

R12.4 Chemical Vapor Deposition (CVD) Reactors

As discussed in Section 6.6, CVD is a very important process in the microelectronics industry. The fabrication of microelectronic devices may include as few as 30 or as many as 200 individual steps to produce chips with up to 10^6 transducers per chip. An abbreviated schematic of the steps involved in producing a typical computer chip is shown in Figure 11-11.

Starting from the upper left we see that single crystal silicon ingots are grown in a Czochralski crystalizer, then sliced into wafers, and chemically and physically polished. These polished wafers serve as a starting material for a variety of microelectronic devices. A typical fabrication sequence is shown for processing the wafer beginning with the formation of an SiO_2 layer on top of the silicon. The SiO_2 layer may be formed either by oxidizing a silicon layer or by laying down a SiO_2 layer by Chemical Vapor Deposition (CVD). Next the wafer is masked with a polymer photoresist (PR), a template with the pattern to be etched onto the SiO_2 layer is placed over the PR and the wafer is exposed to ultraviolet irradiation. If the mask is a positive PR, the light will cause scission in the polymer so that the exposed areas will dissolve when the wafer is placed in the developer. On the other hand, when a negative PR mask is exposed to ultraviolet irradiation, crosslinking of the polymer chains occurs and the *unexposed* areas dissolve in the developer. The undeveloped portion of the PR (in either case) will protect the covered areas from etching.

After the exposed areas of SiO_2 are etched to form trenches (either by wet etching (see P5-11) or plasma etching), the remaining PR is removed. Next the wafer is placed in a furnace containing gas molecules of the desired

