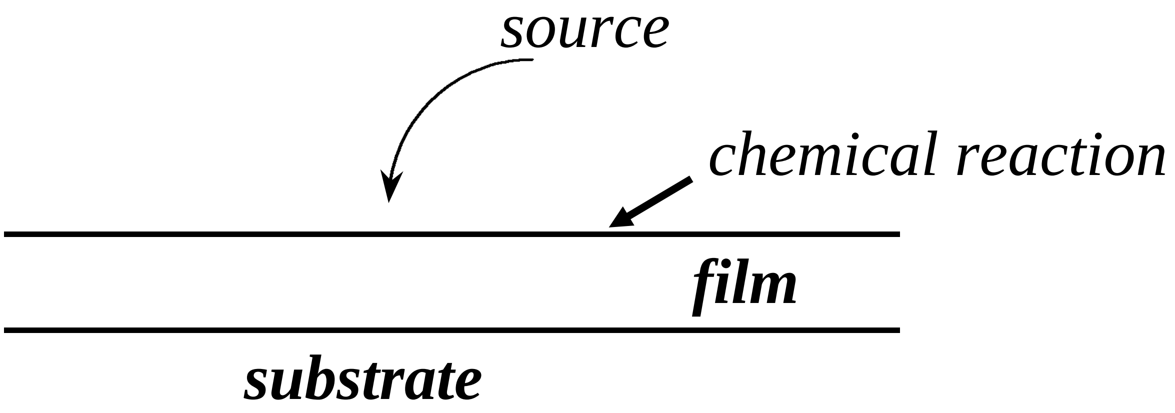
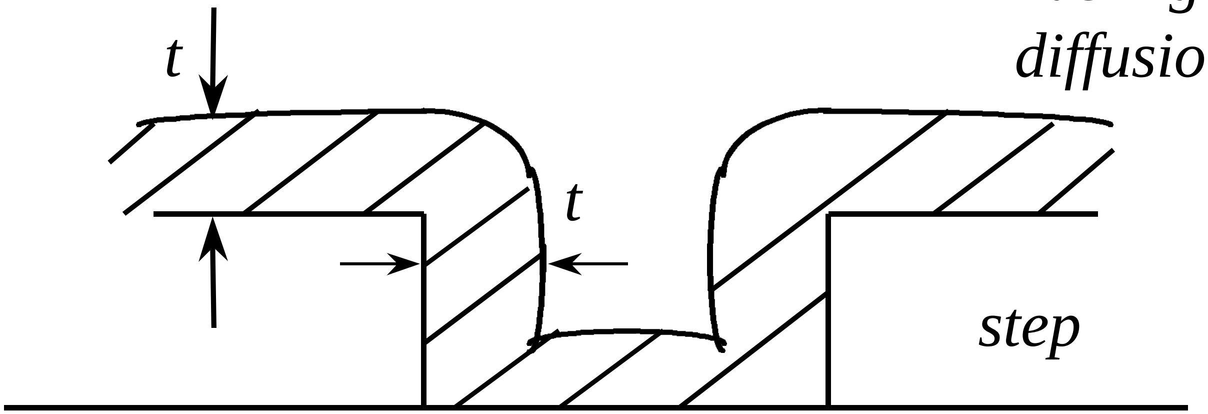
Chemical Vapor Deposition (CVD)

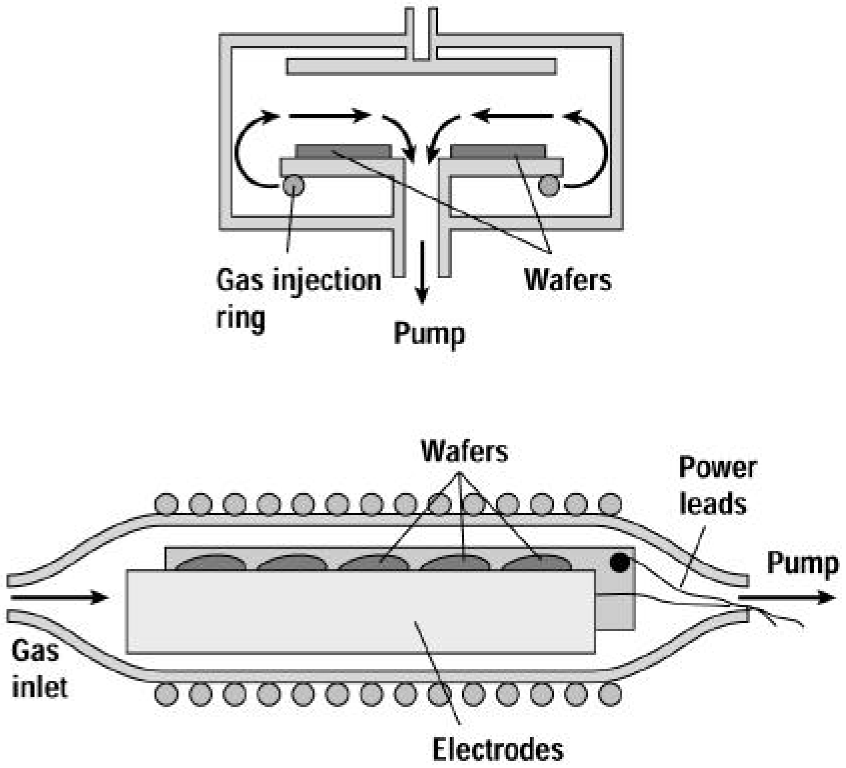


More conformal deposition vs. PVD

(Θ higher temp
has higher surface
diffusion)



