Coupled Mass Transport and Reaction in LPCVD Reactors

Dilute A in B
e.g., SiH$_4$ in H$_2$

Separate reactor into two regions, intrawafer & annular
Continuity Eqn: Convection-Diffusion-Reaction Eqns

Assumptions

- Dilute species $i$ in major carrier gas (e.g., $H_2$) $i=SiH_4$
- Isothermal
- Constant $D_i$ and density

\[ D_i \nabla^2 c_i - \vec{u} \cdot \nabla c_i + R_i = \frac{\partial c_i}{\partial t} \]

- No rxn in the gas
- Assume stagnant in the intrawafer region
- Steady state

$\sim 0$
Equations and Boundary Conditions for the intrawafer region

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} = 0 \]

\[ \frac{\partial c}{\partial r} = 0 \quad @ \quad r = 0 \]
\[ c = c_b \quad @ \quad r = R_w \]
\[ D \frac{\partial c}{\partial z} = r_s \quad @ \quad z = -\Delta / 2 \]
\[ D \frac{\partial c}{\partial z} = -r_s \quad @ \quad z = \Delta / 2 \]

- If \( r_s \) is linear in \( c \) then there is an analytic solution
- If \( r_s \) is nonlinear we have to seek numerical solution

\( r_s \) = surface reaction rate (net loss rate of SiH\(_4\)); related to the deposition rate
Approximate solution – “Fin Approximation”

- Take $r_s = kc$ & average over $z$ direction
- Averaging over the small dimension ($z$) is called the “fin approximation”: an approximation which is very good for 2-D regions with high aspect ratio ($R/\Delta$)

\[
\Delta \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c}{\partial r} \Delta z + \Delta \frac{\partial^2 c}{\partial z^2} \Delta z = 0
\]

\[
\Delta \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial C}{\partial r} \Delta z + \frac{\partial C}{\partial z} \bigg|_{z=\Delta/2} - \frac{\partial C}{\partial z} \bigg|_{z=-\Delta/2} = 0
\]

\[
\Delta \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial C}{\partial r} + \frac{kC}{D} - \frac{kC}{D} = 0
\]

\[
D \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial C}{\partial r} - \frac{2}{\Delta} kC = 0
\]

\[
\Delta = \frac{2\pi R_w^2}{\Delta \pi R_w^2} = \frac{\text{surface area}}{\text{volume}}
\]

note
## Nondimensionalization & Solution

\[ \xi = \frac{r}{R_w} \quad \theta = \frac{C}{c_b} \]

\[ \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \theta}{\partial \xi} \right) = \frac{2kR_w^2}{D\Delta} \]

\[ \Phi^2 = \frac{2kR_w^2}{D\Delta} \]

\[ \frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \theta}{\partial \xi} - \Phi^2 \theta = 0 \]

Bessel’s equation (Mickley Sherwood & Reid, Applied Math in ChE p. 174)

\( \Phi \) is the Thiele Modulus

\[ \frac{\text{reaction rate}}{\text{diffusion rate}} = \frac{\text{reaction time scale}}{\text{diffusion time scale}} \]

\[ \theta = AI_o(\Phi \xi) + BK_o(\Phi \xi) \]

Zero order Bessel functions of the 2\textsuperscript{nd} kind
Concentration profile in the intrawafer region

$K_o$ has logarithmic singularity at $\xi=0 \Rightarrow B = 0$

Using $\theta=1$ at $\xi=1 \Rightarrow 1 = A I_o(\Phi)$

$\theta = \frac{I_o(\Phi \xi)}{I_o(\Phi)}$

- as $\Phi \to 0$ uniformity gets better and $C$ increases; reaction limited; diffusion faster than rxn
- as $\Phi >> 1$ uniformity degrades and $C$ decreases; diffusion limited; rxn faster than diffusion