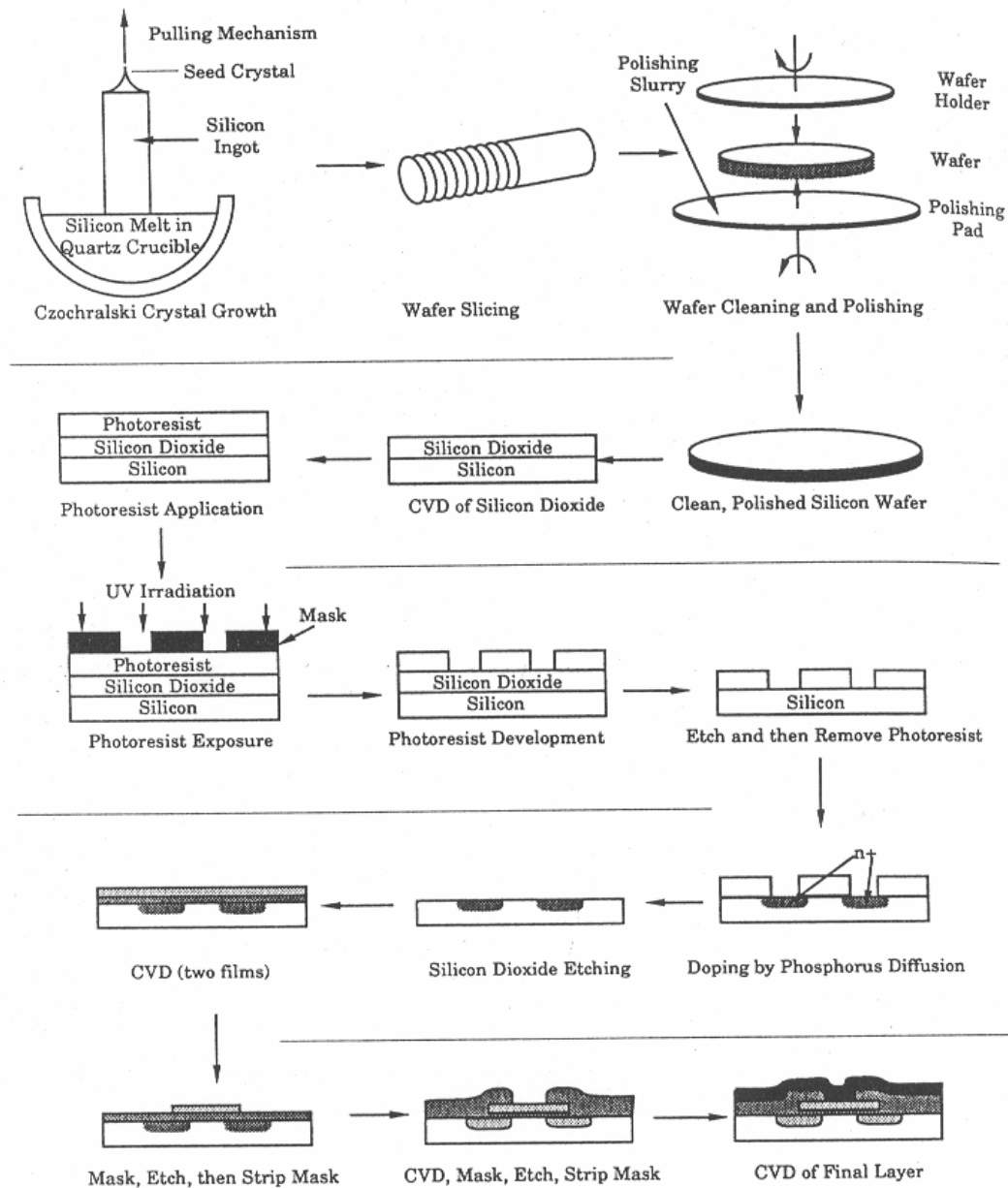


Figure 11-11 Microelectronic fabrication steps.

dopant, which then diffuse into the exposed silicon. After diffusion of dopant to the desired depth in the wafer it is removed and then covered with SiO_2 by CVD. The sequence of masking, etching, CVD, and metallization continues until the desired device is formed. A schematic of a final chip is shown in the lower right-hand corner of Figure 11-11.

One of the key steps in the chip making process is the deposition of different semiconductors and metals on the surface of the chip. This step can be achieved by CVD. CVD mechanisms were discussed in Chapter 6, consequently this section will focus on CVD reactors. A number of CVD reactor types have been used, such as barrel reactors, boat reactors, and

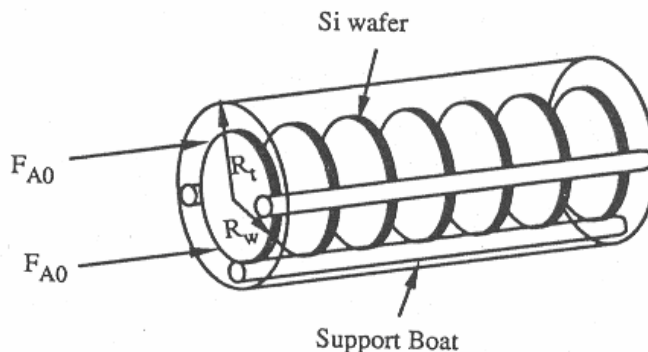
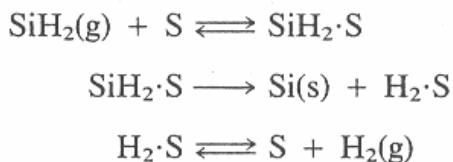


Figure 11-12 LPCVD boat reactor.

horizontal and vertical reactors. A description of these reactors and modeling equations are given by Jensen.⁶

One of the more common CVD reactors is the Horizontal Low Pressure CVD (LPCVD) reactor. This reactor operates at pressures of approximately 100 Pa. The main advantage of the LPCVD is its capability of processing a large number of wafers without detrimental effects to film uniformity. Owing to the large increases in the diffusion coefficient at low pressures (recall Table 10-2) surface reactions are more likely to be controlling than mass transfer. A schematic of a LPCVD reactor is shown in Figure 11-12.

To illustrate LPCVD modeling we shall use a specific but simplified example, the deposition of silicon from a gas stream of SiH_2 . The reaction mechanism is



Here we have assumed that the equilibrium for the dissociation of SiH_4 discussed in Problem 6-3 lies far to the right.

