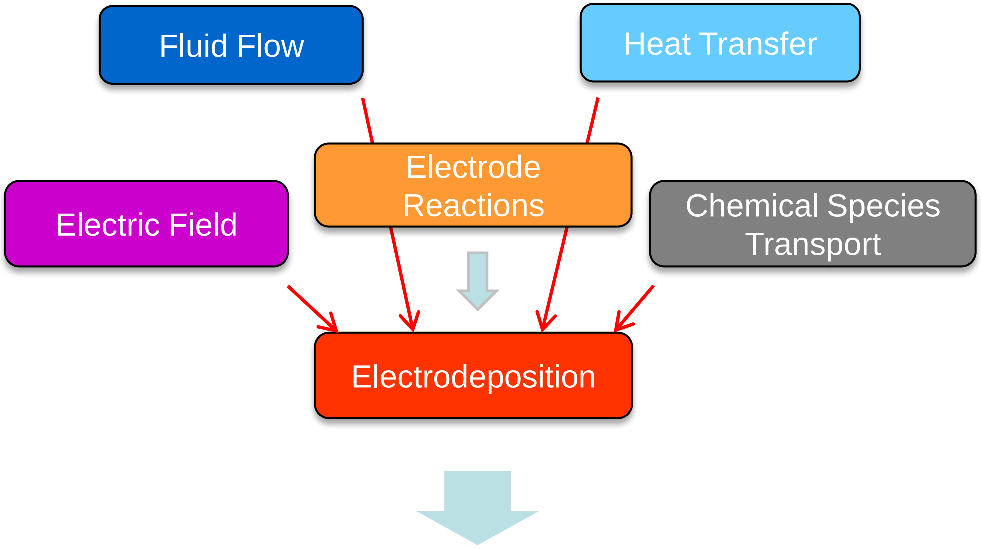
$$\eta = V - \phi_0$$

- Overvoltage at low current density

$$\eta = \frac{i}{i_0}\frac{RT}{(\partial_a+\partial_c)2F}$$

- Exchange current density

$$i_0 = \left(\frac{c_w}{c_b}\right)^{\gamma} i_0(c_b)$$



Fluid Flow

Heat Transfer

Electrode Reactions

Electric Field

Chemical Species Transport

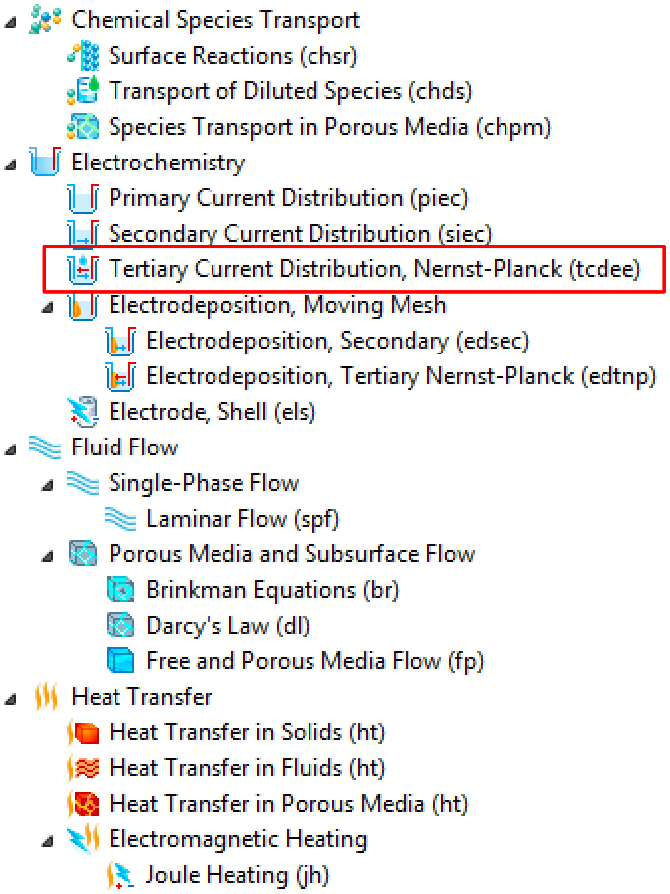
Electrodeposition

Coupled simulation of multiphysics

COMSOL Electrodeposition Module (1)

