Surface Chemistry Tutorial

Introduction

Surface chemistry is often the most important and most overlooked aspect of reacting flow modeling. Surface rate expressions can be hard to find or not even exist at all. Often it is preferable to use sticking coefficients to describe surface reactions because they can be estimated intuitively.

Model Definition

The tutorial model simulates outgassing from a wafer during a chemical vapor deposition (CVD) process. Careful attention is paid to the overall mass balance in the system and the difference between the mass averaged velocity and diffusion velocity is explored. The geometry and operating principle for the model is shown in Figure 1. Initially the closed container is full of 99.9% silicon hydride and 0.1% hydrogen (measured by molar content).

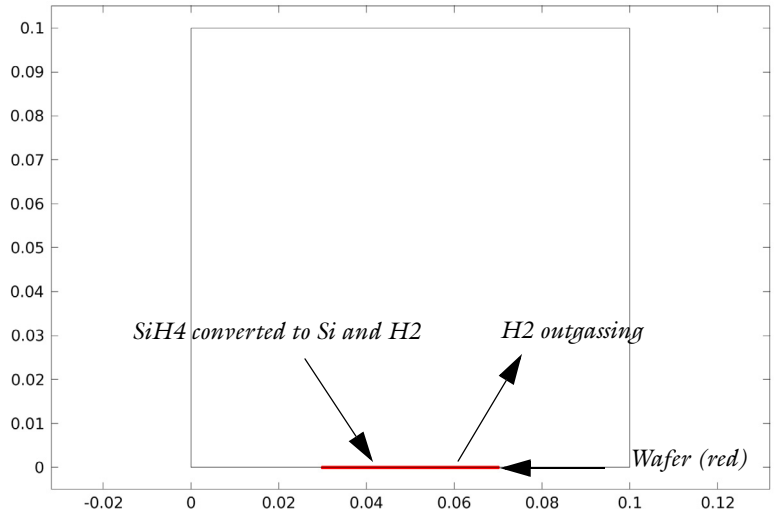

Figure 1: Geometry and basic operating principle for the surface chemistry tutorial model.

A surface reaction begins to occur on the wafer which consumes the silicon hydride, releases hydrogen into the domain, alters the composition of the absorbed species on

the wafer surface and deposits bulk silicon. The following reactions are considered on the surface of the wafer:

TABLE 0-1: SURFACE REACTIONS CONSIDERED

REACTION	STICKING COEFFICIENT
SiH4+2Si(s)=>Si(b)+2SiH(s)+H2	1E-4
SiH(s)=>Si(s)+0.5H2	1E-4

The (s) here denotes "surface species" which means that the species only exists on the surfaces where the reaction is occurring. To indicate that a species is bulk, append (b) to the end of the species. Since bulk species cannot participate in surface reactions, they must only be products and not reactants in a surface reaction. The net result of these two competing reactions is `SiH4=>Si(b)+2H2`, which means it is expected that the silane is replaced by hydrogen inside the reactor, and layers of silicon deposited on the wafer surface.

MODEL EQUATIONS - SURFACE REACTIONS AND SURFACE SPECIES

The surface reaction rate for reaction i is given by:

$$q_i = k_{f,i} \prod_{k=1}^{K} c_k^{\nu_{ki}^f} \tag{1}$$

where the rate constant, k_f is given by:

$$k_{\mathrm{f},i} = \left(\frac{\gamma_i}{1-\gamma_i/2}\right)\frac{1}{(\Gamma_{\mathrm{tot}})^m}\left(\frac{1}{4}\right)\sqrt{\frac{8RT}{\pi M_n}} \tag{2}$$

and c_k is the concentration of species k which may be a volumetric or surface species, m is the reaction order minus 1, T is the surface temperature, R is the gas constant and M_n is the mean molecular weight of the gas mixture. γ_i is the dimensionless sticking coefficient. For the surface species the following equations are solved:

$$\frac{d\Gamma}{dt} = \sum_{i=1}^{N} q_i \Delta\sigma_i \tag{3}$$

where Γ is the surface site concentration (mol/m^2), q_i is the reaction rate for reaction i (mol/m^2), $\Delta\sigma_i$ is the change in site occupancy number for reaction i (dimensionless).

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$$\frac{dZ_k}{dt} = \frac{R}{\Gamma_{tot}} \tag{4}$$

where Γ_{tot} is the total surface site concentration (mol/m^2), Z_k is the site fraction (dimensionless) and R is the surface rate expression (mol/m^2).