The corresponding rate law is

$$r''_{\text{Si}} = \frac{k_1 P_{\text{SiH}_2}}{1 + K_1 P_{\text{H}_2} + K_2 P_{\text{SiH}_2}} \quad (11-75)$$

Recalling that the adsorption constants K_1 and K_2 decrease with increasing temperatures, an excellent approximation at high temperature is

$$1 \gg (K_1 P_{\text{H}_2} + K_2 P_{\text{SiH}_2})$$

consequently, the deposition rate can be modeled as first-order in SiH_2 , i.e.,

$$r''_{\text{Si}} \cong k_1 P_{\text{SiH}_2} \cong k C_{\text{SiH}_2} \equiv k C_A \quad (11-76)$$

where $A \equiv \text{SiH}_2$

CVD Reaction
Sequence in Silicon
Deposition

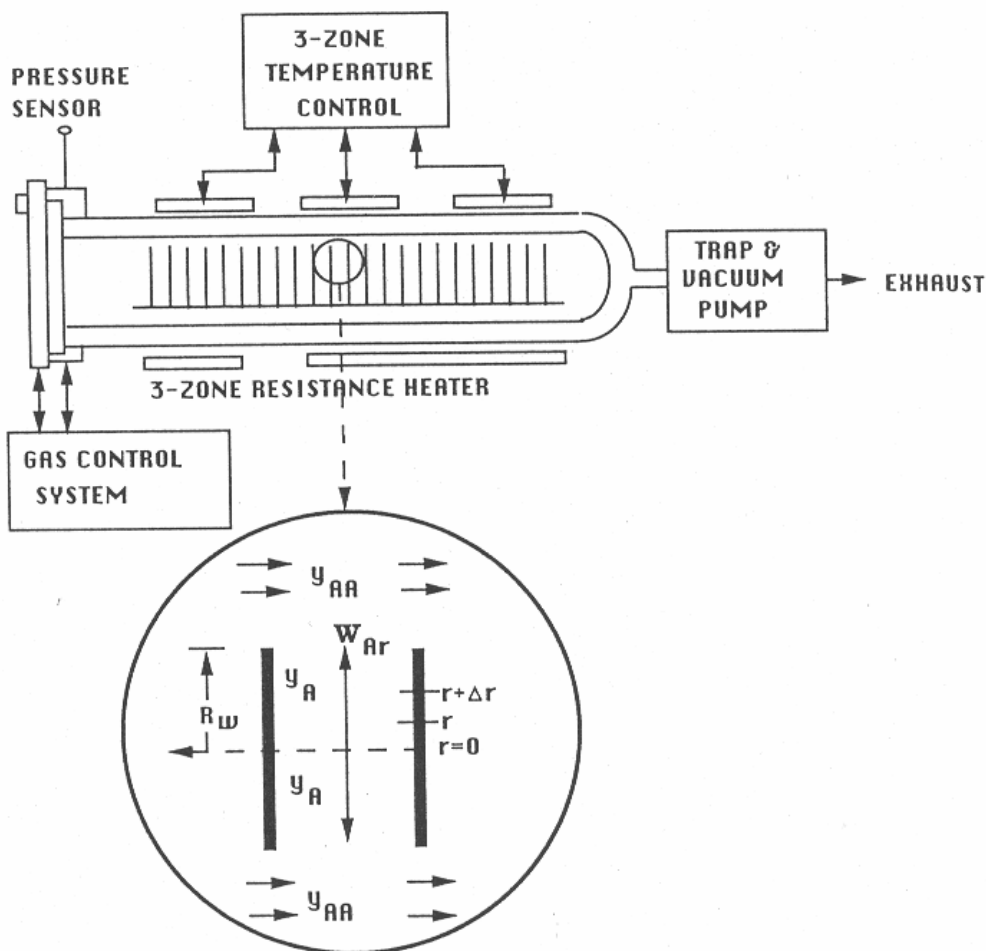


Figure 11-13 LPCVD boat reactor with peripherals.

Modeling Concepts We shall model the axial flow in the annular region as being laminar. This assumption is reasonable because a typical Reynolds number for flow in a LPCVD reactor is less than 1. As the reactant gases flow through the annulus, the reactants diffuse from the annulus radially inward between the wafers to coat them.⁷

The reacting gas flows through the annulus between the outer edges of the cylindrical wafers and the tube wall (see Figure 11-13). The corresponding cross-sectional area of the annulus is

Flow in the
Annulus

$$A_c = \pi(R_t^2 - R_w^2)$$

where R_t and R_w are the radii of the tube and wafer, respectively. Because SiH_2 is being consumed by CVD, the mole fraction of SiH_2 (i.e., the reactant) in the annulus, y_{AA} , decreases as the reactant flows down the length of the annulus.

