Model created in COMSOL Multiphysics 6.4

# 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 circuits, MEMS devices, and 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.

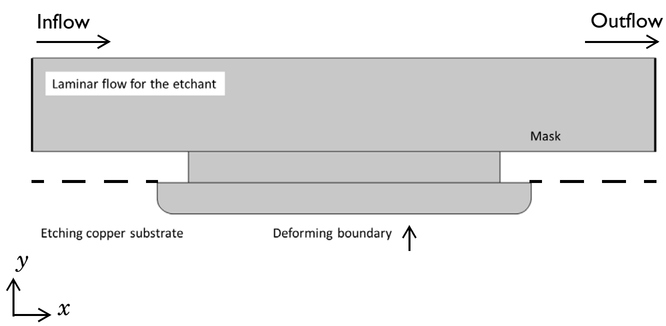


*Figure 1: Schematic diagram of the chemical etching under a laminar flow of the etchant.*

### TRANSPORT OF CHEMICAL SPECIES

The mass flux of the etching species is governed by diffusion and convection according to

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

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

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

where $k$ (SI unit: m/s) is the forward rate constant for linear kinetics of the etching species, and $\mathbf{n}$ 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 the Navier–Stokes equations

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

along with the continuity equation

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

Here ρ is the fluid density (SI unit: $kg/m^3$), $p$ is the pressure (SI unit: Pa), μ 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 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

$$v = -\frac{rM}{\rho} \tag{5}$$

where $v$ is velocity of the moving mesh in the normal direction; $r$, $M$, and ρ are the reaction rate (SI unit: $mol/(m^2{\cdot}s)$, which is the right side $-kc$ in Equation 2 above, molar mass (SI unit: kg/mol), and density (SI unit: $kg/m^3$) of the etching species, respectively.

## *Results and Discussion*

Figure 2 shows the concentration of etchant species $CuCl_2$ at $t$ = 10,800 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.)

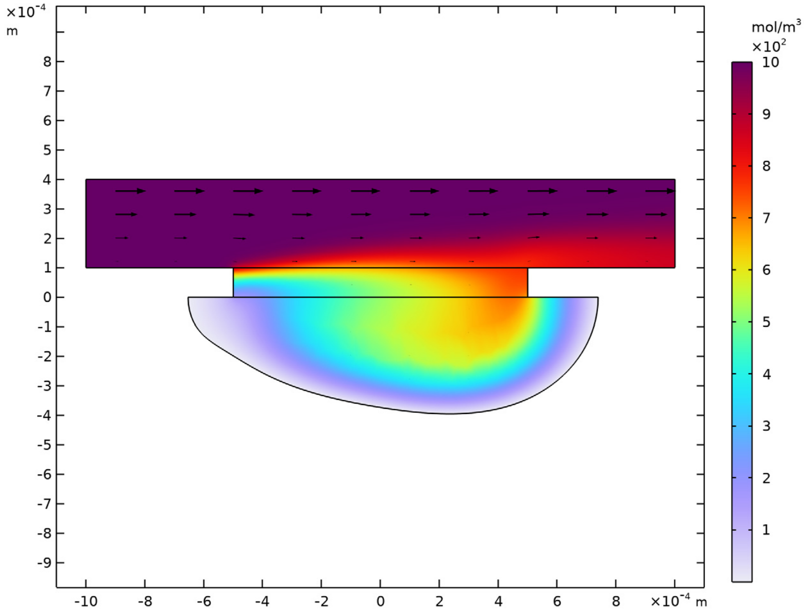


*Figure 2: Concentration profile of $CuCl_2$ etchant at $t = 10{,}800$ s over unmasked copper cavity.*

Figure 3 shows the velocity profile for etchant flow at $t$ = 10,800 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.