For the bulk surface species, the following equation is solved for the deposition height:

$$\frac{dh}{dt} = -\frac{RM_w}{\rho} \tag{5}$$

where h is the total growth height (m), M is the molecular weight (kg/mol) and ρ is the density of the bulk species (kg/m^3).

DOMAIN EQUATIONS

Inside the domain, the Navier-Stokes equations are solved for the fluid velocity. The mass fraction of hydrogen is computed by solving:

$$\rho\frac{\partial}{\partial t}(w) + \rho(\mathbf{u}\cdot\nabla)w = \nabla\cdot\mathbf{j} \tag{6}$$

where w is the mass fraction of hydrogen. For detailed information on the transport of the non-electron species see Theory for the Heavy Species Transport User Interface in the *Plasma Module User's Guide*. The mass fraction of silane is not directly computed. It's value comes from the fact that the sum of the mass fractions must equal one. The gas temperature is computed by solving the energy equation.

BOUNDARY CONDITIONS

Fluid Flow

The following boundary conditions are used. The mass averaged velocity is constrained using:

$$\mathbf{u} = -\frac{M_f}{\rho}\mathbf{n} \tag{7}$$

where M_f is the inward (or outward in this example) mass flux which is defined, from the surface chemistry as:

$$M_f = \sum_{k=1}^{K_g} M_k \dot{s}_k \tag{8}$$

where s_k is the surface rate expression for each species which comes from summing the surface reaction rates multiplied by their stoichiometric coefficients over all surface reactions:

$$\dot{s}_k = \sum_{i=1}^{I} \nu_{ki} q_i \tag{9}$$

Hydrogen Mass Fraction

The flux of hydrogen at the surface of the wafer comes from the surface reactions:

$$\mathbf{n} \cdot \mathbf{j} = M_k s_k \tag{10}$$

Energy Equation

For the energy equation, the following boundary condition is used:

$$\mathbf{n} \cdot \kappa \nabla T = \sum_{i=1}^{I} q_i h_i \tag{11}$$

where hi is the molar enthalpy change due to reaction i.

Results and Discussion

The y-component of the mass averaged velocity is plotted in Figure 2. The mass averaged velocity is negative at the surface of the wafer. This means that overall, mass is leaving the system. This is to be expected since silane is being consumed, which has

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a molecular weight of 0.032 kg/mol and replacing it with hydrogen, which has a lower molecular weight of 0.002 kg/mol.

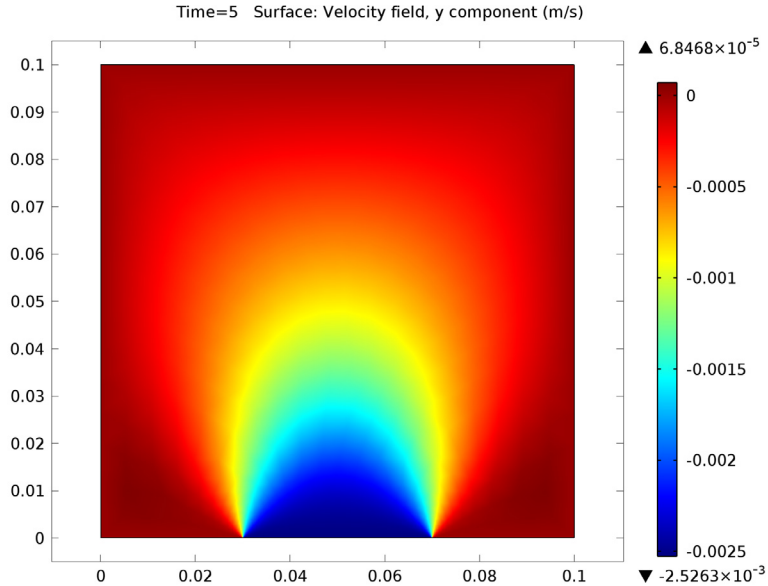

Figure 2: Plot of the mass averaged velocity field after 5 seconds.

The surface reactions begin to consume the silane which results in concentration gradients within the reactor. The outward mass flux at the wafer surface leads to a mass averaged velocity everywhere inside the reactor. The combination of concentration gradients and convection due to the mass averaged velocity tends to draw silane to wards the wafer. The first surface reaction is exothermic while the second surface reaction is endothermic. The amount of heat released by the exothermic reaction dominates, so the temperature begins to increase. The temperature is plotted in Figure 3 and is highest on the wafer surface.