LPCVD Reactors



PECVD Reactors

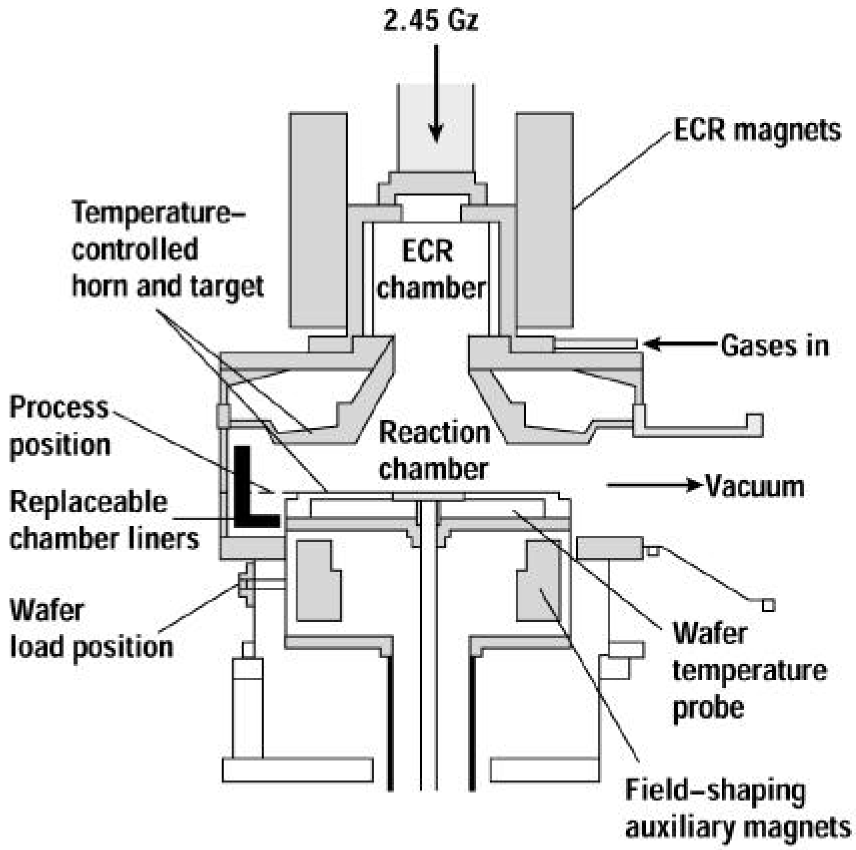


Figure 13.18 Basic PECVD geometries: cold wall parallel plate, hot wall parallel plate, and ECR.

Examples

$(a)SiO_2$

$$\underset{\underset{gas}{\uparrow}}{SiH_4} + \overset{\overset{gas}{\swarrow}}{O_2} \rightarrow \overset{\overset{solid}{\swarrow}}{SiO_2} + 2H_2 \uparrow$$

350°C-500°C

$(b)PSG : phospho\ silicate\ glass. \left[P_2O_5 + SiO_2\right]$

$$4PH3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2$$

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2 \uparrow$$

350°C-500°C

$(c)TEOS : tetraethylene\ orthosilicate.$

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + C_X H_Y O_Z \uparrow$$

$(d)\,Si_3N_4$

$$3SiH_4 + NH_3 \rightarrow Si_3N_4 + 12H_2$$

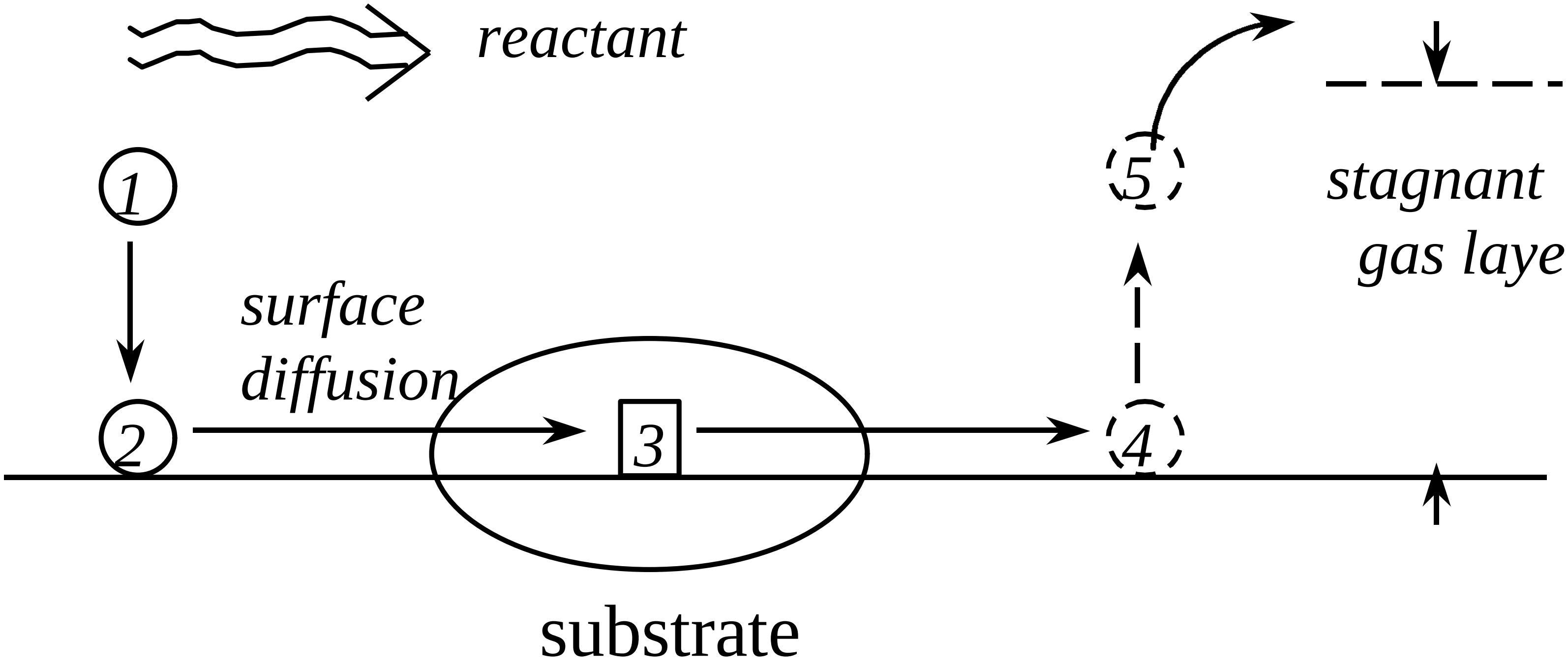
$(e)\,Poly - Si$

$$SiH_4 \xrightarrow{600\,^oC} Si + 2H_2$$

$(f)\,W$

$$WF_6 + 3H_2 \rightarrow W + 6HF \uparrow$$

CVD Mechanisms



1 = **Diffusion of reactant to surface**
2 = **Absorption of reactant to surface**
3 = **Chemical reaction**
4 = **Desorption of gas by-products**
5 = **Outdiffusion of by-product gas**