$\Phi = \frac{\text{reaction rate}}{\text{diffusion rate}}$
Quantifying Uniformity

\[ \eta = \text{“Uniformity Index”} = \frac{\text{actual deposition rate}}{\text{deposition rate if } c = c_b \text{ throughout}} \]

\[
\eta = \frac{2\pi R_w \Delta D \frac{dC}{dr}}{2k_s c_b \pi R_w^2} \\
= \frac{2\pi R_w \Delta \frac{dC}{dr}}{2k_s c_b \pi R_w^2}
\]

\[
\Delta = \frac{dC}{dr} \bigg|_{r=R_w} = \frac{C_b}{R_w} \frac{d\theta}{d\xi} \bigg|_{\xi=1} = \frac{C_b \Phi I_1(\Phi \xi)}{R_w I_o(\Phi)} \bigg|_{\xi=1} = \frac{C_b \Phi I_1(\Phi)}{R_w I_o(\Phi)}
\]

\[
\eta = \frac{2\pi R_w \Delta D c_b \Phi I_1(\Phi)}{2k_s c_b \pi R_w^3 I_o(\Phi)}
\]

\[
\eta = \frac{2 I_1(\Phi)}{\Phi I_o(\Phi)} = f(\Phi)
\]

\[ \Phi \ll 1 \Rightarrow \eta \to 1 \Rightarrow \text{uniform deposition (rxn limited)} \]

\[ \Phi \gg 1 \Rightarrow \eta \to 0 \Rightarrow \text{nonuniform deposition (diffusion limited)} \]
Growth Rate distribution as a function of wafer spacing
Growth Rate distribution as a function of $\Phi$

\[ A \quad \Phi \ll 1 \implies \eta \to 1 \implies \text{uniform deposition (rxn limited)} \]
\[ B \quad \Phi \gg 1 \implies \eta \to 0 \implies \text{nonuniform deposition (diffusion limited)} \]
Annular Region

R_w < r < R_t
0 < z < L

Boundary Conditions:

Dankwertz Boundary Conditions:

\[-D \frac{\partial c}{\partial r} = r_s \quad \text{at} \quad r = R_t\]
\[D \frac{\partial c}{\partial r} = \eta k_s c \frac{2\pi R_w^2}{2\pi R_w \Delta} = \eta k_s c \frac{R_w}{\Delta} \quad \text{at} \quad r = R_w\]
\[-D \frac{\partial c}{\partial z} \bigg|_{z=0} = u_z (c_o - c \bigg|_{z=0}) \quad \text{at} \quad z = 0\]
\[\frac{\partial c}{\partial z} \bigg|_{z=L} = 0 \quad \text{at} \quad z = L\]
r-averaged Eqns. in the Annular Region

\[
D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} \right] - \frac{u_r}{r} \frac{\partial c}{\partial r} - u_z \frac{\partial c}{\partial z} = 0
\]

- We are mostly interested in wafer-to-wafer changes (z variation) and do not care about profiles in the annulus.
- We will average over the r dimension and obtain a single r-averaged equation for C(z) where

\[
\text{let } C(z) = \frac{\int_{R_w}^{R_i} \int_{0}^{2\pi} rc(r, z) r dr d\theta}{\int_{R_w}^{R_i} \int_{0}^{2\pi} r dr d\theta} = \frac{2}{R_i^2 - R_w^2} \int_{R_w}^{R_i} rc(r, z) dr
\]

\[
\bar{u}_z = \frac{\int_{R_w}^{R_i} \int_{0}^{2\pi} ru_z(r) r dr d\theta}{\int_{R_w}^{R_i} \int_{0}^{2\pi} r dr d\theta} = \frac{2}{R_i^2 - R_w^2} \int_{R_w}^{R_i} ru_z dr
\]
Look how boundary conditions in \( r \) end up in the differential equation for \( C(z) \) as if they are in the gas phase (i.e., the domain of diff eq.); surface reactions at radial walls appear as if they are gas phase reactions.