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



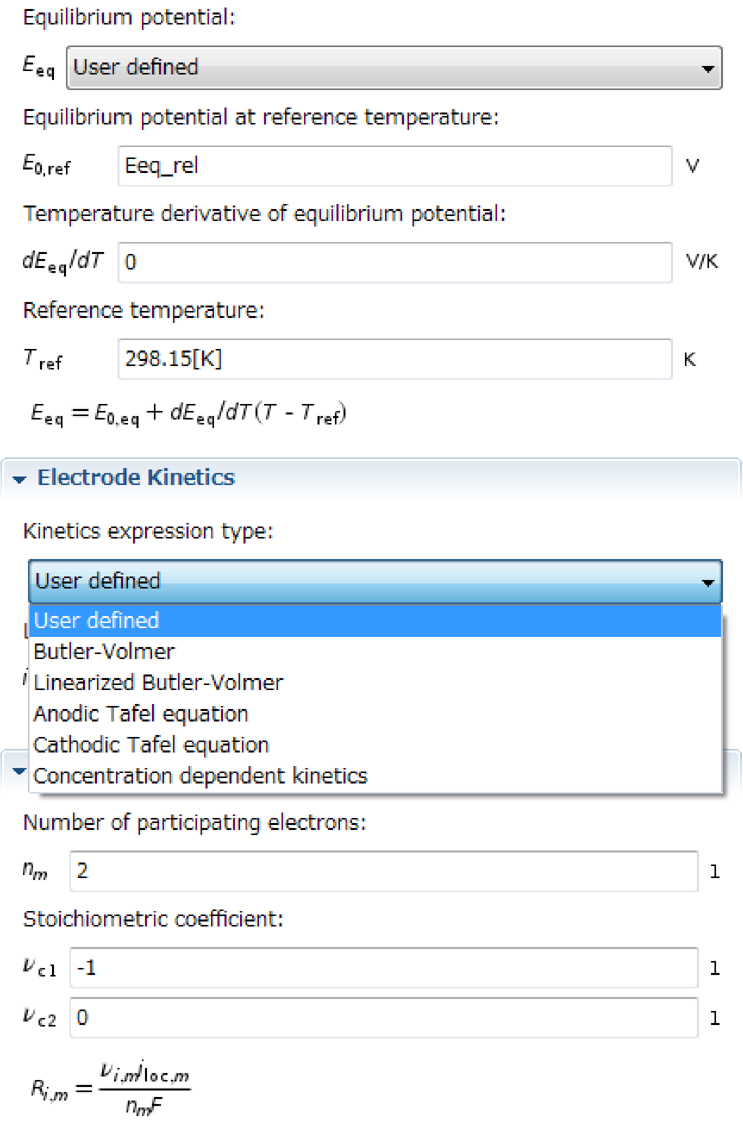
- Chemical Species Transport
  - Surface Reactions (chsr)
  - Transport of Diluted Species (chds)
  - Species Transport in Porous Media (chpm)
- Electrochemistry
  - Primary Current Distribution (piec)
  - Secondary Current Distribution (siec)
  - Tertiary Current Distribution, Nernst-Planck (tcdee)
  - Electrodeposition, Moving Mesh
    - Electrodeposition, Secondary (edsec)
    - Electrodeposition, Tertiary Nernst-Planck (edtnp)
  - Electrode, Shell (els)
- Fluid Flow
  - Single-Phase Flow
    - Laminar Flow (spf)
  - Porous Media and Subsurface Flow
    - Brinkman Equations (br)
    - Darcy's Law (dl)
    - Free and Porous Media Flow (fp)
- Heat Transfer
  - Heat Transfer in Solids (ht)
  - Heat Transfer in Fluids (ht)
  - Heat Transfer in Porous Media (ht)
  - Electromagnetic Heating
    - Joule Heating (jh)