Example Poly-Si Deposition

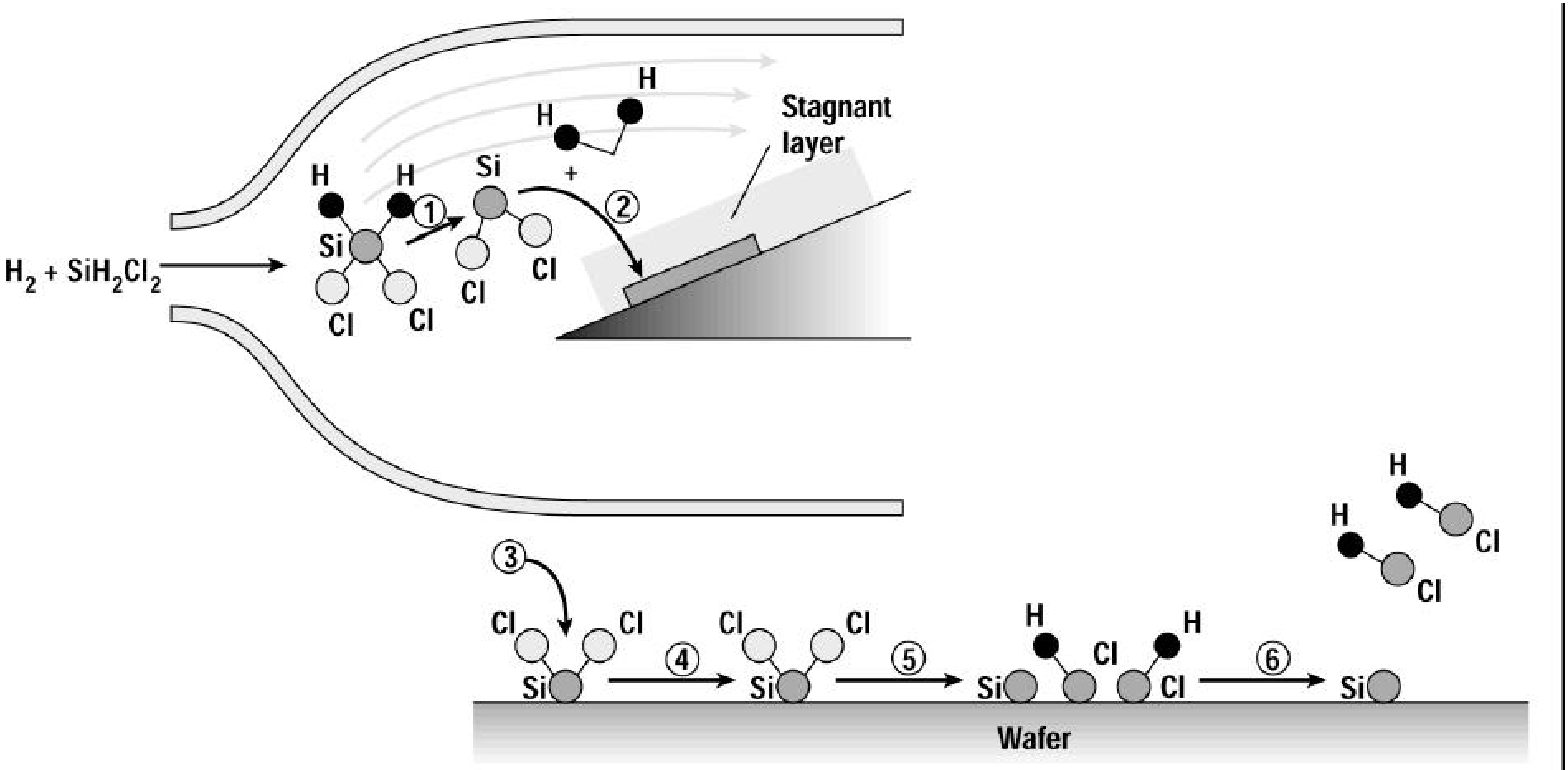
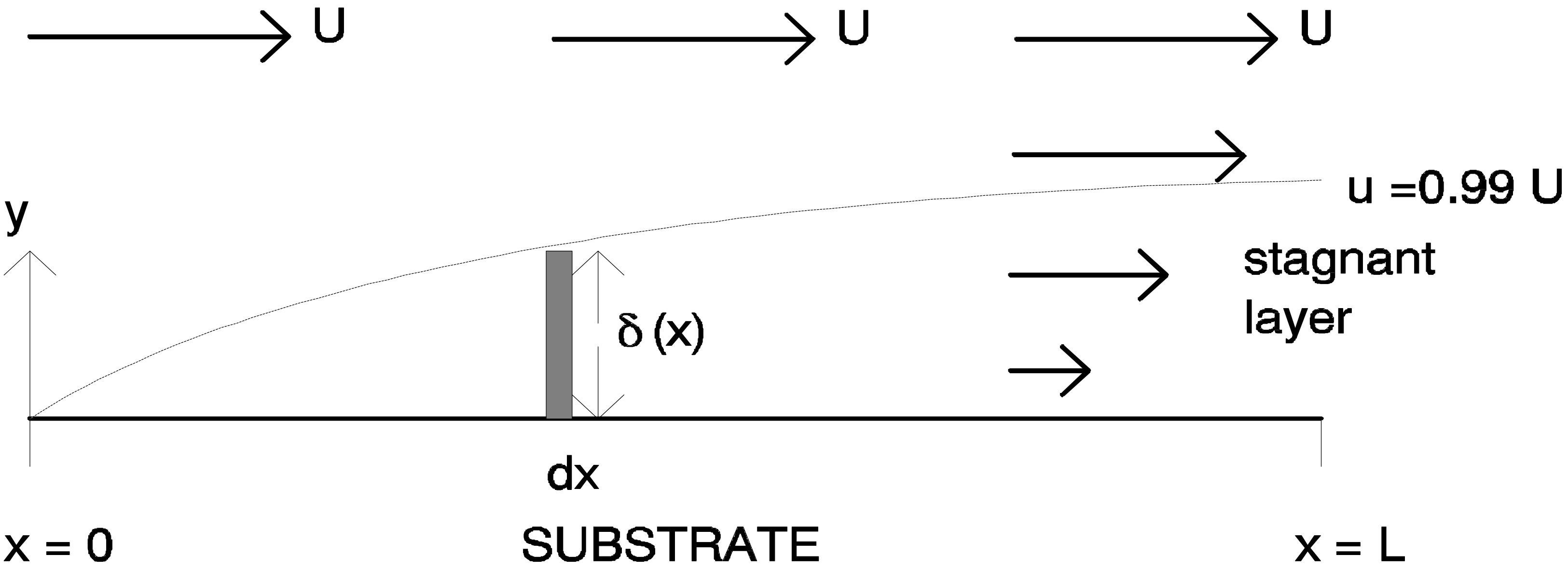