The reacting gases diffuse out of the annular region into the space between the wafers where the mole fraction is represented by y_A . As molecules diffuse radially *inward* some of them are adsorbed and deposited on the wafer surface. The reaction products then diffuse radially *outward* into the gas stream axially flowing in the annulus. This system can be analyzed in a manner analogous to flow through a packed catalyst bed where the reaction gases diffuse into the catalyst pellets. In this analysis we used an effectiveness factor to determine the overall rate of reaction per volume (or mass) of reactor bed. We can extend this idea to LPCVD reactors where the reactants diffuse from the annular flow channel radially inward between the wafers.

R12.4 Effectiveness Factor for a LPCVD Reactor

Silicon will deposit on the wafers, the reactor walls, and on the boat support. Deposition on the walls and support will take place at the reactant concentrations in the annulus. However, the concentration of A between the wafers is less than the concentration in the annulus. Consequently, the rate of deposition on the wafer will be less than the rate at conditions in the annulus. Fortunately these two concentrations can be related by the effectiveness factor. We can determine the effectiveness factor once the concentration profile in the region between the wafers is obtained.

$$\eta = \frac{\text{Actual rate of reaction}}{\text{Rate of reaction when entire wafer surface is exposed to the concentration in the annulus } C_{AA} \text{ (i.e., } y_{AA})}$$
(11-77)

$$\eta = \frac{2 \int_0^{R_w} 2\pi r (-r'_A(r)) dr}{2\pi R_w^2 (-r''_{AA})} = \frac{2\pi R_w \ell (-W_{Ar}|_{r=R_w})}{2\pi R_w^2 (-r''_{AA})} = \frac{\ell D_{AB} \left. \frac{dC_A}{dr} \right|_{r=R_w}}{R_w (-r''_{AA})}$$
(11-78)

where ℓ is the distance between wafers, and $-r''_{AA}$ is the rate of disappearance of A at the concentration of A in the annular region, C_{AA} . We now use η to express the actual rate of reaction per unit surface area of wafer in terms of the rate of reaction at conditions in the annulus.

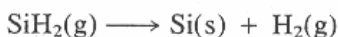
$$\text{Actual Rate} = -r''_{AA} \eta$$
(11-79)

Letting ' a ' be the wafer surface area per unit volume of reactor, the rate of consumption of species A by the wafer per unit volume of reactor is

$$-r_{Aw} = -r''_{AA} a \eta$$
(11-80)

Example 11-4 Diffusion Between Wafers

Derive an equation for the reactant gas concentration as a function of wafer radius and then determine the effectiveness factor.



In terms of the diffusing gas phase components, we can write this reaction as:



Solution

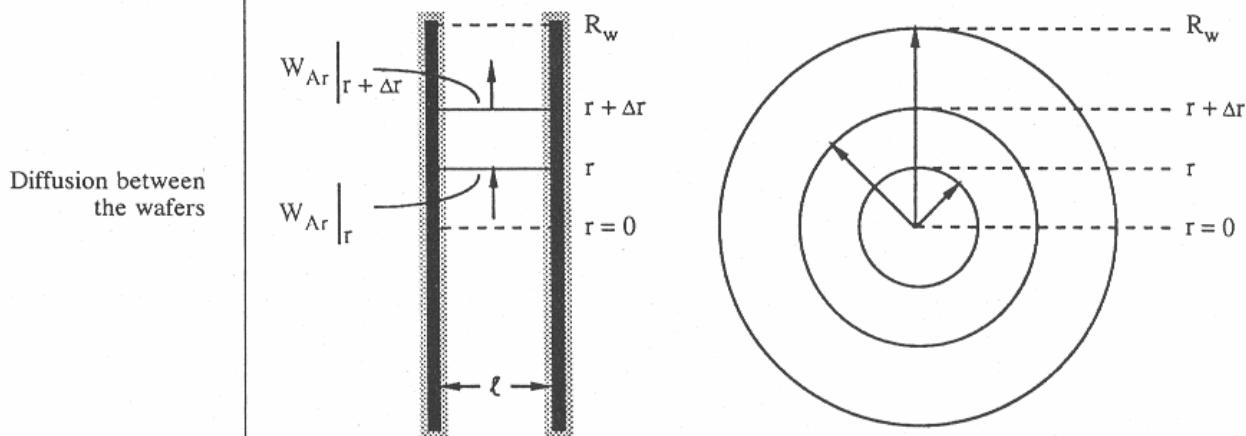


Figure E11-4.1

The shell balance on the reactant diffusing between two wafers separated by a distance ℓ shown in Figure E11-4.1 gives

