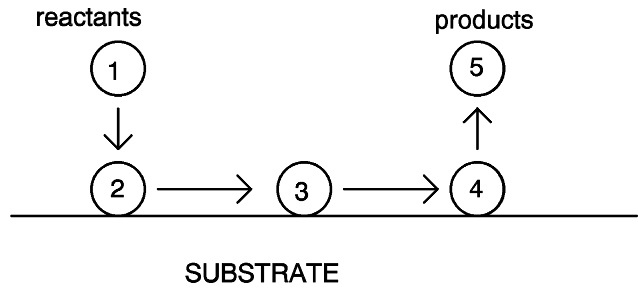
Notes on CVD Kinetics

• Deposition depends on the sequence of events:

(1) Diffusion of Reactants to surface
(2) Absorption of Reactants at surface
(3) Chemical reaction at surface
(4) Desorption of products from surface
(5) Diffusion of products from surface.



* (1) and (5) are mass-transfer mechanisms.

• The *slowest* event will be the rate- determing step.

(1) Temperature Dependence of Deposition rate.

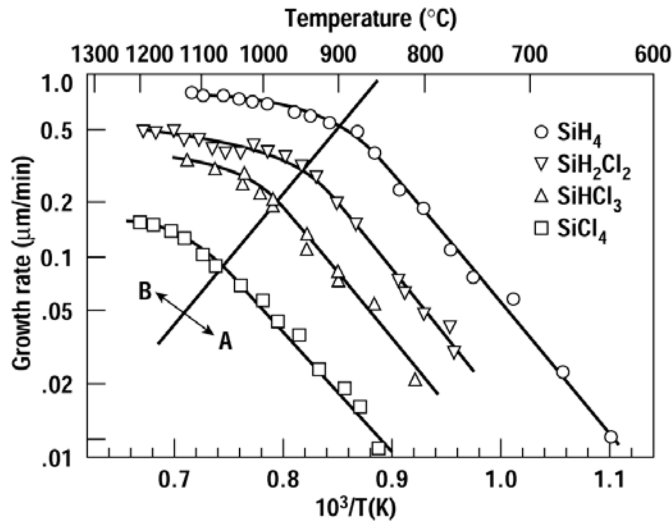


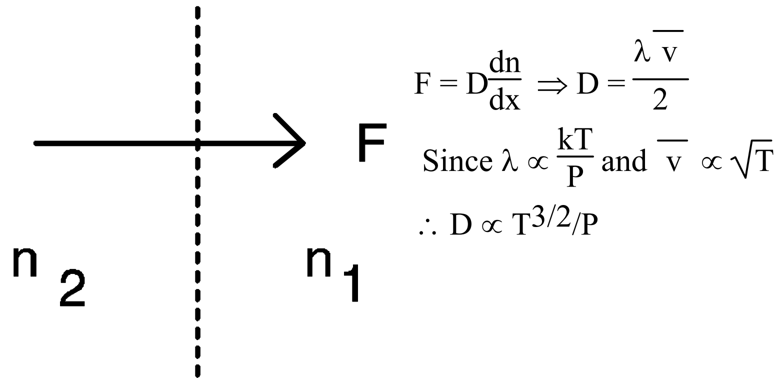
Figure 14.8 Arrhenius behavior of a variety of silicon-containing growth species *(after Eversteyn, reprinted by permission, Philips).*

(i) • From the above Si deposition example, for low T, rate $R \propto e^{-\Delta E/kT}$ (Surface Reaction limited)
where ΔE = 25 - 100 kcal/mole for most CVD processes (or 1- 4 eV/atom).

(ii) For high temperature, $R \propto T^n$ ($1.5 < n$ (experimental) < 2.0) (Mass Transport limited)

For mass-transport limited reactions, $R \propto D$ (diffusion constant) and $D \propto T^{3/2}/P$ for gaseous diffusion.

Proof: $F = \frac{n_1 \overline{v}}{4} - \frac{n_2 \overline{v}}{4} = \frac{\overline{v}}{4} (\lambda \cdot \frac{dn}{dx})$ where λ = mean free path of gas collision.



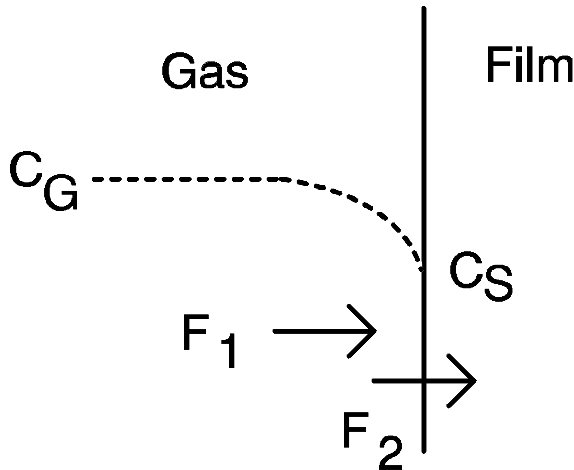
$F = D\frac{dn}{dx} \Rightarrow D = \frac{\lambda \overline{v}}{2}$

Since $\lambda \propto \frac{kT}{P}$ and $\overline{v} \propto \sqrt{T}$

$\therefore D \propto T^{3/2}/P$

(2) Growth Rate Model

[Note] This model is a special case of the Grove-Deal model for thermal oxidation. Here , we don't have to consider the diffusion througfh the oxide layer.