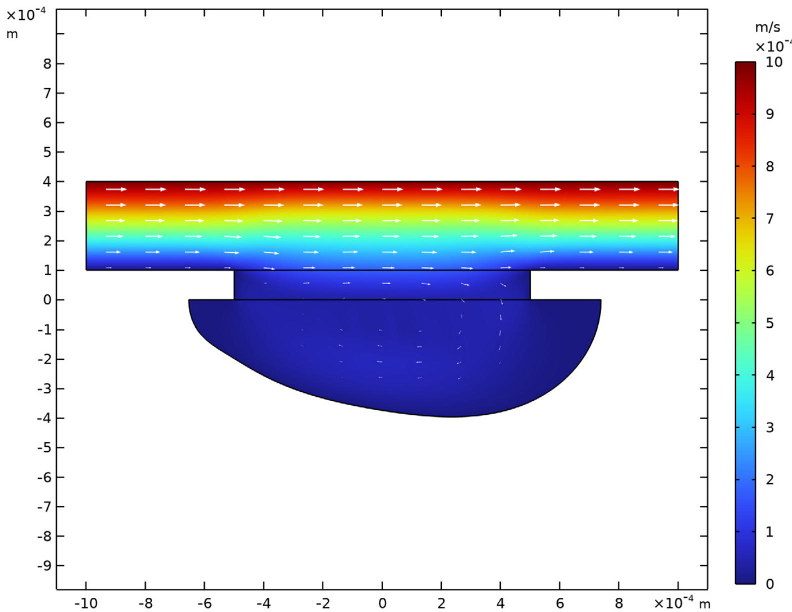


*Figure 3: Arrow surface plot depicting velocity profile of $CuCl_2$ etchant after t = 10,800 s over the deformed geometry of copper cavity.*

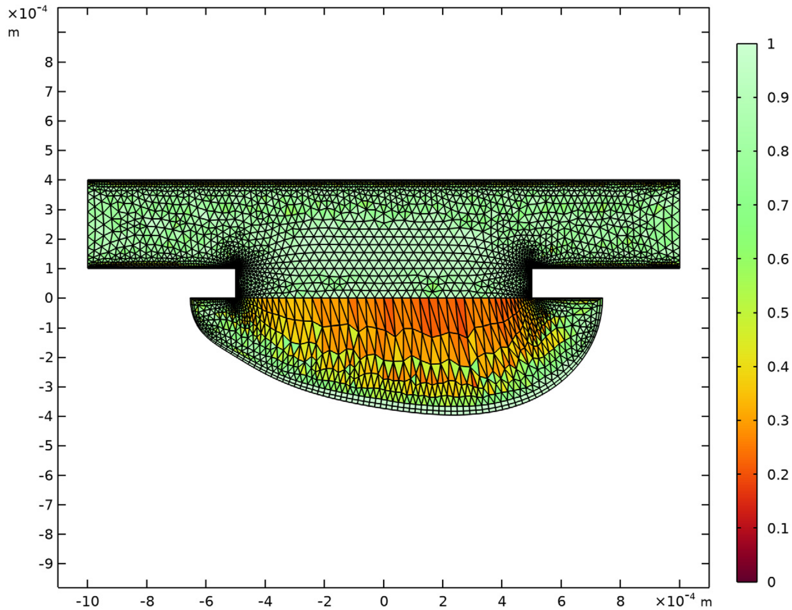


*Figure 4: Mesh deformation after t = 10,800 s over the etching unmasked copper cavity.*

Figure 4 shows mesh deformation for the deforming geometry at $t$ = 10,800 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

**1** 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 (mol/m³)** 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*

**1** In the **Model Builder** window, expand the **Component 1 (comp1)** > **Definitions** node, then click **Global Definitions** > **Parameters 1**.

**2** In the **Settings** window for **Parameters**, locate the **Parameters** section.

**3** Click **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 1*

**1** In the **Model Builder** window, under **Component 1 (comp1)** 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 1

*Rectangle 1 (r1)*

1 In the **Model Builder** window, expand the **Component 1 (comp1)** > **Geometry 1** node.

2 Right-click **Geometry 1** 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`.

6 Locate the **Position** section. In the **x** text field, type `-0.5*d_mask`.

*Rectangle 2 (r2)*

1 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 `-0.5*h_boundary_layer`.

6 In the **y** text field, type `-h_seed_cavity`.

*Fillet 1 (fil1)*

1 In the **Geometry** toolbar, click **Fillet**.

2 Click the **Zoom 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)*

1 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`.

6 In the **y** text field, type `h_mask`.

7 Click **Build All Objects**.

## DEFINITIONS

*Moving Boundary*

1 In the **Definitions** toolbar, click **Box**.

2 In the **Settings** window for **Box**, locate the **Geometric Entity Level** section.

3 From the **Level** list, choose **Boundary**.

4 In the **Label** text field, type `Moving Boundary`.

5 Locate the **Box Limits** section. In the **y maximum** text field, type `-h_seed_cavity*0.001`.

*Bottom*

1 Right-click **Moving Boundary** and choose **Duplicate**.

2 In the **Settings** window for **Box**, type `Bottom` in the **Label** text field.

3 Locate the **Box Limits** section. In the **y maximum** text field, type `-h_seed_cavity*0.999`.

4 Locate the **Output Entities** section. From the **Include entity if** list, choose **Entity inside box**.

## ADD MATERIAL

1 In the **Materials** 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 the **Add to Component** button in the window toolbar.