$$\text{In} - \text{Out} + \text{Generation} = 0$$

$$W_{Ar} 2\pi r \ell \Big|_r - W_{Ar} 2\pi r \ell \Big|_{r+\Delta r} + 2(2\pi r \Delta r r'_{Aw}) = 0$$

where r'_{Aw} = rate of generation of species A per unit wafer surface area. The factor of 2 appears in the generation term because there are two wafer surfaces exposed in each differential volume element. Dividing by $2\pi r \Delta r \ell$, taking the limit as Δr approaches zero, and then rearranging gives

$$\frac{1}{r} \frac{d(W_{Ar} r)}{dr} = \frac{2r'_{Aw}}{\ell} \quad (\text{E11-4.1})$$

Recalling the constitutive equation for the molar flux W_{Ar} in radial coordinates

$$W_{Ar} = -cD_{AB} \frac{dy_A}{dr} + y_A(W_{Ar} + W_{Br}) \quad (\text{E11-4.2})$$

For every one molecule of SiH_2 (i.e., species A) that diffuses *IN* one molecule of H_2 (i.e., species B) diffuses *OUT*.

$$W_{Br} = -W_{Ar}$$

Then

$$W_{Ar} = -cD_{AB} \frac{dy_A}{dr} = -D_{AB} \frac{dC_A}{dr} \quad (\text{E11-4.3})$$

Diffusion with
reaction between
wafers

For a first-order reaction

$$-r''_{Aw} = kC_A \quad (11-76)$$

Substituting equations (11-76) and (E11-4.3) into Equation (E11-4.1) we get

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dC_A}{dr} \right) - \frac{2k}{D_{AB}} \frac{C_A}{\ell} = 0 \quad (E11-4.4)$$

The corresponding boundary conditions are

$$\text{At } r = R_w \quad C_A = C_{AA} \quad (E11-4.5)$$

$$\text{At } r = 0 \quad \frac{dC_A}{dr} = 0 \text{ and } C_A \text{ is finite} \quad (E11-4.6)$$

Let $\lambda = r/R_w$ and $\Psi = C_A/C_{AA}$

then

$$\frac{1}{\lambda} \frac{d}{d\lambda} \left(\lambda \frac{d\Psi}{d\lambda} \right) - \phi_1^2 \Psi = 0 \quad (E11-4.7)$$

$$\text{where } \phi_1^2 = \frac{2kR_w^2}{D_{AB}\ell}$$

The boundary conditions are

$$\text{at } \lambda = 0: \quad \frac{d\Psi}{d\lambda} = 0 \text{ and } \Psi \text{ is finite}$$

$$\text{at } \lambda = 1 \quad \Psi = 1.0$$

Equation (E11-4.7) is a form of Bessel's Equation.

The general form of the solution to Bessel's equation is⁸

$$\Psi = AI_o(\phi_1\lambda) + BK_o(\phi_1\lambda) \quad (E11-4.8)$$

Where I_o is a modified Bessel function of the first kind of order zero and K_o is a modified Bessel function of the second kind of order zero. The second boundary condition requires Ψ to be finite at $\lambda = 0$. Therefore B must be zero because $K_o(0) = \infty$. Using the first boundary condition we get $1 = AI_o(\phi_1)$, then $A = 1/I_o(\phi_1)$. The concentration profile in the space between the wafers is

$$\Psi = \frac{C_A}{C_{AA}} = \frac{I_o(\phi_1\lambda)}{I_o(\phi_1)} \quad (E11-4.9)$$

$$\eta = \frac{-W_{Ar} |_{r=R_w} (2\pi R_w \ell)}{2\pi R_w^2 (-r''_{AA})} \quad (E11-4.10)$$