Figure 14.4 VPE steps include (1) gas-phase decomposition and (2) transport to the surface of the wafer. At the surface the growth species must (3) adsorb, (4) diffuse, and (5) decompose, and (6) the reaction by-products desorb.

Boundary Layer Theory for Stagnant Gas Layer [Planar Geometry]

***See CVD Kinetis Handout for details**

Stream velocity



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

Derivation of boundary layer continued

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

then $\boxed{\delta(x) \approx A \left(\frac{\mu x}{\rho U}\right)^{1/2} - B}$

“parabolic dependence’ where A,B are constants.

The Exact Solution:

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.

$\therefore$ 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 ($\leq$ 2000) , viscous flow dominates. When R_{e_L} very large ($\geq$ 2000) , turbulent flow dominates.

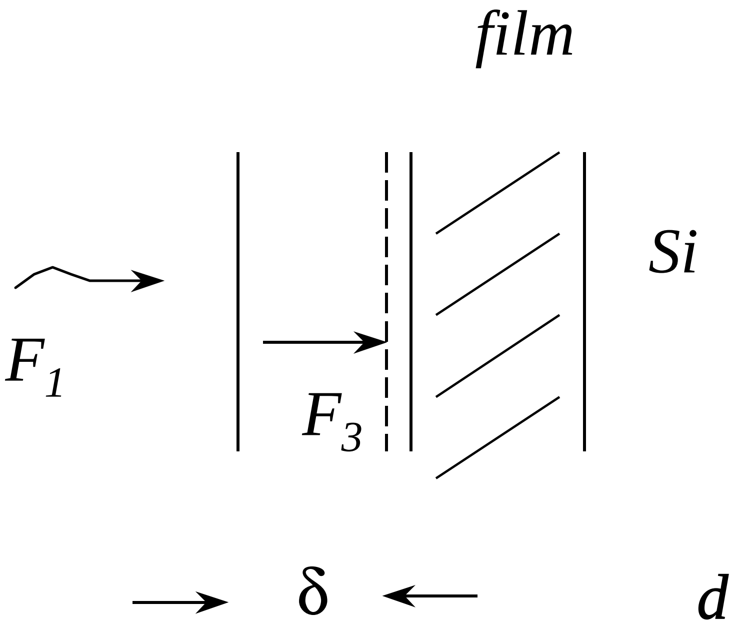
In the CVD growth rate model, it was assumed that mass transport across stagnant layer proceeds by diffusion,

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

For mass-transfer limited deposition, model ⇒

$$\frac{dy}{dt} \propto h_G \propto \frac{1}{\bar{\delta}} \propto \sqrt{U}$$

CVD Deposition Rate [Grove Model]



$$\frac{D}{d} = h_G$$

$$k_s = k_o e^{-\Delta E/kT}$$

d = thickness of stagnant layer

$$F_1 = D\,[\,C_G - C_S]\,/\,\delta$$

$$F_3 = k_S\,C_S$$

$$F_1 = F_3$$

$$\therefore \boldsymbol{F}_3 = \frac{\boldsymbol{k_s h_G}}{\boldsymbol{k_s + h_G}} \cdot \boldsymbol{C_G}$$