\[
D \int_{R_w}^{R_t} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \, dr + \int_{R_w}^{R_t} \frac{\partial^2 c}{\partial z^2} \, r \, dr - \int_{R_w}^{R_t} ru_z \frac{\partial c}{\partial z} \, dr = 0
\]

\[
D \left[ r \frac{\partial c}{\partial r} \right]_{r=R_w}^{r=R_t} + \frac{1}{2} \frac{(R_t^2 - R_w^2)}{D} \frac{d^2 C}{dz^2} - \frac{1}{2} \frac{(R_t^2 - R_w^2)}{u_z} \frac{dC}{dz} = 0
\]

\[
- \left( R_t k_s C + \eta \frac{k_s C R_w^2}{\Delta} \right) + \frac{1}{2} \frac{(R_t^2 - R_w^2)}{D} \frac{d^2 C}{dz^2} - \frac{1}{2} \frac{(R_t^2 - R_w^2)}{u_z} \frac{dC}{dz} = 0
\]

\[
D \frac{d^2 C}{dz^2} - \bar{u}_z \frac{dC}{dz} - \left[ \frac{2k_s R_t}{(R_t^2 - R_w^2)} + 2\eta \frac{k_s R_w^2}{\Delta(R_t^2 - R_w^2)} \right] C = 0
\]

Looks like:

\[
D \frac{d^2 c}{dz^2} - u_z \frac{dc}{dz} + R_{gas} = 0
\]
Dimensional analysis

\[ \Theta = \frac{C}{C_b}, \quad \zeta = \frac{z}{L} \]

\[
\frac{D}{\bar{u}_z L} \frac{d^2 \Theta}{d\zeta^2} - \frac{d\Theta}{d\zeta} - \left[ \frac{2k_s R_t L}{\bar{u}_z (R_t^2 - R_w^2)} + \eta \frac{2k_s R_w^2 L}{\Delta \bar{u}_z (R_t^2 - R_w^2)} \right] \Theta = 0
\]

\[
P_e = \frac{\bar{u}_z L}{D} = \frac{\text{convective transport}}{\text{diffusive transport}}
\]

\[
Da_1 = \frac{2k_s R_t L}{\bar{u}_z (R_t^2 - R_w^2)} = \frac{\text{reaction rate (deposition on walls)}}{\text{convection rate}}
\]

\[
Da_2 = \frac{2k_s R_w^2 L}{\Delta \bar{u}_z (R_t^2 - R_w^2)} = \frac{\text{reaction rate (deposition on wafers)}}{\text{convection rate}}
\]

\[
\frac{1}{Pe} \frac{d^2 \Theta}{d\zeta^2} - \frac{d\Theta}{d\zeta} - [Da_1 + \eta Da_2] \Theta = 0
\]
Boundary conditions and Solution

\[
\frac{d\Theta}{d\zeta} = 0 \quad @ \quad \zeta = 1
\]

\[
- \frac{1}{Pe} \frac{d\Theta}{d\zeta} = (1 - \Theta) \quad @ \quad \zeta = 0
\]

\[
\Theta = \frac{2[(1 + \beta) \exp\{M(1 + \beta) + M(1 - \beta)\zeta\} - (1 - \beta) \exp\{M(1 + \beta)\zeta + M(1 - \beta)\}]}{(1 + \beta)^2 \exp\{M(1 + \beta)\} - (1 - \beta)^2 \exp\{M(1 - \beta)\}}
\]

where \( \beta = \sqrt{1 + \frac{4(Da_1 + \eta Da_2)}{Pe}} \) and \( M = \frac{Pe}{2} \)

Dankwertz “continuous flow systems” *Chemical Engineering Science* 2 (1), 1 (1953).
Limiting Cases: PFR limit

- $\text{Pe} \to \infty$ (i.e., $D \to 0$ or $u_z \to \infty$)

small diffusion rate compared to convection

$\Rightarrow$ Plug flow reactor (PFR) limit

\[
\beta = \sqrt{1 + \frac{4(Da_1 + \eta Da_2)}{Pe}} \to 1 \quad \text{and} \quad M \to \infty \quad Da^* = (Da_1 + \eta Da_2)
\]

\[
M(1 - \beta) = \frac{1}{2} Pe \left[1 - \sqrt{1 + \frac{4(Da_1 + \eta Da_2)}{Pe}}\right] = -\frac{2 Da^*}{\sqrt{1 + \frac{4 Da^*}{Pe}}} = -Da^*
\]

\[
\lim_{Pe \to \infty} \Theta = e^{-Da^* \zeta}
\]
Limiting Cases: PFR limit

Another way of seeing this is to look at $\text{Pe} \to \infty$ of the differential equation and boundary condition at $\zeta = 0$