$$\eta = \frac{-\left(-D_{AB} \frac{dC_A}{dr}\right)_{r=R_w} (2\pi R_w \ell)}{2kC_{AA}\pi R_w^2} = 2 \frac{\frac{d\Psi}{d\lambda}\bigg|_{\lambda=1}}{\frac{2kR_w^2}{D_{AB}\ell}} \quad (\text{E11-4.11})$$

$$\eta = 2 \frac{\frac{d\Psi}{d\lambda}\bigg|_{\lambda=1}}{\phi_1^2}$$

$$\eta = \frac{2I_1(\phi_1)}{\phi_1 I_0(\phi_1)} \quad (\text{E11-4.12})$$

The concentration profile along the radius of the wafer disk as well as the wafer shape is shown in Figure E11-4.2 for different values of the Thiele modulus.

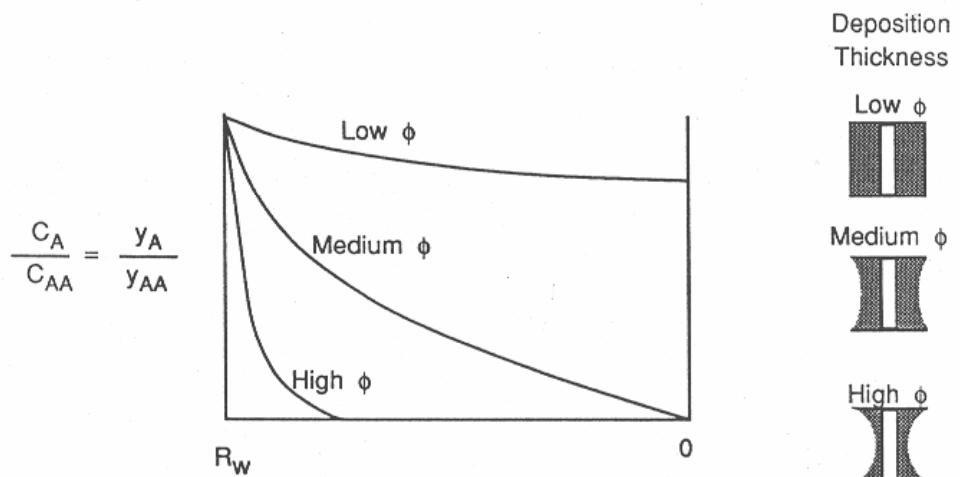


Figure E11-4.2 Radial concentration profile.

Accounting for Si deposition on the walls and support

Deposition on the Peripherals Silicon will deposit on the walls of a reactor and on the boat support in addition to the wafers. This rate of deposition on the walls and support is

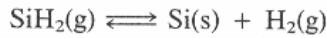
$$-r''_{Si,p} = -r''_{AA} = (1 + \alpha)kC_{AA}$$

$$\alpha = \frac{\text{surface area of boat support}}{\text{surface area of tube}}$$

Owing to high temperature and low pressure, radiation is the dominant heat transfer mechanism, therefore small temperature differences exist between the wafer and reactor wall. Consequently, there is no need to couple the mole and energy balances for these small temperature gradients.

Example 11-5 CVD Boat Reactor

Silicon is to be deposited on wafers in a LPCVD reactor. We want to obtain an analytical solution for the silicon deposition rate and reactant concentration profile for the simplified version of the LPCVD reactor just discussed. Analytical solutions of this type are important in that an engineer can rapidly gain an understanding of the important parameters and their sensitivities, without making a number of 'runs' on the computer. The reaction that is taking place is



Sections of the reactor are shown in Figures E11-5.1 and E11-5.2.

