Course name: Growth and Characterization of Nanoelectronic Materials (EE728)

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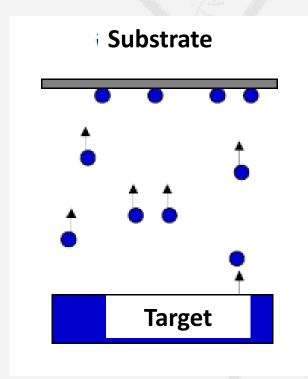


Outline

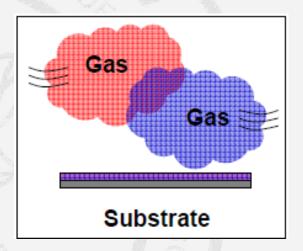
- > Introduction
- > Thin film growth
- Chemical Vapor Deposition: Design, Fundamental and Application
- > Epitaxy: Physics and application

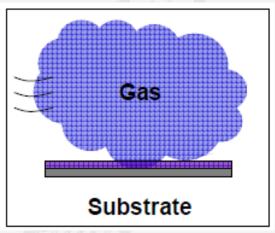
Introduction: Thin films deposition

Physical Vapor Deposition (PVD)



Chemical Vapor Deposition (CVD)





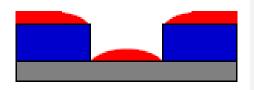
Chemical Vapor Deposition

- ➤ CVD is the formation of a solid film on a substrate, by the chemical reaction of vapors (precursors). The reaction parameters are controlled such that the reaction only occurs at the surface of the substrate, and not in the gas phase.
- External energy is required to supply the required activation energy for the CVD reaction, in the form of elevated temperature, or plasma excitation.
- > Therefore the substrate as well as reactant temperature play a role in the rate of reaction
- The process can produce amorphous, polycrystalline, or single crystal films (epitaxy).

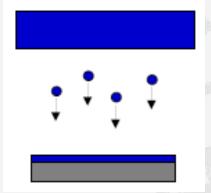
PVD vs. CVD

Physical Vapor Deposition (PVD)

Non-conformal deposition

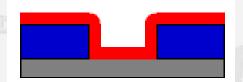


> Highly directional deposition

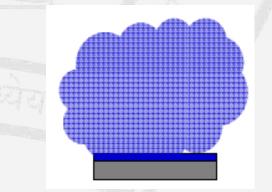


Chemical Vapor Deposition (CVD)

Conformal deposition the coating bends as the surface



> Multidirectional deposition



Advantages of CVD

- > Uniform distribution over large areas
- > No compositional gradients across substrate
- > No need to break vacuum for source changes
- > More selective area deposition because of higher activation energy for reaction with foreign substances.

Disadvantages of CVD

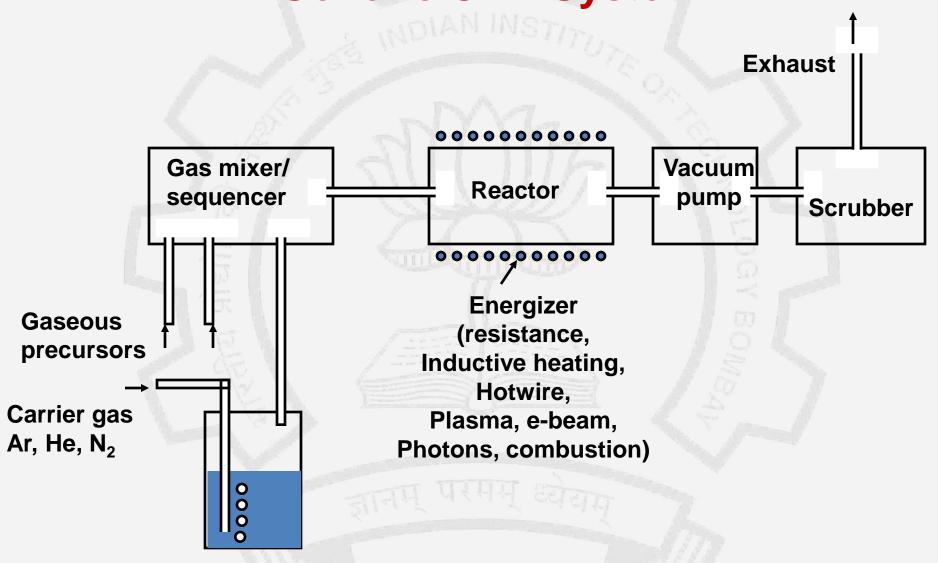
- > Mostly involve safety and contamination
- > Hydrides and carbonyls are poisonous (especially arsine)
- > Metalorganics are pyrophoric (ignite in contact with air)
- > High cost for compounds with sufficient purity

What is CVD used for?