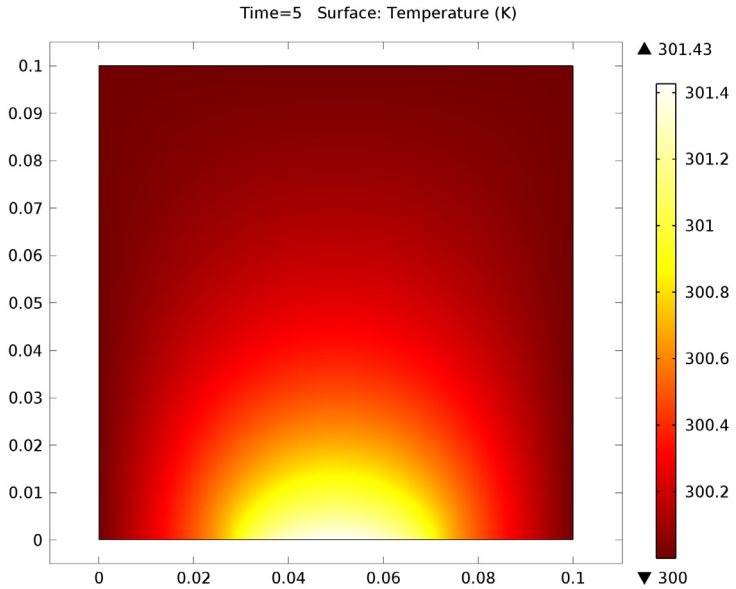

Figure 3: Plot of the gas temperature after 5 seconds. The higher temperature is observed at the wafer surface due to the heat released in the surface reactions.

From the net reaction `SiH4=>Si(b)+2H2` there should be a molar inflow of hydrogen at twice the rate that silane is leaving. Although this condition is not applied explicitly, it is implicit from the equations solved in the Heavy Species transport interface. Despite the fact that there is a negative mass averaged velocity, there is a positive diffusion velocity for the hydrogen at the wafer surface. The y-component of the diffusion velocity for hydrogen is plotted in Figure 4.

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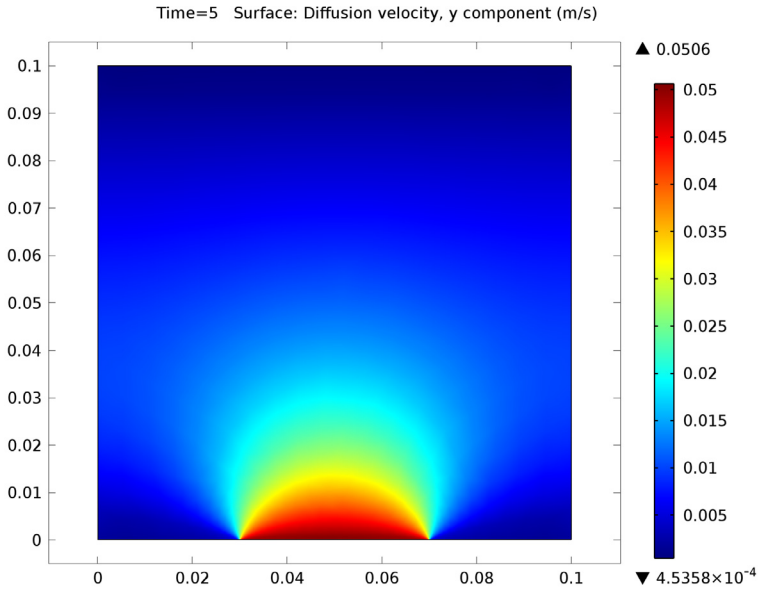

Figure 4: Plot of the y-component of the diffusion velocity for hydrogen after 5 seconds. Even though the mass averaged velocity is negative, the diffusion velocity is positive indicating an inflow of hydrogen and a net outflow of total mass.

Figure 5 plots the integrated pressure in the reactor divided by the initial average pressure in the reactor. Once the problem reaches steady state the average pressure in the reactor has increased by a factor of 2. This is expected since every mole of silane is being replaced by two moles of hydrogen. The silane in the reactor is completely consumed after around 200 seconds.