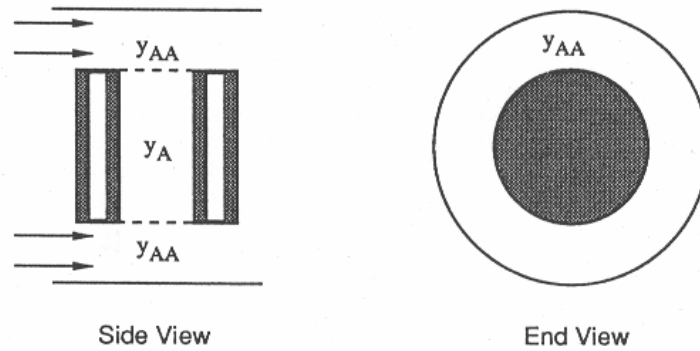


Figure E11-5.1

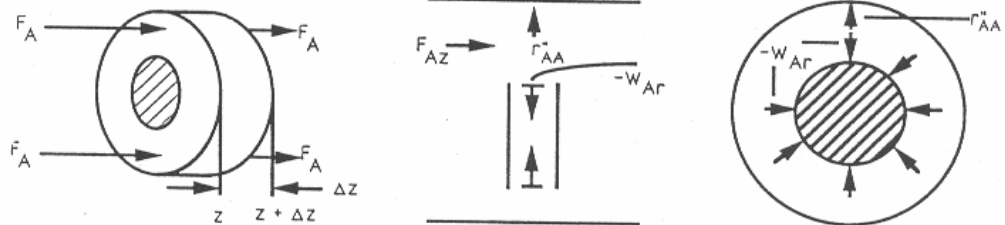


Figure E11-5.2

- Balances:** In forming our shell balance on the annular region we shall assume there are no radial gradients in the annulus and include the outer tube walls and the boat which consume some of the reactant by deposition on the walls in the balance. In addition we shall neglect any dispersion or diffusion in the axial direction.

Balance on reactant A

<u>IN</u>	<u>OUT</u>	<u>GENERATION</u>	<u>GENERATION</u>	<u>GENERATION</u>	
By	By	By	By	By	
Convection	Convection	reaction on wafer surface	reaction on tube walls	reaction on boat support	= 0

$$F_{Az} \Big|_z - F_{Az} \Big|_{z+\Delta z} + r''_{AA} \eta a \pi R_i^2 \Delta z + r''_{AA} 2\pi R_i \Delta z + r''_{AA} \alpha 2\pi R_i \Delta z = 0 \tag{E11-5.1}$$

Dividing through by Δz and taking the limit as $\Delta z \rightarrow 0$

$$-\frac{dF_{Az}}{dz} + \overbrace{r''_{AA}[(1 + \alpha)2\pi R_t + \eta a\pi R_t^2]}^{R''_{AA}} = 0 \quad (\text{E11-5.2})$$

Mole balance on
the reacting gas

2. **Rate laws:** The rate of silicon deposition, r''_{Si} , (mol/dm²·s) is equal to the rate of depletion of SiH₂.

$$r''_{Si} = -r''_A = kC_A \quad (11-76)$$

where the units of C_A and k are (mol/dm³) and (dm/s), respectively. Deposition takes place on the reactor walls, the support, and on the wafer surfaces. The corresponding depletion of reactant gas on each of these surfaces is

$$\text{Wafer (mol/s): } kC_{AA}\eta a\pi R_t^2\Delta z$$

$$\text{Reactor wall (mol/s): } kC_{AA}2\pi R_t\Delta z$$

$$\text{Boat support (mol/s): } kC_{AA}\alpha 2\pi R_t\Delta z$$

$$\text{Total: } -R''_{AA}\Delta z = -r''_{AA}(2\pi R_t + \alpha 2\pi R_t + \eta a\pi R_t^2)\Delta z$$

$$-R''_{AA} = kC_{AA}(2\pi R_t + \alpha 2\pi R_t + \eta a\pi R_t^2) \quad (\text{E11-5.3})$$

Radial
concentration
profile

3. **Concentration profile and effectiveness factor:** From Example 11-4 we derived the radial concentration profile between the wafers as

$$\frac{C_A}{C_{AA}} = \frac{I_o(\phi_1\lambda)}{I_o(\phi_1)} \quad (\text{E11-4.9})$$

the corresponding effectiveness factor was

$$\eta = \frac{2I_1(\phi_1)}{\phi_1 I_o(\phi_1)} \quad (\text{E11-4.12})$$

4. **Concentration profile in the annular region:** Combining equations (E11-5.2) and (E11-5.3) yields

$$-\frac{dF_{Az}}{dz} = kC_{AA}[(1 + \alpha)2\pi R_t + \eta a\pi R_t^2] \quad (\text{E11-5.4})$$

Writing F_{Az} and C_{AA} in terms of conversion we have

$$\begin{aligned} F_{Az} &= F_{A0}(1 - X) \\ C_{AA} &= \frac{C_{A0}(1 - X)}{(1 + \epsilon X)} \end{aligned} \quad (\text{E11-5.5})$$

Axial
concentration
profile

Where C_{A0} and F_{A0} refer to the reactant concentration and molar flow rates at the entrance to the reactor.