- > Typically used to deposit dielectrics
 - \circ SiO₂, Si₃N₄, SiO_xN_y
- > Other materials can also be deposited via CVD
 - Most common are W and TiN for semiconductors
 - o Al, B, C, Co, Fe, Mo, Ni, Nb, Ta

CVD is the single most widely used deposition method in IC manufacture

A Generic CVD System



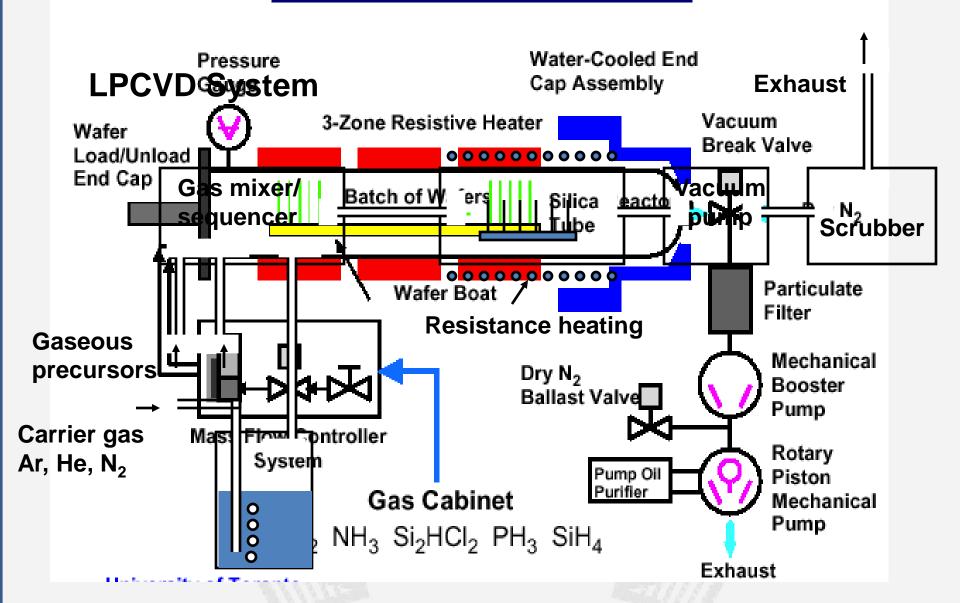
CVD: Classification

Classified by operating conditions:

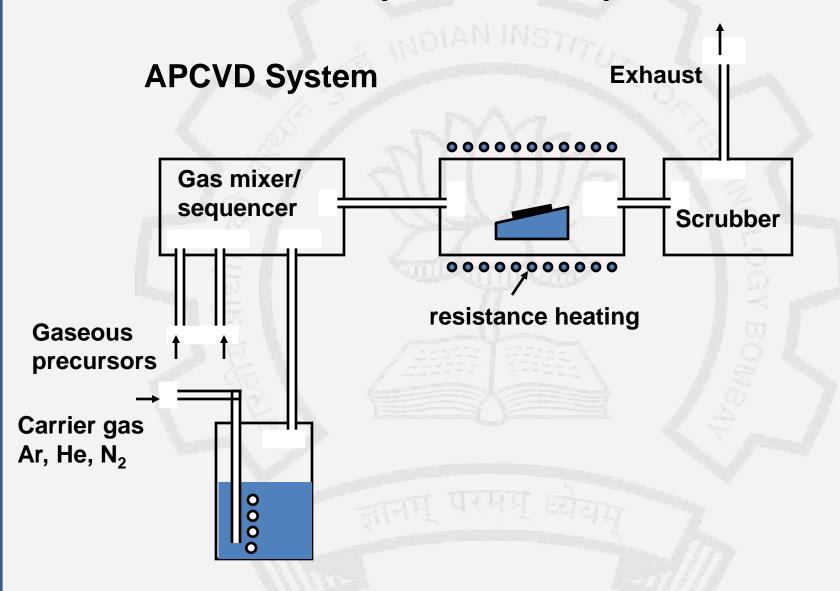
- > Atmospheric pressure CVD (APCVD) CVD at atmospheric pressure.
- Low-pressure CVD (LPCVD) CVD at sub-atmospheric pressures.
 Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
- \triangleright Ultrahigh vacuum CVD (UHVCVD) − CVD at very low pressure, typically below 10^{-6} Pa ($\approx 10^{-8}$ torr). Note that in other fields, a lower division between high and ultra-high vacuum is common, often 10^{-7} Pa.