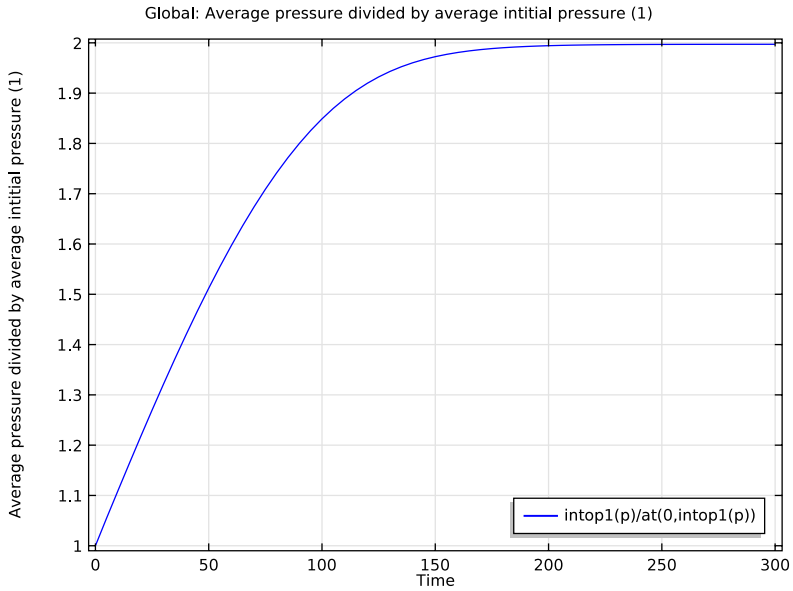

Figure 5: Plot of the ratio of the average pressure at time t divided by the average initial pressure.

In Figure 6 the total mass initially present in the reactor divided by the total mass in the reactor is plotted. The total mass in the reactor drops by a factor of 8, which is expected since the silane with molecular mass 0.032 kg/mol is replaced with two moles of hydrogen which has a molecular weight of 2·0.002=0.004 kg/mol.

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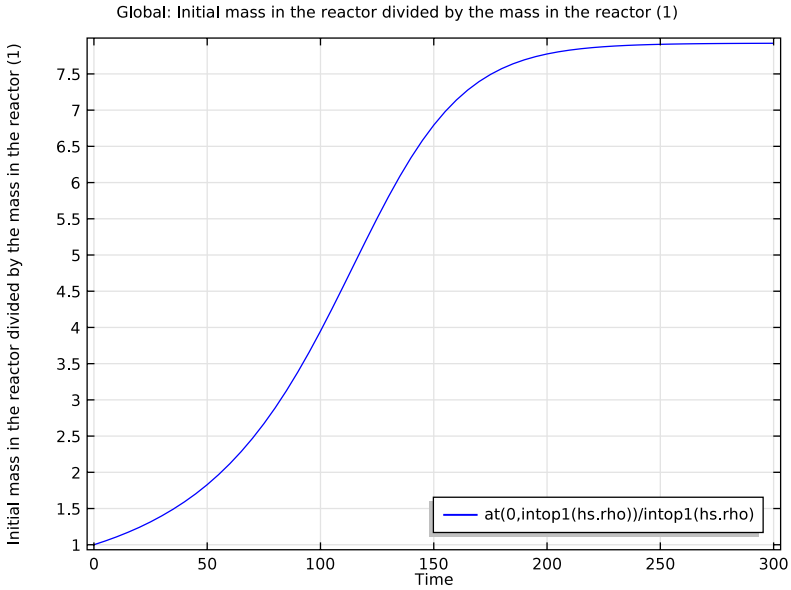

Figure 6: Plot of the total mass in the reactor at t = 0 divided by the total mass at t = t.

Another way of verifying the correctness of the model is to compare the mass lost inside the reactor to the mass accumulated on the wafer surface. The two quantities should be equal. The total gain in mass from surface and bulk species is compared to the total loss in mass from the reactor in Figure 7. The two curves agree very well indicating that the total mass in the entire system is conserved.