Combining equations (E11-5.4) and (E11-5.5) gives

$$F_{A0} \frac{dX}{dz} = kC_{A0}[(1 + \alpha)2\pi R_t + \eta a\pi R_t^2] \frac{(1 - X)}{(1 + \epsilon X)} \quad (\text{E11-5.6})$$

$$\epsilon = y_{A0}\delta = 1 \cdot (1 - 1 - 0) = 0$$

Collecting terms we can obtain an expression involving the Damköhler number, Da.

$$\frac{dX}{dz} = \frac{\text{Da}}{L}(1 - X) \quad (\text{E11-5.7})$$

where

$$\text{Da} = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}}$$

and

$$\text{Da} = \frac{kC_{A0}[(1 + \alpha)2\pi R_t + \eta a\pi R_t^2]L}{F_{A0}}$$

Solving for conversion as a function of distance along the length of the reactor yields

$$X = 1 - \exp[-\text{Da}z/L] \quad (\text{E11-5.8})$$

or, in terms of concentration

$$C_{AA}/C_{A0} = \exp[-\text{Da}(z/L)] \quad (\text{E11-5.9})$$

The deposition rate as a function of r and z can now be obtained as follows. The deposition rate at a location r and z is

$$-r''_{Aw}(r, z) = kC_A(r, z)$$

First, using Equation (E11-4.9) to relate $C_A(r, z)$ and $C_{AA}(z)$ we obtain

$$-r''_{Aw}(r, z) = kC_A(r, z) = kC_{AA}(z) \frac{I_0(\phi_1 r/R_w)}{I_0(\phi_1)} \quad (\text{E11-5.10})$$

Next, we use Equation (E11-5.9) to determine the rate as a function of distance down the reactor.

$$-r''_{Aw}(r, z) = kC_{A0} \frac{I_0(\phi_1 r/R_w)}{I_0(\phi_1)} \exp[-\text{Da}(z/L)] \quad (\text{E11-5.11})$$

The thickness, T , of the deposit is obtained by integrating the deposition rate with respect to time, i.e.,

$$\frac{dT}{dt} = \frac{2(-r''_{Aw})}{\rho}$$

where ρ = molar density of the material deposited, gmole/cm³. The *two* accounts for deposition on both sides of the wafer. Integrating, we obtain

$$T(r, z) = \frac{-r''_{Aw}(r, z)}{\rho} 2t \quad (\text{E11-5.12})$$

The reactant concentration profile and deposition thickness along the length of the reactor is shown schematically below in Figure E11-5.3 for the case of small values of the Thiele modulus ($\eta \approx 1$).

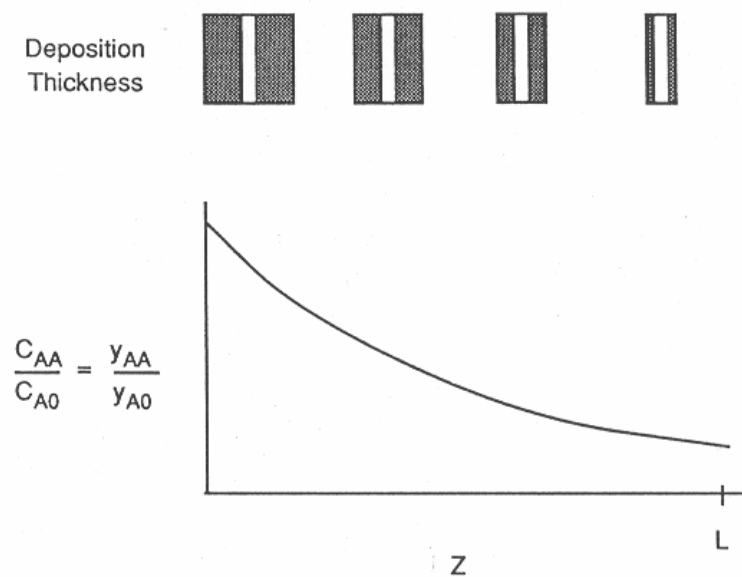


Figure E11-5.3 Axial concentration profile.