Most modern CVD is either LPCVD or UHVCVD.

Horizontal LPCVD Reactor

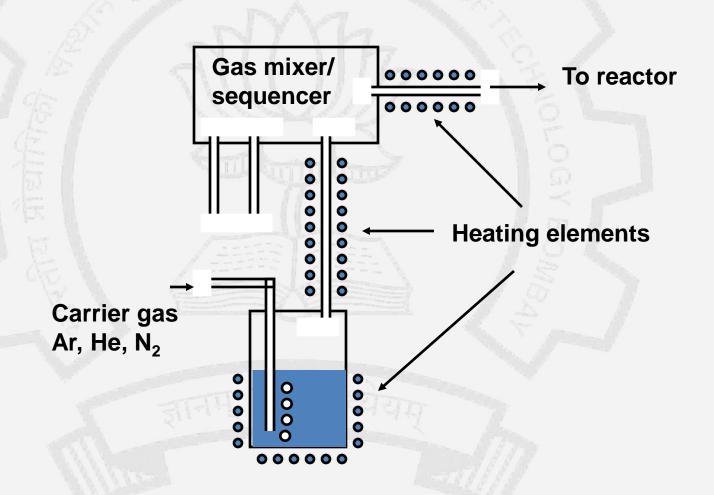


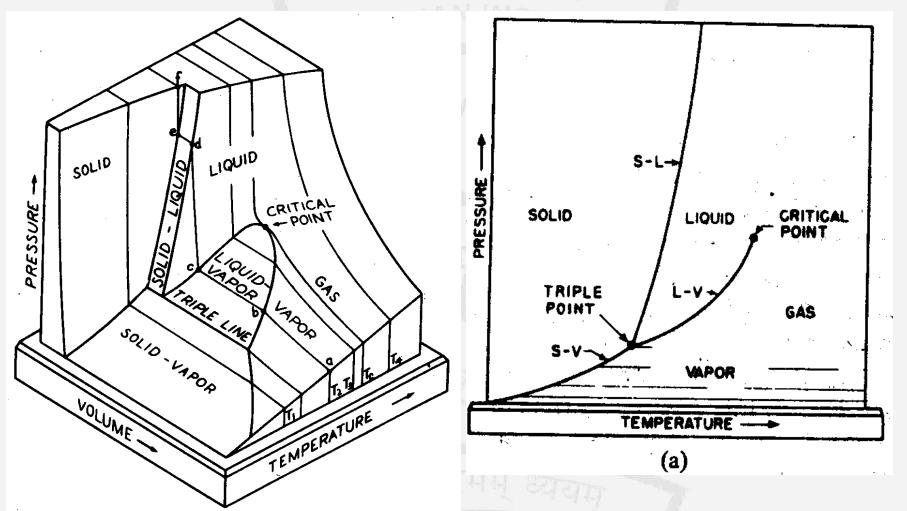
CVD System: Example



- Has to be vaporized and transported to the reaction chamber
- Two designs
 - Vaporizer with carrier gas
 - Flash vaporizer

Vaporizer with carrier gas (bubbler)