COMSOL Electrodeposition Module (2)

- 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)

$Cu(s) \rightarrow Cu^{2+} + 2e^-$

$$\nu_{Cu(s)} = 1$$
$$\nu_{Cu^{2+}} = -1$$



Equilibrium potential:

E_{eq}: User defined

Equilibrium potential at reference temperature:

$E_{0,ref}$: Eeq_rel V

Temperature derivative of equilibrium potential:

dE_{eq}/dT: 0 V/K

Reference temperature:

T_{ref}: 298.15[K] K

$$E_{eq} = E_{0,eq} + dE_{eq}/dT(T - T_{ref})$$

Electrode Kinetics

Kinetics expression type:

User defined

Number of participating electrons:

n_m: 2 1

Stoichiometric coefficient:

ν_{c1}: -1 1

ν_{c2}: 0 1

$$R_{i,m} = \frac{\nu_{i,m} i_{loc,m}}{n_m F}$$

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, δ: 2-6 mm

Electrolyte properties

Density: 1000 kg/m^3

Kinematic viscosity: 1×10^{-6} m^2/s

Bulk concentration of cupric ions: 9.6 mol/m^3

Diffusion coefficient of cupric ions: 5.37×10^{-10} m^2/s

Electrode characteristics

Factor for the effect of concentration, γ: 0.6

Exchange current density, $i_0(c_b)$: 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.

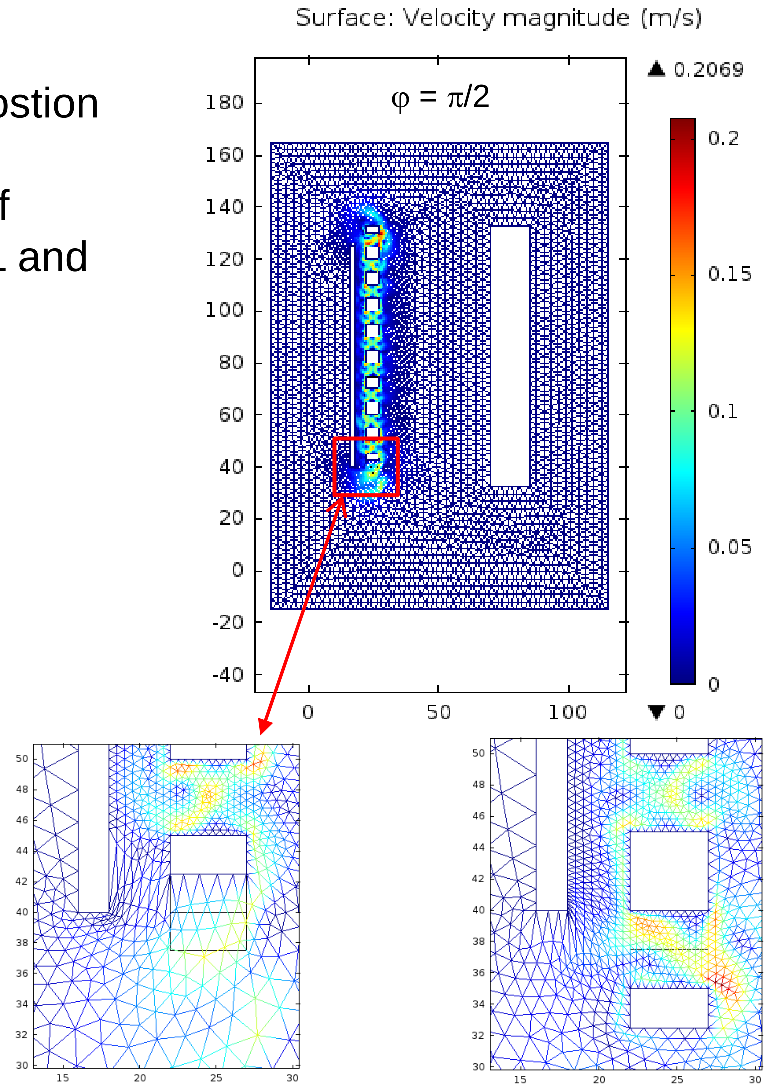
The bottom and side boundaries as well as the surfaces of electrodes are stationary no-silp walls.