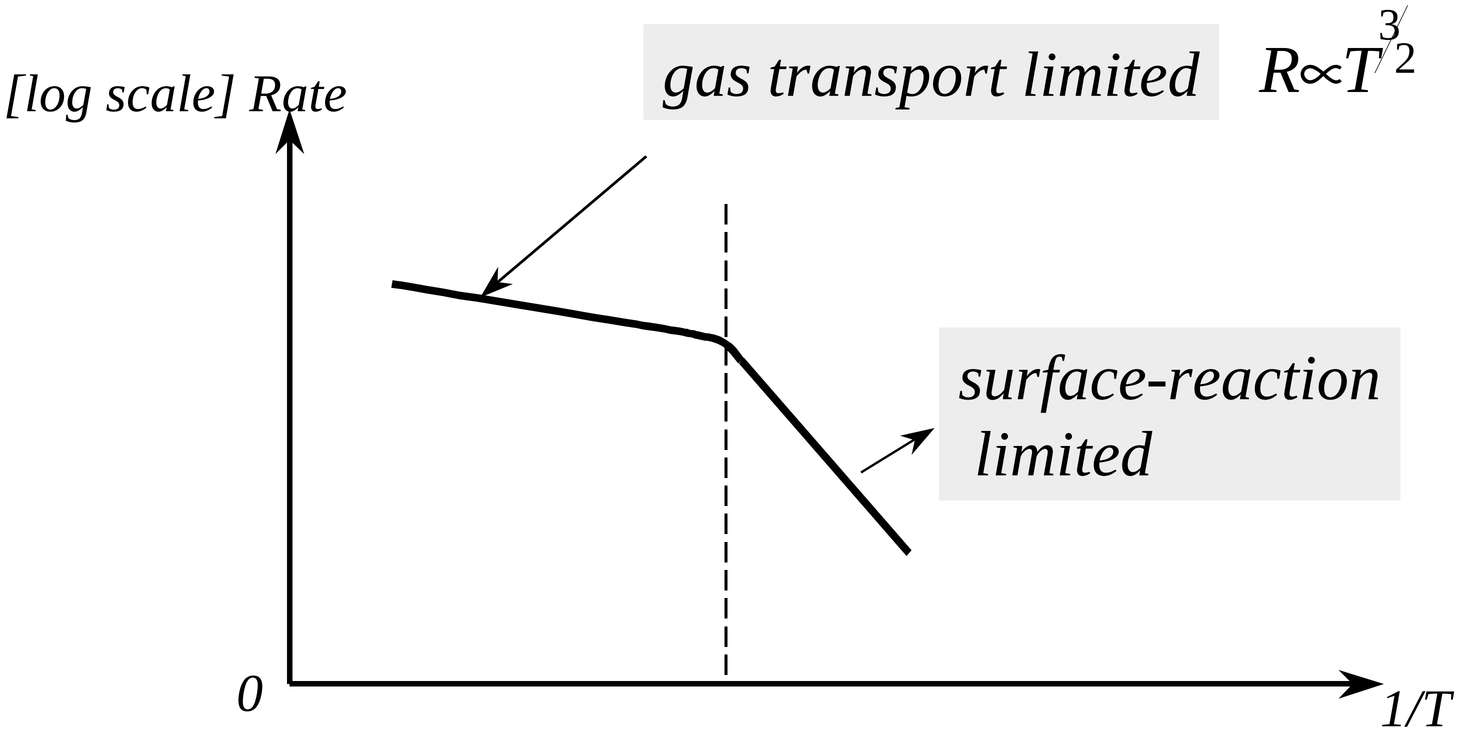
Film growth rate = $\mathbf{F_3}$ / N

N = atomic density of deposited film

$$\therefore \frac{dx}{dt} = \frac{F_3}{N} = contant\ with\ time$$

$$\left(cm/\text{sec}\right)$$

Deposition Rate



gas transport limited $R \propto T^{3/2}$

surface-reaction limited

high T ⟵ ⟶ *low T*

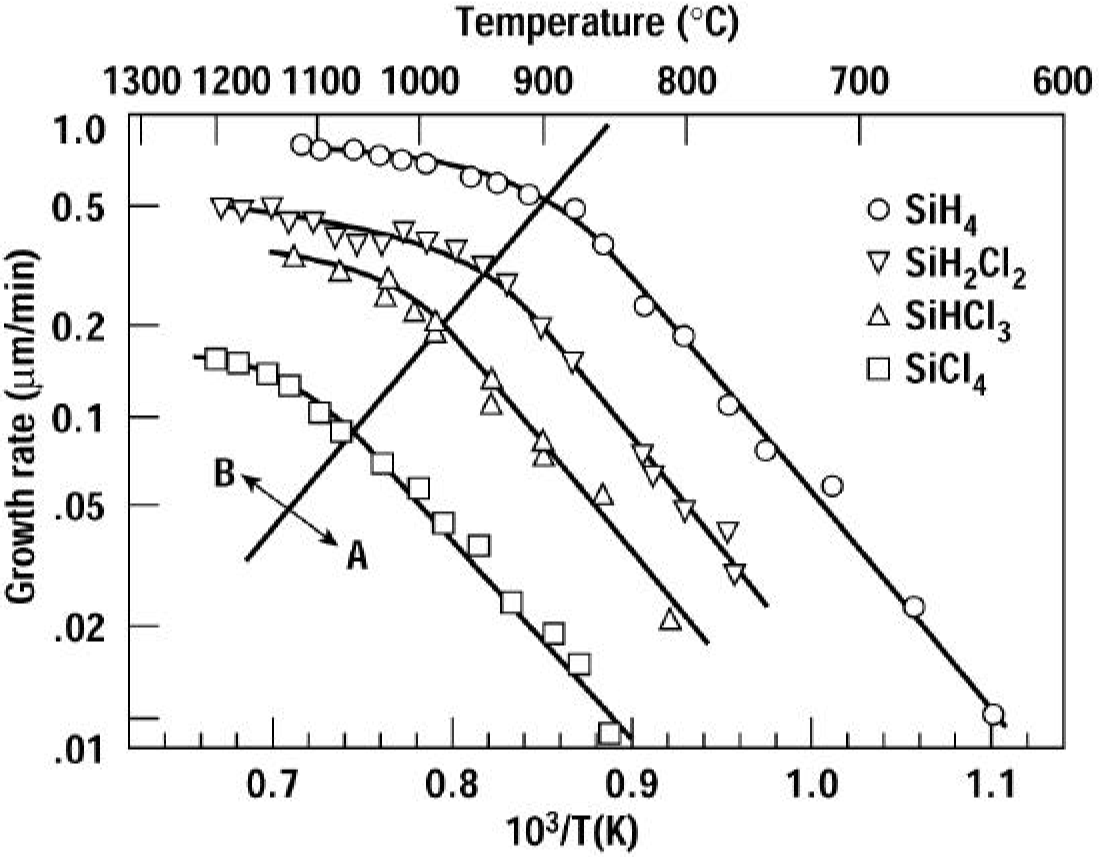
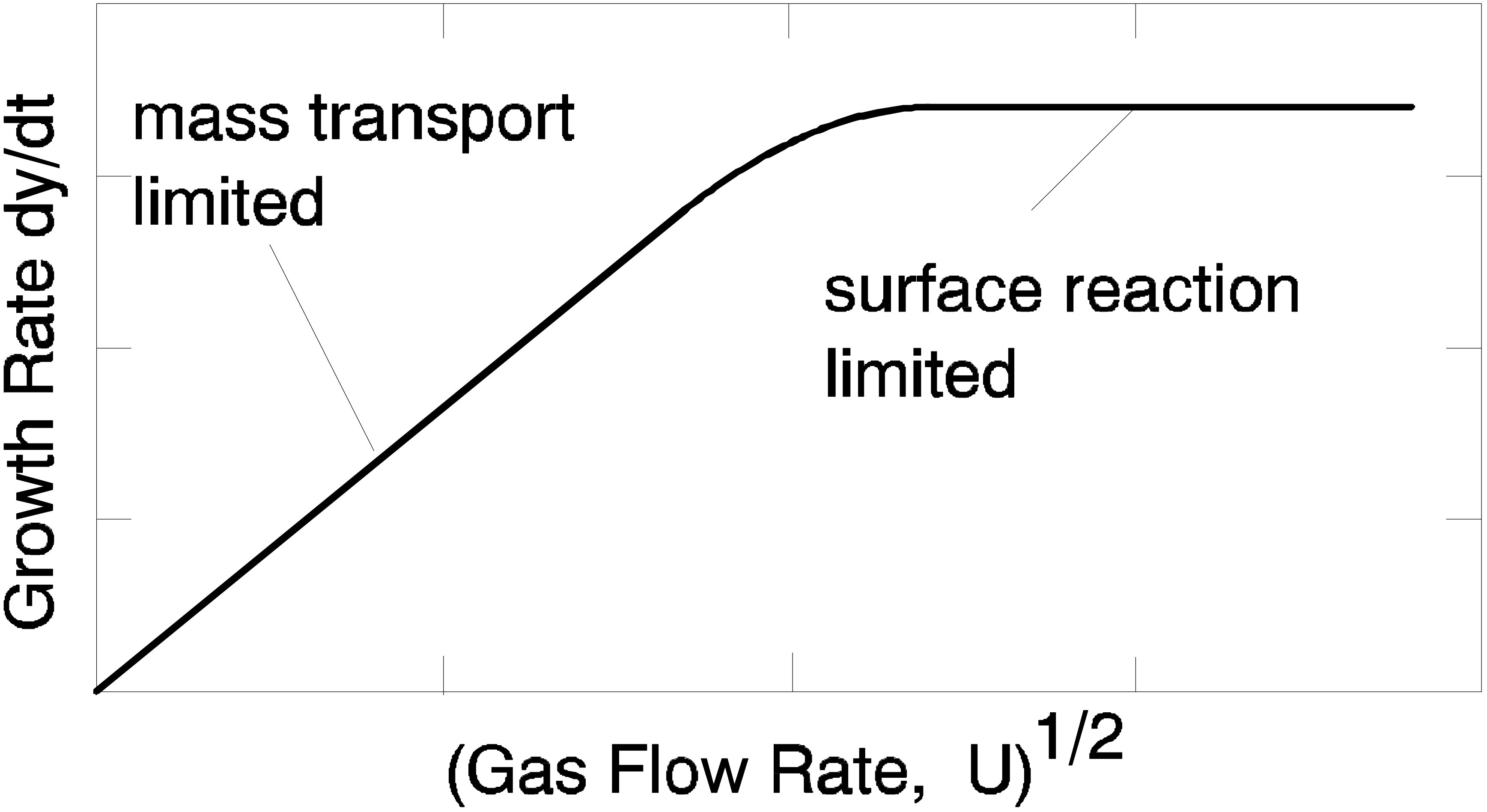


Figure 14.8 Arrhenius behavior of a variety of silicon-containing growth species *(after Eversteyn, reprinted by permission, Philips).*