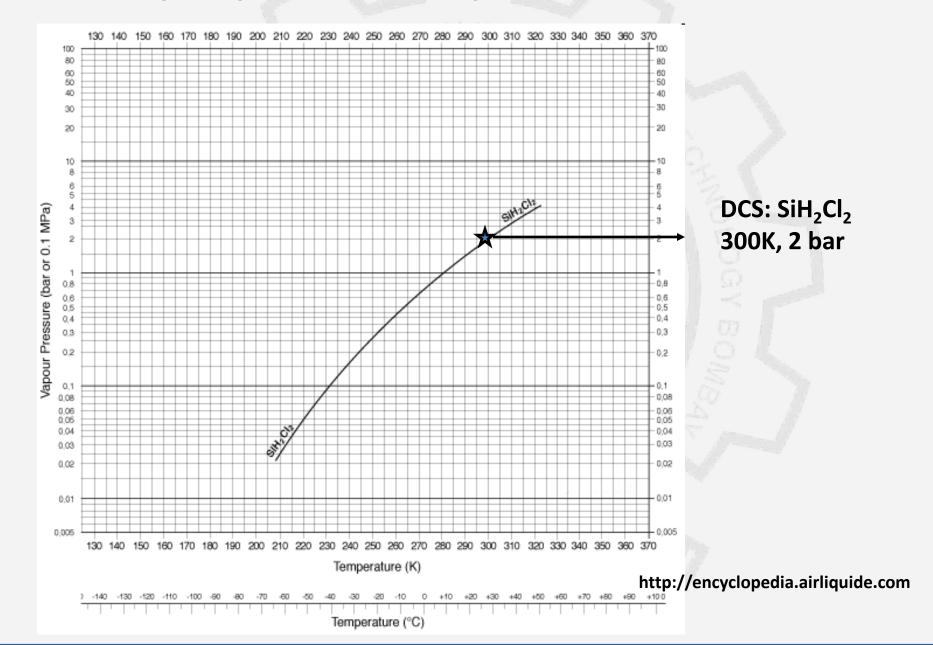




P-T diagram is unique for each liquid-vapor system

Example: Sears and Salinger, "Thermodynamics, Kinetic Theory and Statistical Thermodynamics

Liquid precursor: Vapor Pressure



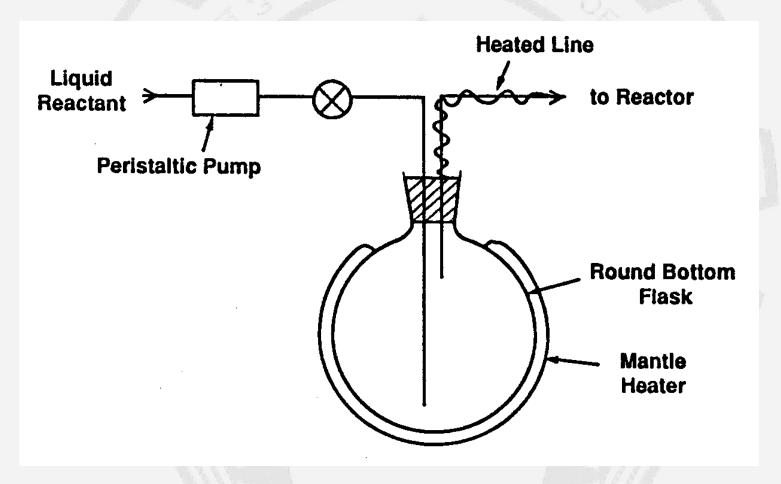
- Vaporizer with carrier gas (bubbler)
 - In the presence of a carrier gas, the vapor pressure could change

$$\ln\frac{p}{p_0} = \frac{v}{RT}(P - p_0)$$

 p is the vapor pressure of the vapor in the bubbler, p₀ is the vapor pressure when there is no carrier gas, P is the total pressure, T is the temperature, v is the specific volume of the liquid at T, R is the ideal gas constant

Example: Sears and Salinger, "Thermodynamics, Kinetic Theory and Statistical Thermodynamics

Flash Vaporizer



Hugh O. Pierson, "Handbook of chemical vapor deposition (CVD)"