Results (1)

The copper electrodepostion from an acid sulfate electrolyte composed of $CuSO_4 \cdot 5H_2O$ of 2.4 g/L and H_2SO_4 of 90 g/L was considered in this work.

Reference:
B.Q. Wu, Z. Liu, A. Keigler, J. Harrell, *J. Electrochem. Soc.* **152** (5), C272 (2005).

Flow velocity

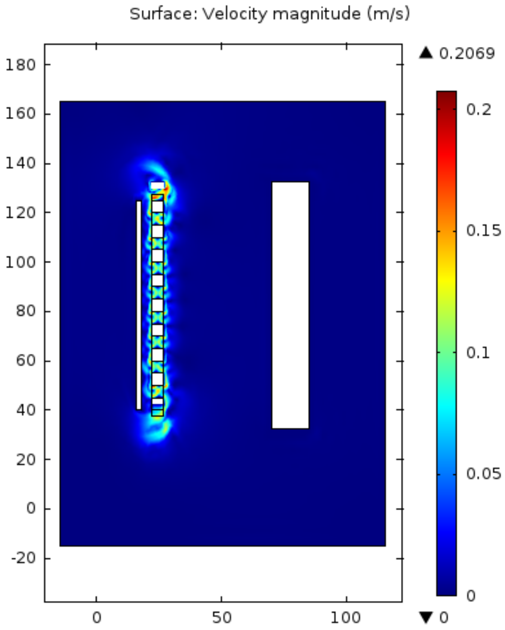


φ = π/2

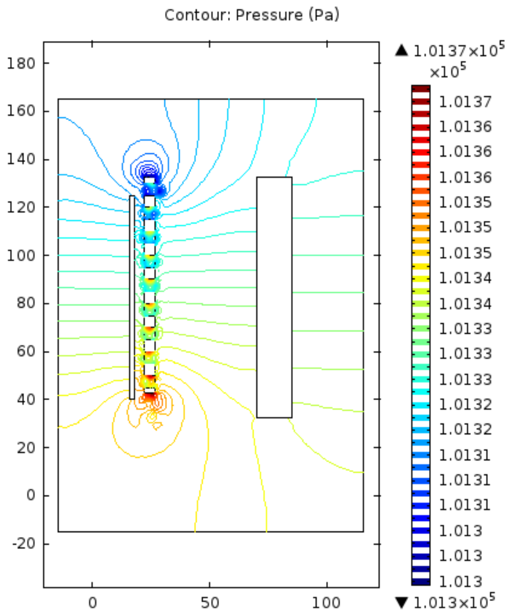
φ = 3π/4

Results (2)