In this model, fluxes of products are ignored (i.e., their mass-transfer coefficients >> those of reactant).

Let F_1 = flux from bulk of gas to substrate surface.

$\equiv h_G \cdot (C_G - C_S)$

where h_G = mass-transfer coefficient.

C_G, C_S = reactant conc. at bulk of gas and substrate surface respectively.

Let F_2 = flux consumed in film-growth reaction.

$= k_S \cdot C_S$ where k_S = surface-reaction rate coefficient.

Steady state $\Rightarrow F_1 = F_2 = F$

$$\therefore C_S = \frac{C_G}{1 + k_S/h_G} \text{ and } F = \frac{k_S h_G}{k_S + h_G} \cdot C_G$$

Since $C_G = Y \cdot C_T$ where Y = mole fraction of reactant.

C_T = total # of molecules/cm^3 in gas mixture.

and $\frac{dy}{dt}$ (thickness growth rate) = $\frac{F}{\rho}$ where ρ = atomic density of film.

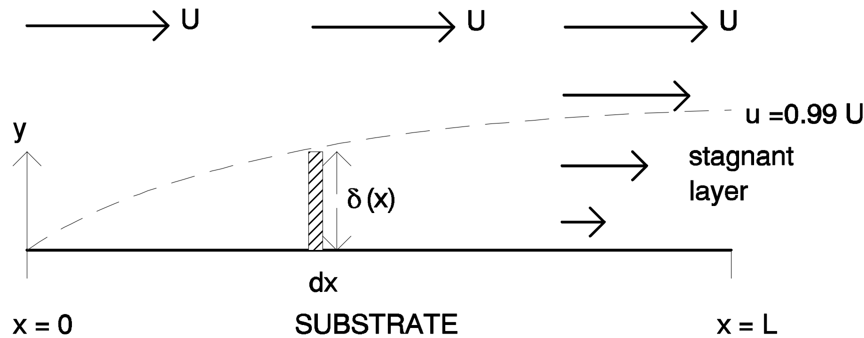
$$\therefore \frac{dy}{dt} = \frac{k_S h_G}{k_S + h_G} \cdot \frac{C_T}{\rho} \cdot Y = \frac{1}{(\frac{1}{k_s} + \frac{1}{h_G})} \cdot \frac{C_T}{\rho} \cdot Y$$

Comments:

(a) $\frac{dy}{dt}$ is determined by the smaller of h_G and k_S (i.e., mass-transfer control or surface-reaction control).

(b) $\frac{dy}{dt} \propto Y$ (mole fraction of reactant in bulk of gas mixture)

(3) Boundary Layer Theory for Stagnant Gas Layer



The boundary layer thickness δ(x) is shown in the figure below and L is the length of the substrate (e.g. substrate or wall of reactor).

The gas velocity u is a function of x and y and is equal to zero at plate's surface and is equal to U in the free gas stream.

Let μ = viscosity of gas. Then frictional force / unit area along the x-direction = $\mu \times \frac{\partial u}{\partial y}$

Let us consider a volume element of unit depth (i.e., into the paper) , height δ(x) and width dx.

Total friction force on element = $\mu \times \frac{\partial u}{\partial y} \times (1 \times dx) = \mu \frac{\partial u}{\partial y} dx =$ decelerating force

Total accelerating force on element.

$= \rho \times \delta(x)dx \times \frac{du}{dt} = \rho \times \delta(x)dx \times \frac{du}{dx} \times \frac{dx}{dt} = \rho \times \delta(x)dx \times \frac{du}{dx} \times u$

where ρ is the gas mass density

Balanced forces : $\mu \frac{\partial u}{\partial y} = \rho \times \delta(x)u\frac{du}{dx}$ and u(x,y) can be solved exactly.

Approximate Solutions

Let u » U ; $\frac{\partial u}{\partial y} \approx \frac{U}{\delta(x)}$; $\frac{\partial u}{\partial y} \approx \frac{U}{x}$

then $\delta(x) \approx A \left(\frac{\mu x}{\rho U}\right)^{1/2} - B$ "parabolic dependence' where A,B are constants.

∴ The "average" boundary layer thickness $\overline{\delta} = \frac{1}{L}\int_0^L \delta(x)\, dx = \frac{2}{3}\frac{L}{\sqrt{\frac{\rho UL}{\mu}}} = \frac{2}{3}\frac{L}{\sqrt{R_{e_L}}}$

R_{e_L} is called the Reynold Number of the reactor. When R_{e_L} is small (≤ 2000) , viscous flow dominates. When R_{e_L} very large (≥ 2000) , turbulent flow dominates.

The Exact Solutions:

The stagnant layer thickness with u= 0.99U is equal to :

$$\delta(x) \approx 5.0 \left(\frac{\mu x}{U}\right)^{1/2}$$

See H. Blasius, NACA Tech. Mem., 1949, p. 1217.

In the CVD growth rate model, it was assumed that mass transport across stagnant layer proceeds by diffusion,

then. $F_1 \equiv D_G \cdot \frac{C_G - C_S}{\bar{\delta}} \Rightarrow h_G = \frac{D_G}{\bar{\delta}}$ where D_G = diffusivity

For mass-transfer limited deposition, model $\Rightarrow$ $\frac{dy}{dt} \propto h_G \propto \frac{1}{\bar{\delta}} \propto \sqrt{U}$