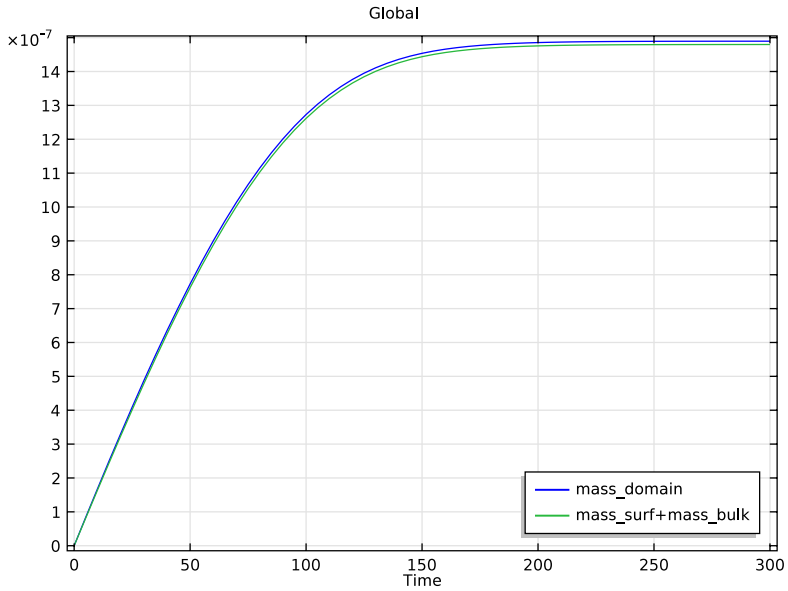

Figure 7: Plot of the total mass lost in the domain (blue) and the total mass gained due to Silicon deposition on the wafer surface (green).

The ultimate goal of most CVD models is to determine the total growth height and growth rate on the surface of the wafer. The total growth height is plotted in Figure 8 and saturates at about 159 Angstroms. The total growth rate saturates because all the silane in the reactor is consumed after around 200 seconds. The accumulated growth height is also very uniform across the surface of the wafer.

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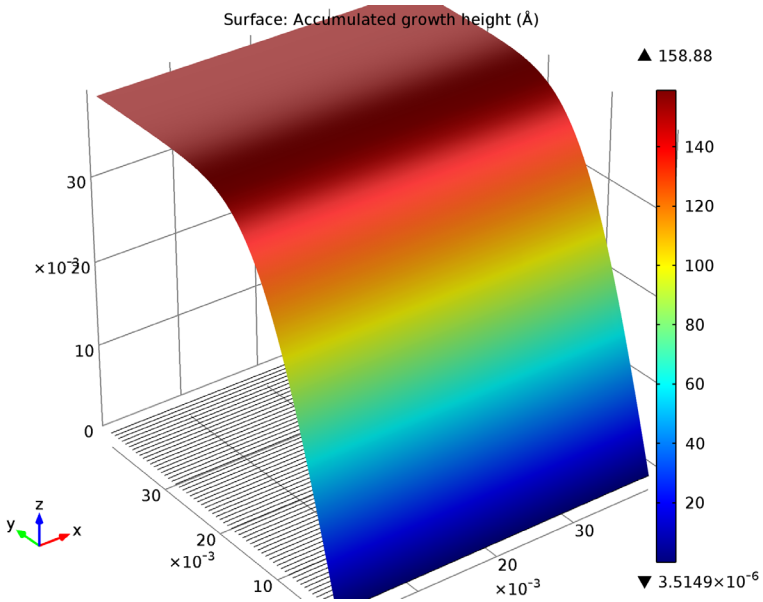

Figure 8: Plot of the growth height (surface and z-axis) vs. the wafer arc length (x-axis) and time (y-axis). The final height of deposited silicon is 158 Å.

Reference

1. R.J. Kee, M.E. Coltrin, and P. Glarborg, *Chemically Reacting Flow Theory and Practice*, Wiley, 2003.

Model Library path: `Plasma_Module/Chemical_Vapor_Deposition/surface_chemistry_tutorial`

Modeling Instructions

In the **Model Builder** window's toolbar, click the **Show** button and select **Stabilization** in the menu.

In the **Model Builder** window's toolbar, click the **Show** button and select **Discretization** in the menu.

In the **Model Builder** window's toolbar, click the **Expand sections** button and select **Stabilization** in the menu.

In the **Model Builder** window's toolbar, click the **Expand sections** button and select **Discretization** in the menu.

MODEL WIZARD

1 Go to the **Model Wizard** window.

2 Click the **2D** button.

3 Click **Next**.

4 In the **Add physics** tree, select **Plasma>Heavy Species Transport (hs)**.

5 Click **Add Selected**.

6 In the **Add physics** tree, select **Fluid Flow>Single-Phase Flow>Laminar Flow (spf)**.

7 Click **Add Selected**.

8 In the **Add physics** tree, select **Heat Transfer>Heat Transfer in Fluids (ht)**.

9 Click **Add Selected**.

10 Click **Next**.

11 Find the **Studies** subsection. In the tree, select **Preset Studies for Selected Physics>Time Dependent**.

12 Click **Finish**.

GEOMETRY 1

Square 1

1 In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Square**.

2 In the **Square** settings window, locate the **Size** section.

3 In the **Side length** edit field, type `0.1`.

4 Click the **Build All** button.

Polygon 1

1 In the **Model Builder** window, right-click **Geometry 1** and choose **Polygon**.

2 In the **Polygon** settings window, locate the **Coordinates** section.

3 In the **x** edit field, type `0.03 0.07`.

4 In the **y** edit field, type `0 0`.

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DEFINITIONS

In the **Model Builder** window, expand the **Model 1>Definitions** node.