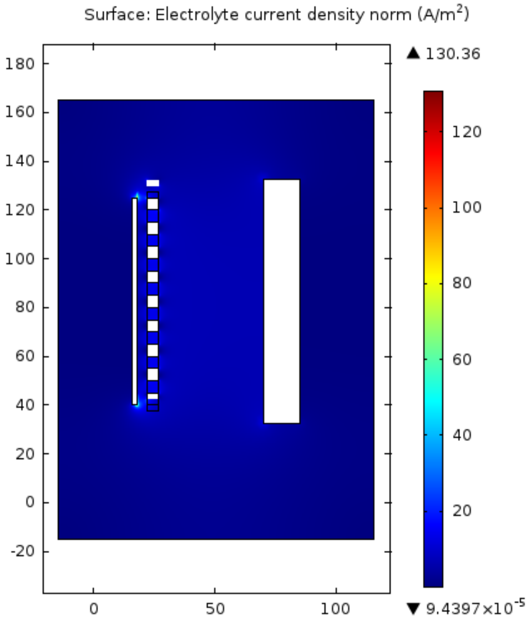
Flow velocity



Pressure

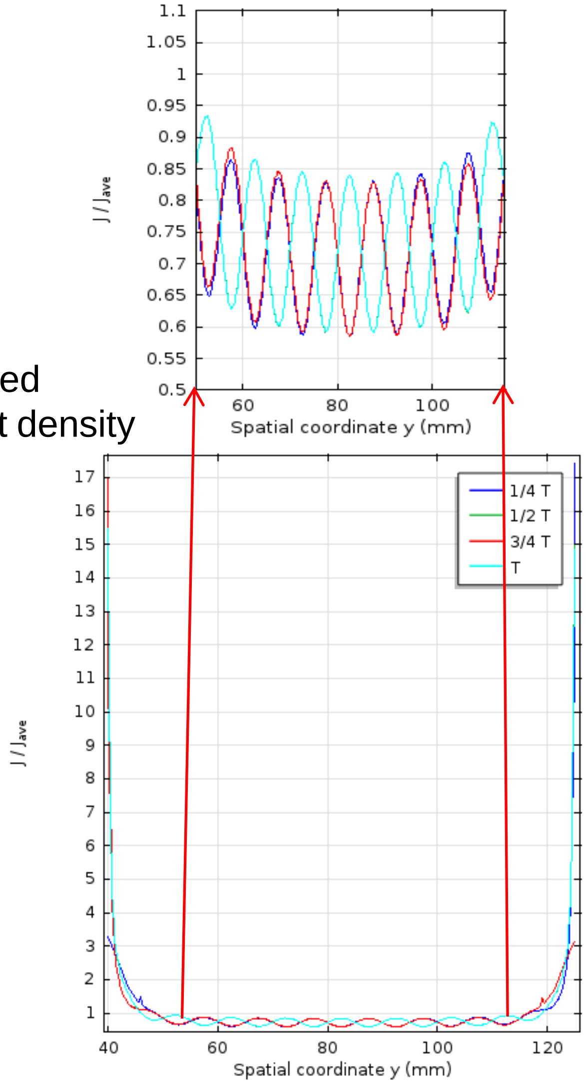


Current density



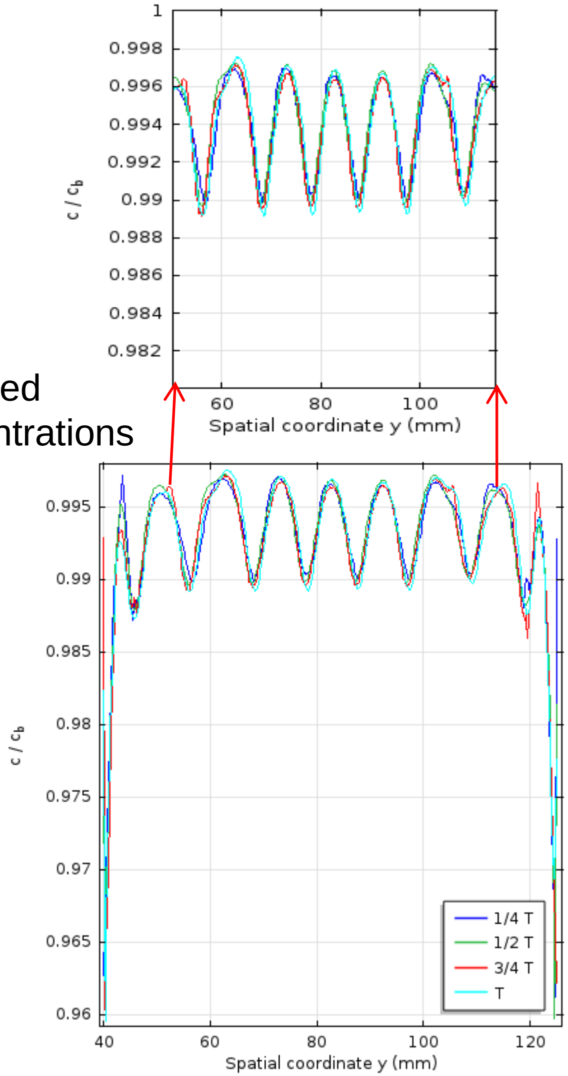
Results (3)