5 In the **Materials** toolbar, click **Add Material** to close the **Add Material** window.

## TRANSPORT OF DILUTED SPECIES (TDS)

*Fluid 1*

1 In the **Model Builder** window, expand the **Component 1 (comp1)** > **Transport of Diluted Species (tds)** > **Fluid 1** node, then click **Fluid 1**.

2 In the **Settings** window for **Fluid**, locate the **Convection** section.

3 From the $\mathbf{u}$ list, choose **Velocity field (spf)**.
4 Locate the **Diffusion** section. In the $D_{\mathrm{cCuCl2}}$ text field, type `D`.

*Concentration 1*

1 In the **Model Builder** window, expand the **Component 1 (comp1)** > **Transport of Diluted Species (tds)** > **No Flux 1** 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** checkbox.
6 In the $c_{0,\mathrm{cCuCl2}}$ text field, type `cCuCl2_bulk`.

*Outflow 1*

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

*Flux 1*

1 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** checkbox.
5 In the $J_{0,\mathrm{cCuCl2}}$ text field, type `r_surface`.

## LAMINAR FLOW (SPF)

In the **Model Builder** window, under **Component 1 (comp1)** click **Laminar Flow (spf)**.

*Wall 2*

1 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 $\mathbf{u}_{\mathrm{tr}}$ vector as

| | |
|---|---|
| 1[mm/s] | x |
| 0 | y |

### *Boundary Stress 1*

1 In the **Physics** toolbar, click **Boundaries** and choose **Boundary Stress**.
2 Select Boundaries 1 and 14 only.
3 In the **Settings** window for **Boundary Stress**, locate the **Boundary Condition** section.
4 From the **Boundary condition** list, choose **Normal stress, normal flow**.

## COMPONENT 1 (COMP1)

### *Deforming Domain 1*

1 In the **Physics** toolbar, click **Deformed Geometry** and choose **Free Deformation**.
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 1*

1 In the **Deformed Geometry** toolbar, click **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 1*

1 In the **Deformed Geometry** toolbar, click **Prescribed Normal Mesh Displacement**.
2 Select Boundaries 5 and 11 only.

### *Prescribed Mesh Displacement 1*

1 In the **Deformed Geometry** toolbar, click **Prescribed Mesh Displacement**.
2 Select Boundary 8 only.

## STUDY 1

### *Step 1: Stationary*

1 In the **Model Builder** window, under **Study 1** click **Step 1: Stationary**.
2 In the **Settings** window for **Stationary**, locate the **Physics and Variables Selection** section.
3 In the **Solve for** column of the table, under **Component 1 (comp1)**, clear the checkbox for **Deformed Geometry**.

*Step 2: Time Dependent*

1 In the **Study** toolbar, click **Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `range(0,0.05*tmax,tmax)`.

4 In the **Study** toolbar, click **Compute**.

## RESULTS

*Concentration (tds)*

1 In the **Settings** window for **2D Plot Group**, locate the **Color Legend** section.

2 Select the **Show units** checkbox.

3 Click the **Zoom Extents** button in the **Graphics** toolbar.

4 In the **Concentration (tds)** toolbar, click **Plot**.

*Velocity (spf)*

1 In the **Model Builder** window, click **Velocity (spf)**.

2 In the **Settings** window for **2D Plot Group**, locate the **Color Legend** section.

3 Select the **Show units** checkbox.

*Arrow Surface 1*

1 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 **Plot**.

*Pressure (spf)*

1 In the **Model Builder** window, under **Results** click **Pressure (spf)**.

2 In the **Settings** window for **2D Plot Group**, locate the **Color Legend** section.

3 Select the **Show units** checkbox.

4 Click the **Zoom Extents** button in the **Graphics** toolbar.

5 In the **Pressure (spf)** toolbar, click **Plot**.

*Mesh*

1 In the **Results** toolbar, click **2D Plot Group**.

2 Right-click **2D Plot Group 5** and choose **Rename**.

3 In the **Rename 2D Plot Group** dialog, type `Mesh` in the **New label** text field.

4 Click **OK**.

5 In the **Settings** window for **2D Plot Group**, type `Mesh` in the **Label** text field.

*Mesh 1*

1 Right-click **Mesh** and choose **Mesh**.

2 In the **Mesh** toolbar, click **Plot**.

*Animation 1*

1 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.