Variables 1

1 Right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Variables** section.

3 In the table, enter the following settings:

Name	Expression	Description
mass_domain	at(0,intop1(hs.rho)) -intop1(hs.rho)	Mass change in the domain
mass_bulk	intop2(h_Si_bulk*2329[kg/m^3])	Total mass of bulk species
mass_Si_surf	intop2(Zk_Si_surf*gamman_Si_surf/ hs.sigmak_Si_surf*0.028[kg/mol])	Total mass of Si surface species
mass_SiH_surf	intop2(Zk_SiH_surf*gamman_SiH_surf/ hs.sigmak_SiH_surf*0.029[kg/mol])	Total mass of SiH surface species
dmass_Si_surf	mass_Si_surf-at(0,mass_Si_surf)	Total mass minus initial mass of Si surface species
dmass_SiH_surf	mass_SiH_surf-at(0,mass_SiH_surf)	Total mass minus initial mass of SiH surface species
mass_surf	dmass_Si_surf+dmass_SiH_surf	Total mass minus initial mass of all surface species

Integration 1

1 Right-click **Definitions** and choose **Model Couplings>Integration**.

2 Select Domain 1 only.

Integration 2

1 Right-click **Definitions** and choose **Model Couplings>Integration**.

2 In the **Integration** settings window, locate the **Source Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 4 only.

HEAVY SPECIES TRANSPORT

1 In the **Model Builder** window, under **Model 1** click **Heavy Species Transport**.

2 In the **Heavy Species Transport** settings window, locate the **Transport Settings** section.

3 Select the **Calculate thermodynamic properties** check box.

4 Clear the **Migration in electric field** check box.

5 Select the **Convection** check box.

Surface Reaction 1

1 Right-click **Model 1>Heavy Species Transport** and choose **Surface Reaction**.

2 In the **Surface Reaction** settings window, locate the **Reaction Formula** section.

3 In the **Formula** edit field, type `SiH4+2Si(s)=>Si(b)+2SiH(s)+H2`.

4 Select Boundary 4 only.

5 Locate the **Kinetics Expressions** section. In the γ_f edit field, type `1E-4`.

Surface Reaction 2

1 In the **Model Builder** window, right-click **Heavy Species Transport** and choose **Surface Reaction**.

2 In the **Surface Reaction** settings window, locate the **Reaction Formula** section.

3 In the **Formula** edit field, type `SiH(s)=>Si(s)+0.5H2`.

4 Select Boundary 4 only.

5 Locate the **Kinetics Expressions** section. In the γ_f edit field, type `1E-4`.

Species: SiH4

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: SiH4**.

2 In the **Species** settings window, locate the **Species Formula** section.

3 Select the **From mass constraint** check box.

4 Locate the **General Parameters** section. From the **Preset species data** list, choose **SiH4**.

Species: H2

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: H2**.

2 In the **Species** settings window, locate the **General Parameters** section.

3 From the **Preset species data** list, choose **H2**.

4 In the x_0 edit field, type `1E-3`.

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Species: Si(s)

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: Si(s)**.

2 In the **Surface Species** settings window, locate the **General Parameters** section.

3 From the **Preset species data** list, choose **Si**.

4 Locate the **Surface Species Parameters** section. In the $Z_{k,0}$ edit field, type `0.995`.

Species: Si(b)

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: Si(b)**.

2 In the **Surface Species** settings window, locate the **General Parameters** section.

3 From the **Preset species data** list, choose **Si**.

Species: SiH(s)

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: SiH(s)**.

