

# Chemical Etching

# Introduction

This example illustrates the principle of wet chemical etching. Wet chemical etching is particularly important for microelectronics industry for patterning of integrated circuit, MEMS devices, optoelectronic and pressure sensors. Wet etching processes use solution based ("wet") etchants, where the substrate to be etched is immersed in a controlled flow of etchant. Wet etching process is selective isotropic, fast (usually reaction rate limited) and reproducible. Due to its reproducibility the technique is often used for micropatterning of substrates.

A wet etching process involves chemical reaction that consume the original reactant and produce new reactant. The wet etch process can be described by three basic steps:

- Transport of the liquid etchant to the structure that is to be removed.
- The reaction between the liquid etchant and the material being etched away. A reduction-oxidation (redox) reaction usually occurs. This reaction entails the oxidation of the material followed by dissolution.
- Transport of the by products in the reaction from the reacted surface.

The purpose of this tutorial is to examine how the copper substrate material is depleted and how the cavity shape evolves during the wet etching process. The rate of the etching reaction depends on the local concentration of a reactant, which is transported to the surface by coupled convection-diffusion. The laminar flow profile of the etchant fluid changes due to the shape evolution of the etched cavity.

# Model Definition

The simplified 2D model geometry consists of a masked copper substrate with an exposed surface which is to be wet etched. The geometry is shown in Figure 1. The top rectangular

domain has fluid flowing over the exposed copper substrate as marked in the x direction. The fluid reacts only with the unmasked copper as the etching proceeds.



Figure 1: Schematic diagram of the chemical etching under a laminar flow of the etchant.

# TRANSPORT OF CHEMICAL SPECIES

Equation 1 describes mass flux of the etching species as given by diffusion and convection

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot (D \nabla c) \tag{1}$$

where D (SI unit: m<sup>2</sup>/s) denotes the diffusion coefficient and c (SI unit: mol/m<sup>3</sup>) is the concentration. The modeled species has a diffusion coefficient of  $1 \cdot 10^{-9}$  m<sup>2</sup>/s. At the inlet and top boundary of the flow, concentration is equal to the bulk concentration the etchant solution. At the etching surface (moving boundary) the flux condition is considered as in Equation 2:

$$D\nabla c \cdot \mathbf{n} = -kc \tag{2}$$

where k (SI unit: m/s) is the etching rate constant for linear kinetics of the etching species and **n** is the normal vector. k is assumed to be independent of the position on the surface. A No Flux condition is used for all other boundaries except the moving boundary.

## LAMINAR FLOW

At the cavity, the flow field can be calculated by Equation 3:

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

where  $\rho$  is the fluid density (SI unit: kg/m<sup>3</sup>), *p* is the pressure (SI unit: Pa),  $\mu$  is the dynamic viscosity (SI unit: Pa·s), **F** is the volume force vector (indicated as the boundary stress in the modeling instructions), and **u** is the fluid velocity (SI unit: m/s). Along with continuity Equation 4

$$\mathbf{p}\nabla\cdot\mathbf{u}\,=\,0\tag{4}$$

Along the moving wall, a no slip condition is applied.

# DEFORMED GEOMETRY

The movement of the boundary is defined by an interfacial condition on the boundary,

$$\upsilon = \frac{DM}{\rho} \tag{5}$$

where v is velocity of the moving mesh in the normal direction, D, M, and  $\rho$  are the diffusion coefficient (SI unit: m<sup>2</sup>/s), molar mass (SI unit: kg/mol), and density (SI unit: kg/m<sup>3</sup>) of the etching species, respectively.

# Results and Discussion

Figure 2 shows the concentration of etchant species  $CuCl_2$  at t = 10,000 s for an initial cavity radius of 0.5 mm. The etch profile is asymmetric owing to the fluid flow in the x direction. The etch rate is higher around the area where laminar flow first encounters the boundary layer in fluid direction. Concentration becomes uniform deeper into the cavity

as laminar flow can no longer transport reactant to the boundary layer owing to larger aspect ratio. (See also the velocity profile in Figure 3.)



Time=10000 s Surface: Concentration (mol/m<sup>3</sup>) Streamline: Total flux (spatial and material frames)

Figure 2: Concentration profile of CuCl<sub>2</sub> etchant at t = 10000 s over unmasked copper cavity.

Figure 3 shows the velocity profile for etchant flow at t = 10000 s. The velocity is zero close to the moving boundary. The fluid flow eventually becomes weak deeper as the aspect ratio of cavity increases with time.



Time=10000 s Surface: Velocity magnitude (m/s) Arrow Surface: Total flux (spatial and material frames)

Figure 3: Arrow surface plot depicting velocity profile of CuCl<sub>2</sub> etchant after t=10000 s over the deformed geometry of copper cavity.