Distributions of tertiary current densities and concentrations on the wafer



Reduced current density

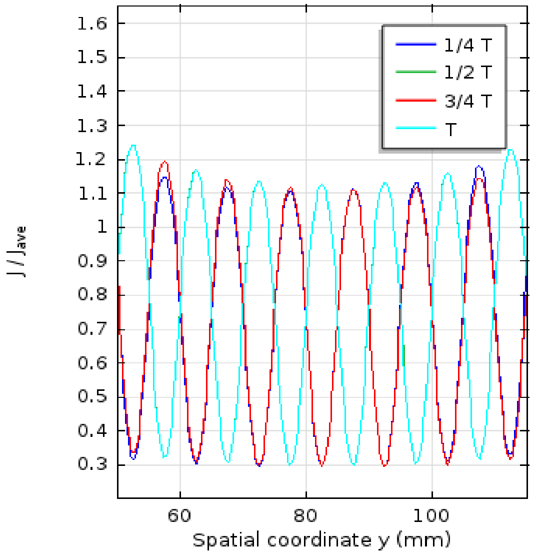
Reduced concentrations



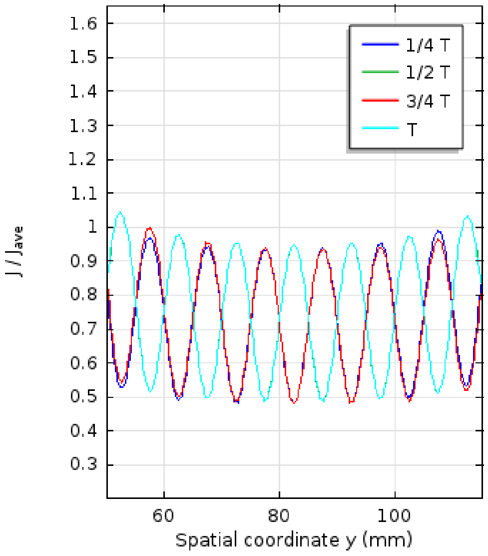
Results (4)

Tertiary current distributions on the wafer for δ = 2 , 3, 4 mm

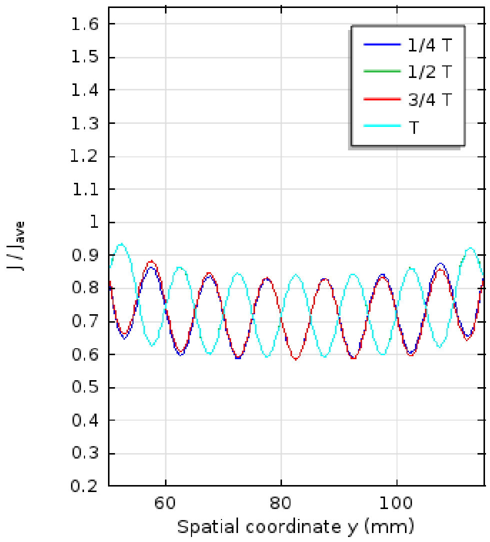
at the different phases of the reciprocating cycle



δ = 2 mm



δ = 3 mm



δ = 4 mm

Conclusions

- 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 ?