2 In the **Surface Species** settings window, locate the **General Parameters** section.

3 From the **Preset species data** list, choose **SiH**.

4 Locate the **Surface Species Parameters** section. In the $Z_{k,0}$ edit field, type `0.005`.

Convection and Diffusion

1 In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Convection and Diffusion**.

2 In the **Convection and Diffusion** settings window, locate the **Model Inputs** section.

3 From the $\mathbf{u}$ list, choose **Velocity field (spf/fp1)**.

4 From the T list, choose **Temperature (ht)**.

5 From the p_A list, choose **Pressure (spf/fp1)**.

6 Clear the **Reference pressure** check box.

LAMINAR FLOW

Fluid Properties 1

1 In the **Model Builder** window, expand the **Model 1>Laminar Flow** node, then click **Fluid Properties 1**.

2 In the **Fluid Properties** settings window, locate the **Fluid Properties** section.

3 From the ρ list, choose **Density (hs/cdm1)**.

4 From the μ list, choose **Dynamic viscosity (hs/cdm1)**.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Laminar Flow** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the p edit field, type `13.3`.

4 In the **Model Builder** window, click **Laminar Flow**.

5 In the **Laminar Flow** settings window, locate the **Consistent Stabilization** section.

6 Find the **Navier-Stokes equations** subsection. Clear the **Crosswind diffusion** check box.

7 Click to expand the **Discretization** section. From the **Discretization of fluids** list, choose **P2 + P1**.

Inlet 1

1 Right-click **Laminar Flow** and choose **Inlet**.

2 Select Boundary 4 only.

3 In the **Inlet** settings window, locate the **Boundary Condition** section.

4 From the **Boundary condition** list, choose **Mass flow**.

5 Locate the **Mass Flow Rate** section. From the **Mass flow type** list, choose **Pointwise mass flux**.

6 From the M_f list, choose **Inward mass flux (hs)**.

HEAT TRANSFER IN FLUIDS

Heat Transfer in Fluids 1

1 In the **Model Builder** window, expand the **Model 1>Heat Transfer in Fluids** node, then click **Heat Transfer in Fluids 1**.

2 In the **Heat Transfer in Fluids** settings window, locate the **Model Inputs** section.

3 From the p_A list, choose **Pressure (spf/fp1)**.

4 Clear the **Reference pressure** check box.

5 From the $\mathbf{u}$ list, choose **Velocity field (spf/fp1)**.

6 Locate the **Heat Conduction, Fluid** section. From the k list, choose **Thermal conductivity (hs/cdm1)**.

7 Locate the **Thermodynamics, Fluid** section. From the **Fluid type** list, choose **Ideal gas**.

8 From the **Gas constant type** list, choose **Mean molar mass**.

9 From the M_n list, choose **Mean molar mass (hs/cdm1)**.

10 From the C_p list, choose **Mass-averaged mixture specific heat (hs/cdm1)**.

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Temperature 1

1 In the **Model Builder** window, right-click **Heat Transfer in Fluids** and choose **Temperature**.

2 Select Boundaries 1, 3, and 6 only.

3 In the **Temperature** settings window, locate the **Temperature** section.

4 In the T_0 edit field, type `300`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Heat Transfer in Fluids** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the T edit field, type `300`.

Boundary Heat Source 1

1 In the **Model Builder** window, right-click **Heat Transfer in Fluids** and choose **Boundary Heat Source**.

2 Select Boundary 4 only.

3 In the **Boundary Heat Source** settings window, locate the **Boundary Heat Source** section.

4 From the Q_b list, choose **Total surface heat source of reaction (hs)**.

MESH 1

Size 1

1 In the **Model Builder** window, under **Model 1** right-click **Mesh 1** and choose **Size**.

2 In the **Size** settings window, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Point**.

4 Select Points 3 and 4 only.

5 In the **Size** settings window, locate the **Element Size** section.

6 From the **Predefined** list, choose **Extremely fine**.

7 Click the **Custom** button.

8 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.

9 In the associated edit field, type `0.0002`.

Edge 1

1 In the **Model Builder** window, right-click **Mesh 1** and choose **More Operations>Edge**.

2 Select Boundary 4 only.

Size 1

1 Right-click **Model 1>Mesh 1>Edge 1** and choose **Size**.

2 In the **Size** settings window, locate the **Element Size** section.

3 From the **Predefined** list, choose **Extremely fine**.

Free Triangular 1

1 In the **Model Builder** window, right-click **Mesh 1** and choose **Free Triangular**.

2 In the **Settings** window, click **Build All**.

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, expand the **Study 1** node, then click **Step 1: Time Dependent**.