Growth Rate Dependence on Flow Velocity



With Low Pressure and high gas velocity due to pumping $h_G \uparrow$

P~1 Torr

$$D \propto \frac{1}{P} \; From \; 760\, Torr \rightarrow 1\, Torr \quad D \uparrow 1000\text{X}$$

$$d \propto \sqrt{\frac{m}{\rho v L}} \propto \sqrt{\frac{1000}{100}} \approx 3$$

velocity of gas flow 100X

Gas density $\rho \propto P$

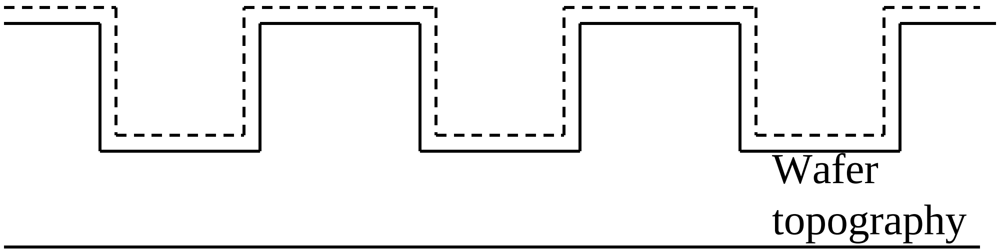
$$\underset{\substack{||\\ D/d}}{h_G} \rightarrow \frac{1000}{3} \rightarrow 300\text{X}$$