Figure 4: Mesh deformation after t=10000 s over the etching unmasked copper cavity.

Figure 4 shows mesh deformation for deforming geometry at t = 10000 s.

# Reference

1. D.J. Economou and others, "Effect of transport and reaction on the shape evolution of cavities during wet chemical etching", *J. Electrochem. Soc.*, vol. 136, no. 7, pp. 1997–2004, 1989.

Application Library path: COMSOL\_Multiphysics/Chemical\_Engineering/ chemical\_etching

# Modeling Instructions

From the File menu, choose New.

#### NEW

In the New window, click 🔗 Model Wizard.

# MODEL WIZARD

I In the Model Wizard window, click **2D**.

Add the required physics.

- 2 In the Select Physics tree, select Chemical Species Transport> Transport of Diluted Species (tds).
- 3 Click Add.
- **4** In the **Concentration** text field, type cCuCl2.
- 5 In the Select Physics tree, select Fluid Flow>Single-Phase Flow>Laminar Flow (spf).
- 6 Click Add.
- 7 Click 🔿 Study.
- 8 In the Select Study tree, select General Studies>Stationary.
- 9 Click 🗹 Done.

# **GLOBAL DEFINITIONS**

Parameters 1

- I In the Model Builder window, expand the Component I (compl)>Definitions node, then click Global Definitions>Parameters I.
- 2 In the Settings window for Parameters, locate the Parameters section.
- 3 Click **b** Load from File.
- **4** Browse to the model's Application Libraries folder and double-click the file chemical\_etching\_parameters.txt.

Next, define the variable v\_surface corresponding to the velocity of the moving boundary.

# DEFINITIONS

Variables I

- I In the Model Builder window, under Component I (compl) right-click Definitions and choose Variables.
- 2 In the Settings window for Variables, locate the Variables section.

**3** In the table, enter the following settings:

Name	Expression	Unit	Description
v_surface	-r_surface*M_Cu/ rho_Cu	m/s	Surface normal velocity
r_surface	-kf*cCuCl2	mol/(m²·s)	

# GEOMETRY I

Rectangle 1 (r1)

- I In the Model Builder window, expand the Component I (compl)>Geometry I node.
- 2 Right-click Geometry I and choose Rectangle.
- 3 In the Settings window for Rectangle, locate the Size and Shape section.
- 4 In the Width text field, type d\_mask.
- 5 In the Height text field, type h\_mask.

Rectangle 2 (r2)

- I In the Geometry toolbar, click 📃 Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type h\_boundary\_layer.
- 4 In the Height text field, type h\_seed\_cavity.
- 5 Locate the Position section. In the x text field, type -h\_seed\_cavity.
- 6 In the y text field, type -h\_seed\_cavity.

### Fillet I (fill)

- I In the **Geometry** toolbar, click *Fillet*.
- **2** Click the **Come Extents** button in the **Graphics** toolbar.
- 3 On the object r2, select Points 1 and 2 only.
- 4 In the Settings window for Fillet, locate the Radius section.
- 5 In the Radius text field, type h\_seed\_cavity/2.

#### Rectangle 3 (r3)

- I In the Geometry toolbar, click 📃 Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type d\_mask\*2.
- 4 In the **Height** text field, type 3\*h\_mask.

- **5** Locate the **Position** section. In the **x** text field, type -d\_mask/2.
- 6 In the y text field, type h\_mask.
- 7 Click 🟢 Build All Objects.

#### DEFINITIONS

#### Moving Boundary

- I In the **Definitions** toolbar, click **here Explicit**.
- 2 In the Settings window for Explicit, type Moving Boundary in the Label text field.
- 3 Locate the Input Entities section. From the Geometric entity level list, choose Boundary.
- **4** Select Boundaries 4, 6, 13, 15, and 16 only.

#### ADD MATERIAL

- I In the Home toolbar, click 🙀 Add Material to open the Add Material window.
- 2 Go to the Add Material window.
- 3 In the tree, select **Built-in>Water**, liquid.
- 4 Click Add to Component in the window toolbar.
- 5 In the Home toolbar, click 🙀 Add Material to close the Add Material window.

# TRANSPORT OF DILUTED SPECIES (TDS)

Transport Properties 1

- In the Model Builder window, expand the Component I (comp1)>
  Transport of Diluted Species (tds)>Transport Properties I node, then click
  Transport Properties I.
- 2 In the Settings window for Transport Properties, locate the Convection section.
- **3** From the **u** list, choose **Velocity field (spf)**.
- **4** Locate the **Diffusion** section. In the  $D_{cCuCl2}$  text field, type D.