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

3 In the **Times** edit field, type `range(0,5,300)`.

4 In the **Model Builder** window, right-click **Study 1** and choose **Show Default Solver**.

5 Expand the **Study 1>Solver Configurations** node.

Solver 1

1 In the **Model Builder** window, expand the **Study 1>Solver Configurations>Solver 1** node.

2 In the **Model Builder** window, under **Study 1>Solver Configurations>Solver 1** click **Time-Dependent Solver 1**.

3 In the **Time-Dependent Solver** settings window, click to expand the **Absolute Tolerance** section.

4 From the **Global method** list, choose **Unscaled**.

5 Click to expand the **Time Stepping** section. In the **Initial step** edit field, type `0.001`.

6 In the **Model Builder** window, right-click **Study 1** and choose **Compute**.

RESULTS

Velocity (spf)

1 In the **2D Plot Group** settings window, locate the **Data** section.

2 From the **Time** list, choose **5**.

3 In the **Model Builder** window, under **Results>Velocity (spf)** click **Surface 1**.

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4 In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Laminar Flow>Velocity field>Velocity field, y component (v)**.

5 Click the **Plot** button.

Temperature (ht)

1 In the **Model Builder** window, under **Results** click **Temperature (ht)**.

2 In the **2D Plot Group** settings window, locate the **Data** section.

3 From the **Time** list, choose **5**.

4 Click the **Plot** button.

2D Plot Group 6

1 In the **Model Builder** window, right-click **Results** and choose **2D Plot Group**.

2 In the **2D Plot Group** settings window, locate the **Data** section.

3 From the **Time** list, choose **5**.

4 Right-click **Results>2D Plot Group 6** and choose **Surface**.

5 In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Heavy Species Transport>Species>Species wH2>Diffusion velocity>Diffusion velocity, y component (hs.Vdy_wH2)**.

6 Click the **Plot** button.

1D Plot Group 7

1 In the **Model Builder** window, right-click **Results** and choose **1D Plot Group**.

2 In the **1D Plot Group** settings window, click to expand the **Legend** section.

3 From the **Position** list, choose **Lower right**.

4 Right-click **Results>1D Plot Group 7** and choose **Global**.

5 In the **Global** settings window, click to expand the **Legends** section.

6 Find the **Include** subsection. Select the **Expression** check box.

7 Clear the **Description** check box.

8 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
`intop1(p)/at(0,intop1(p))`	1	`Average pressure divided by average initial pressure`

9 Click the **Plot** button.

1D Plot Group 8

1 In the **Model Builder** window, right-click **Results** and choose **1D Plot Group**.

2 In the **1D Plot Group** settings window, click to expand the **Legend** section.

3 From the **Position** list, choose **Lower right**.

4 Right-click **Results>1D Plot Group 8** and choose **Global**.

5 In the **Global** settings window, click to expand the **Legends** section.

6 Find the **Include** subsection. Select the **Expression** check box.

7 Clear the **Description** check box.

8 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
`at(0,intop1(hs.rho))/ intop1(hs.rho)`	1	Initial mass in the reactor divided by the mass in the reactor

9 Click the **Plot** button.

1D Plot Group 9

1 In the **Model Builder** window, right-click **Results** and choose **1D Plot Group**.

2 In the **1D Plot Group** settings window, click to expand the **Legend** section.

3 From the **Position** list, choose **Lower right**.

4 Right-click **Results>1D Plot Group 9** and choose **Global**.

5 In the **Global** settings window, click to expand the **Legends** section.

6 Find the **Include** subsection. Select the **Expression** check box.

7 Clear the **Description** check box.

8 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
`mass_domain`		Total mass in the domain
`mass_surf+mass_bulk`		Total mass of surface plus bulk species

9 Click the **Plot** button.

Data Sets

1 In the **Model Builder** window, under **Results** right-click **Data Sets** and choose **Edge 2D**.

2 Select Boundary 4 only.

3 In the **Model Builder** window, right-click **Data Sets** and choose **More Data Sets>Parametric Extrusion 1D**.

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2D Plot Group 10

1 Right-click **Results** and choose **2D Plot Group**.

2 In the **2D Plot Group** settings window, locate the **Data** section.

3 From the **Data set** list, choose **Parametric Extrusion 1D 1**.

4 Right-click **Results>2D Plot Group 10** and choose **Surface**.

5 In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Heavy Species Transport>Etching and deposition>Si bulk>Accumulated growth height (h_Si_bulk)**.

6 Locate the **Expression** section. From the **Unit** list, choose **Å**.

7 Right-click **Results>2D Plot Group 10>Surface 1** and choose **Height Expression**.

8 In the **Settings** window, click **Plot**.

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