Therefore, more likely to be surface reaction limited

LPCVD Features

(1) **R ↑, since h_G ↑**

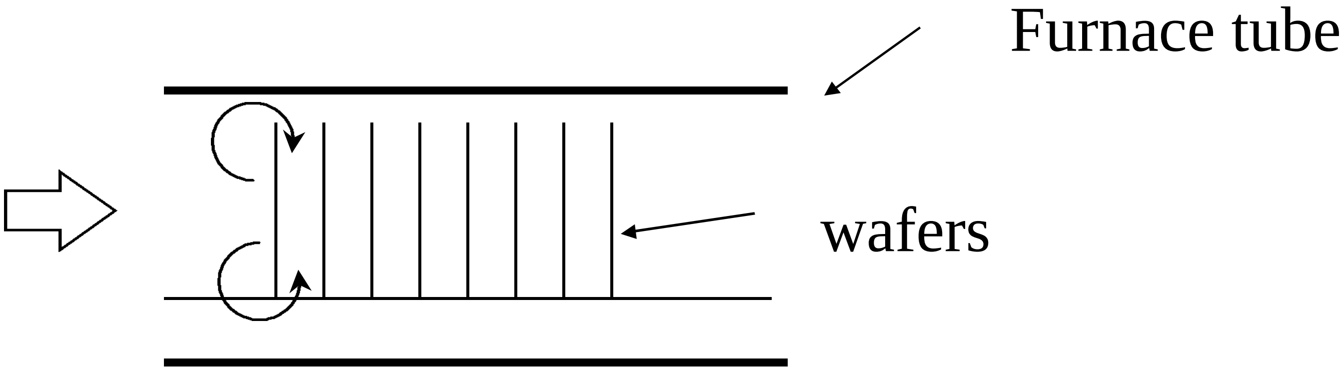
(2) **More conformal deposition**, if T is uniform



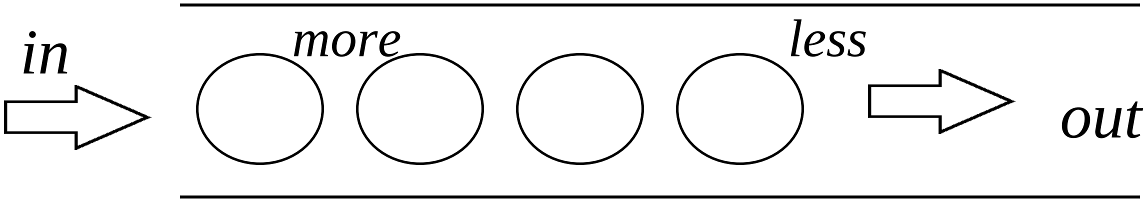
(3) Inter-wafer and intra-wafer thickness uniformity less sensitive to gas flow patterns. (i.e. wafer placement).

Comments

(1) d depends on gas flow pattern



(2) **Mass depletion problem**



Solutions

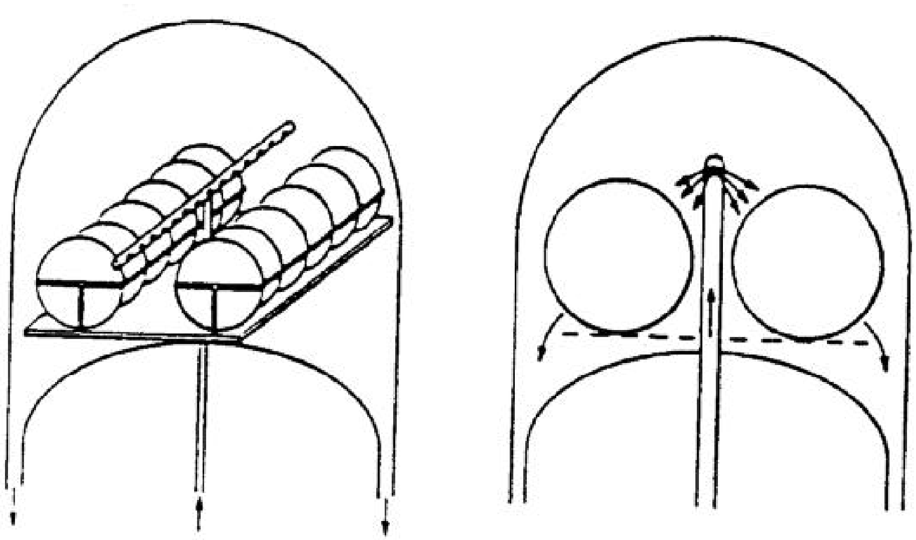
(1) Temperature Ramping along reactor length

For reaction - limited regime :

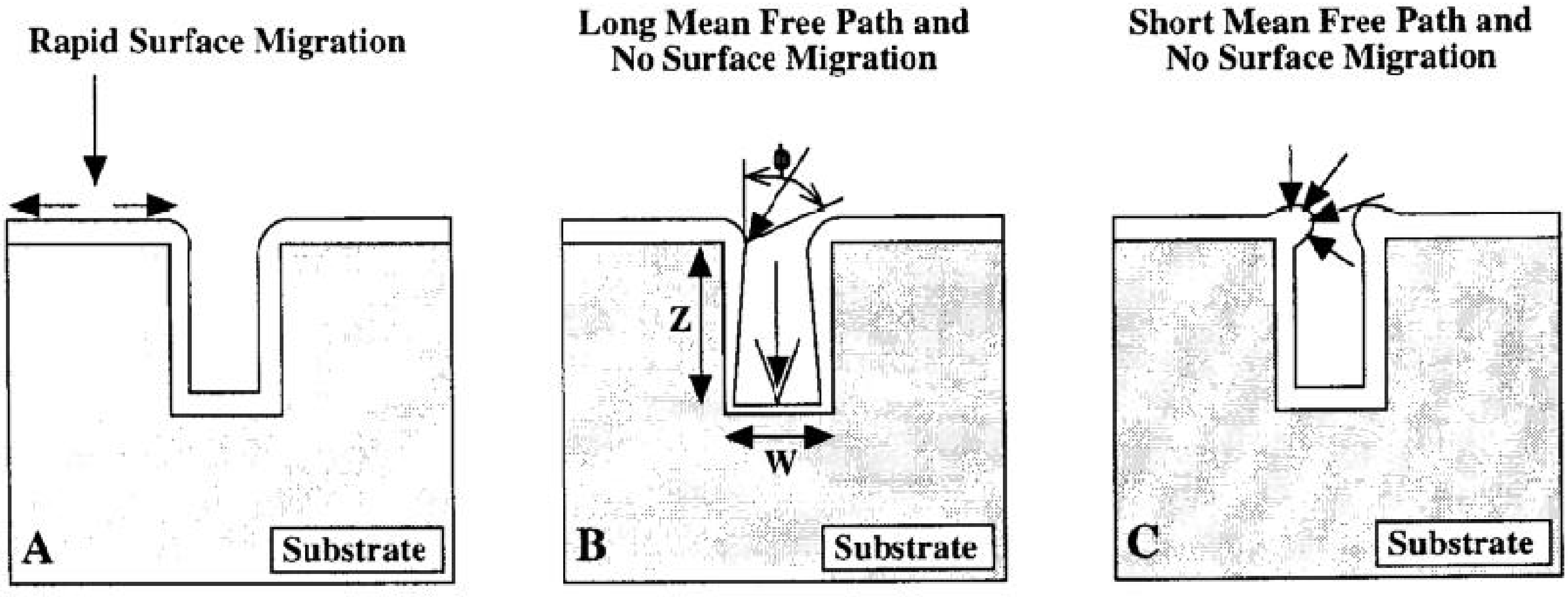
$R(x) = A \exp[-\Delta E/kT] \times C(x)$ [where $C(x) =$ SiH_4 Conc.]