#### Concentration 1

- I In the Model Builder window, expand the Component I (compl)> Transport of Diluted Species (tds)>No Flux I node.
- 2 Right-click Transport of Diluted Species (tds) and choose Concentration.
- **3** Select Boundaries 1 and 3 only.
- 4 In the Settings window for Concentration, locate the Concentration section.
- 5 Select the Species cCuCl2 check box.

**6** In the  $c_{0,cCuCl2}$  text field, type cCuCl2\_bulk.

## Outflow I

- I In the Physics toolbar, click Boundaries and choose Outflow.
- 2 Select Boundary 14 only.

#### Flux I

- I In the Physics toolbar, click Boundaries and choose Flux.
- 2 In the Settings window for Flux, locate the Boundary Selection section.
- 3 From the Selection list, choose Moving Boundary.
- 4 Locate the Inward Flux section. Select the Species cCuCl2 check box.
- **5** In the  $J_{0,cCuCl2}$  text field, type r\_surface.

# LAMINAR FLOW (SPF)

In the Model Builder window, under Component I (compl) click Laminar Flow (spf).

## Wall 2

- I In the Physics toolbar, click Boundaries and choose Wall.
- **2** Select Boundary **3** only.
- 3 In the Settings window for Wall, click to expand the Wall Movement section.
- 4 From the Translational velocity list, choose Manual.
- **5** Specify the **u**<sub>tr</sub> vector as

# 1[mm/s] x 0 y

Boundary Stress I

- I In the Physics toolbar, click Boundaries and choose Boundary Stress.
- 2 Select Boundaries 1 and 14 only.

# COMPONENT I (COMPI)

# Deforming Domain 1

- I In the Definitions toolbar, click ••• Deformed Geometry and choose Domains> Deforming Domain.
- **2** Select Domain 2 only.
- 3 In the Settings window for Deforming Domain, locate the Smoothing section.
- 4 From the Mesh smoothing type list, choose Hyperelastic.

# Prescribed Normal Mesh Velocity I

- I In the Definitions toolbar, click • • Deformed Geometry and choose Boundaries> Prescribed Normal Mesh Velocity.
- 2 In the Settings window for Prescribed Normal Mesh Velocity, locate the Boundary Selection section.
- **3** From the Selection list, choose Moving Boundary.
- **4** Locate the **Prescribed Normal Mesh Velocity** section. In the  $\mathbf{v}_n$  text field, type v\_surface.

# Prescribed Normal Mesh Displacement I

- I In the Definitions toolbar, click • • Deformed Geometry and choose Boundaries> Prescribed Normal Mesh Displacement.
- 2 Select Boundaries 5 and 11 only.

Prescribed Mesh Displacement I

- I In the Definitions toolbar, click • Deformed Geometry and choose Boundaries> Prescribed Mesh Displacement.
- 2 Select Boundary 8 only.

# STUDY I

Step 1: Stationary

- I In the Model Builder window, under Study I click Step I: Stationary.
- 2 In the Settings window for Stationary, locate the Physics and Variables Selection section.
- **3** In the table, enter the following settings:

Physics interface	Solve for	Equation form
Deformed geometry (Component 1)		Automatic

Time Dependent

- I In the Study toolbar, click Study Steps and choose Time Dependent> Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.
- 3 In the **Output times** text field, type range(0,500,10000).
- **4** In the **Study** toolbar, click **= Compute**.

#### RESULTS

Concentration (tds)

- I Click the 4 Zoom Extents button in the Graphics toolbar.
- 2 In the Concentration (tds) toolbar, click **O** Plot.

#### Arrow Surface 1

- I In the Model Builder window, right-click Velocity (spf) and choose Arrow Surface.
- 2 In the Settings window for Arrow Surface, locate the Coloring and Style section.
- 3 From the Arrow length list, choose Logarithmic.
- 4 From the Color list, choose White.
- 5 In the Velocity (spf) toolbar, click **I** Plot.

Pressure (spf)

- I Click the 🕂 Zoom Extents button in the Graphics toolbar.
- 2 In the Model Builder window, under Results click Pressure (spf).
- 3 In the Pressure (spf) toolbar, click 🗿 Plot.

#### Mesh

- I In the Home toolbar, click 🚛 Add Plot Group and choose 2D Plot Group.
- 2 Right-click 2D Plot Group 4 and choose Rename.
- 3 In the Rename 2D Plot Group dialog box, type Mesh in the New label text field.
- 4 Click OK.
- Mesh I
- I Right-click Mesh and choose Mesh.
- 2 In the Mesh toolbar, click 💿 Plot.

#### Animation I

- I In the **Results** toolbar, click **Animation** and choose **Player**.
- 2 In the Settings window for Animation, click Show Frame.
- 3 Locate the Frames section. From the Frame selection list, choose All.
- 4 In the Frame number text field, type 101.
- **5** Click the **Play** button in the **Graphics** toolbar.

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