\[
\frac{1}{\text{Pe}} \frac{d^2 \Theta}{d \zeta^2} - \frac{d \Theta}{d \zeta} - [\text{Da}_1 + \eta \text{Da}_2] \Theta = 0
\]

\[- \frac{1}{\text{Pe}} \frac{d \Theta}{d \zeta} = (1 - \Theta) \quad @ \quad \zeta = 0
\]

becomes

\[\Theta = 1 \quad @ \quad \zeta = 0\]

\[
\frac{d \Theta}{d \zeta} = -\text{Da}^* \Theta
\]

\[\Theta = e^{-\text{Da}^* \zeta}
\]
Limiting Cases: CSTR limit

- $\text{Pe} \to 0$ (i.e., $D \to \infty$ or $u_z \to 0$)

  small flow rate (convection) compared to diffusion

  $\Rightarrow$ Continuous stirred tank reactor (CSTR) limit

\[
\frac{d^2 \Theta}{d \zeta^2} - \text{Pe} \left\{ \frac{d \Theta}{d \zeta} - Da* \Theta \right\} = 0
\]

as $\text{Pe} \to 0$ \quad \frac{d^2 \Theta}{d \zeta^2} = 0

\[
\frac{d \Theta}{d \zeta} = 0 \quad \Rightarrow \quad \zeta = 1
\]

\[
- \frac{1}{\text{Pe}} \frac{d \Theta}{d \zeta} = (1 - \Theta) \quad \Rightarrow \quad \zeta = 0
\]

as $\text{Pe} \to 0$ \quad \frac{d \Theta}{d \zeta} = 0 \quad \Rightarrow \quad \zeta = 0

\[
\lim_{\text{Pe} \to 0} \Theta = \text{constant}
\]
Limiting Cases: CSTR limit

To find the concentration we average over z-direction too

\[
\frac{1}{Pe} \int_0^1 \frac{d^2 \Theta}{d\zeta^2} d\zeta - \int_0^1 \frac{d\Theta}{d\zeta} d\zeta - Da^* \int_0^1 \Theta d\zeta = 0
\]

\[
\frac{1}{Pe} \left[ \frac{d\Theta}{d\zeta} \bigg|_{\zeta=1} - \frac{d\Theta}{d\zeta} \bigg|_{\zeta=0} + \Theta(1) - \Theta(0) - Da^* \Theta = 0 \right]
\]

\[
\frac{1}{Pe} \left[ Pe(1-\Theta) - 0 \right] - Da^* \Theta = 0
\]

\[
\Theta = \frac{1}{1 + Da^*}
\]

Increasing \(Da^*\)

\(Da^* \sim 0\)

\(Da^* \gg 1\)

CSTR limit
Wafer-to-wafer uniformity

Uniformity index often defined as

\[ U = \frac{R_{\text{max}} - R_{\text{min}}}{R_{\text{avg}}} = \frac{C_{\text{max}} - C_{\text{min}}}{C_{\text{avg}}} = \frac{\Theta_{\text{max}} - \Theta_{\text{min}}}{\Theta_{\text{avg}}} \]

- U=0 : good uniformity
- U × 100 = % is variance with respect to average
- As U increases uniformity degrades
- For fixed Da* as Pe↑ U also ↑
- Pe ↑ means D ↓
- Since D ~ 1/P ⇒ lower P ⇒ better uniformity

\[ Pe = \frac{\bar{u}_z L}{D} = \frac{\text{convective transport}}{\text{diffusive transport}} \]
Often we are interested in deposition rate, $R_D$ in thickness/time, e.g., Å/s, Å/min, nm/s, nm/min, μm/min, etc.

$deposition\ flux\ (\#/\ cm^2/s) \times film\ area\ (\ cm^2) = film\ density\ (\#/\ cm^3) \times \dot{V}\ (\ cm^3/s)$

$$r_sA = N_fAR_D = N_fA\frac{dh}{dt}$$

$$R_D = \frac{r_s}{N_f} = \frac{kc}{N_f}$$

$$N_f = \frac{\rho_f}{M_{wf}}N_{Avogadro}$$