∴***Creating a temperature gradient of 20 - 40 °C along the tube*** will give better uniformity

(2) **Distributed Feed Reactors**



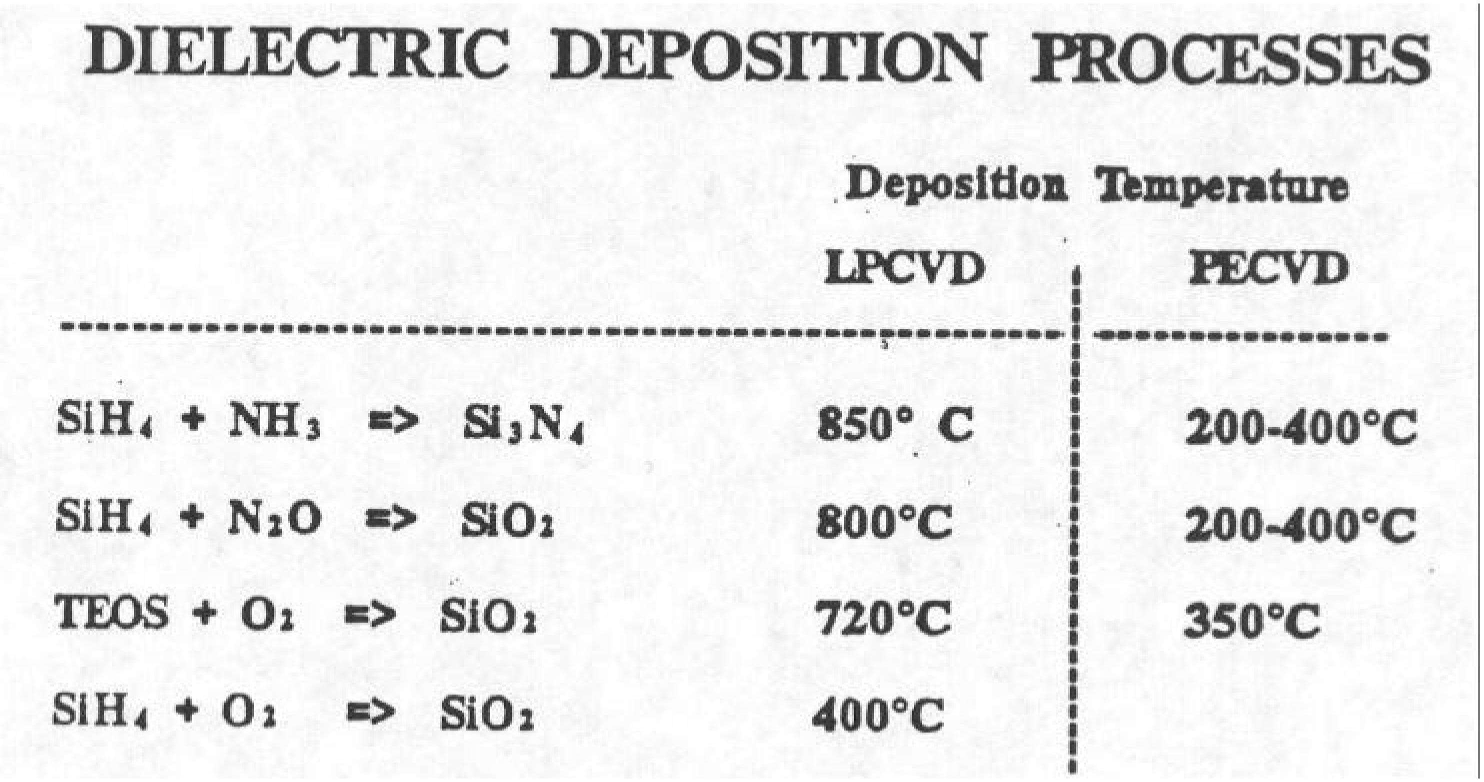
Effect of Surface Diffusion and Gas Mean Free Path on Deposition morphology



Plasma Enhanced CVD

*Ionized chemical species allows a lower process temperature to be used

- Film properties (e.g. mechanical stress) can be tailored by controllable ion bombardment with substrate bias voltage



DIELECTRIC DEPOSITION PROCESSES

	Deposition Temperature	
	LPCVD	PECVD
$SiH_4 + NH_3 \Rightarrow Si_3N_4$	850° C	200-400°C
$SiH_4 + N_2O \Rightarrow SiO_2$	800°C	200-400°C
$TEOS + O_2 \Rightarrow SiO_2$	720°C	350°C
$SiH_4 + O_2 \Rightarrow SiO_2$	400°C	