CVD System: Solid Source, Vapor pressure

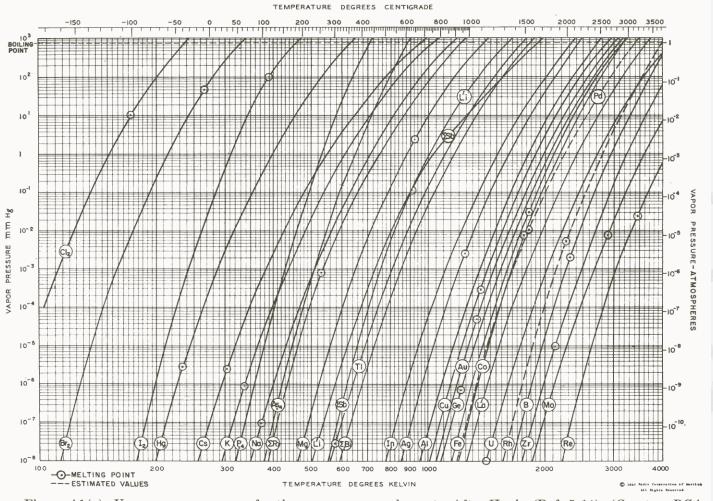


Figure A1(a). Vapor pressure curves for the more common elements. After Honig (Ref. 5:14). (Courtesy RCA

Vapor pressure or equilibrium vapor pressure: The pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases at a given temperature in a closed system.

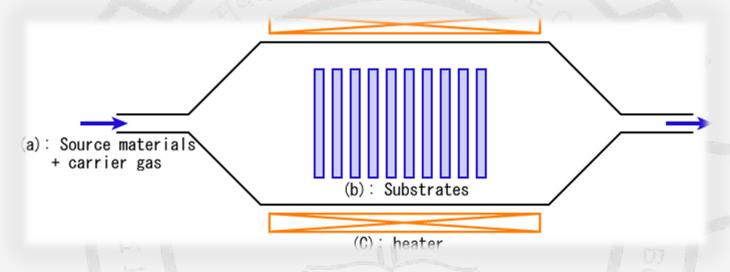
CVD System: Solid Source

- Solids that are easily evaporated may be used in an arrangement similar to the flash vaporizer with an optional carrier gas
- Some solid sources are difficult to vaporize
 - Example: W, vapor pressure at 2000 C is 7 x 10⁻⁹ Torr* (5.2 x 10⁻³ mbar)
 - In such cases, react them with an appropriate gas to give a gaseous product, which is then carried to the reactor
 - Example: $W + 3Cl_2 \rightarrow WCl_6$ (800C)

Langmuir,"The vapor pressure of metallic Tungsten", Physical Review, November 1913

Thermal CVD Reactor Designs

Horizontal, hot wall reactors

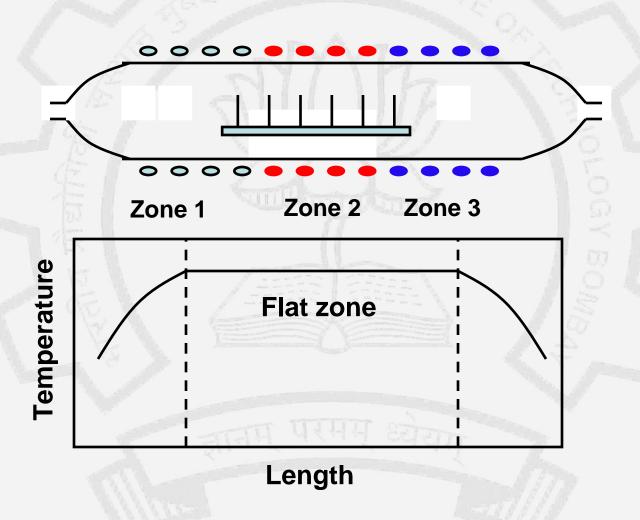


LPCVD, RPCVD

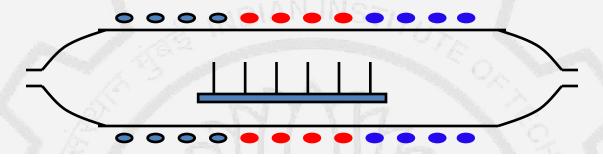
Dielectrics, poly-Si, a-Si

- Excellent temperature profiles
- Deposition on the walls of the reaction chamber, flaking,
- Contamination from the reaction chamber

Horizontal Furnaces



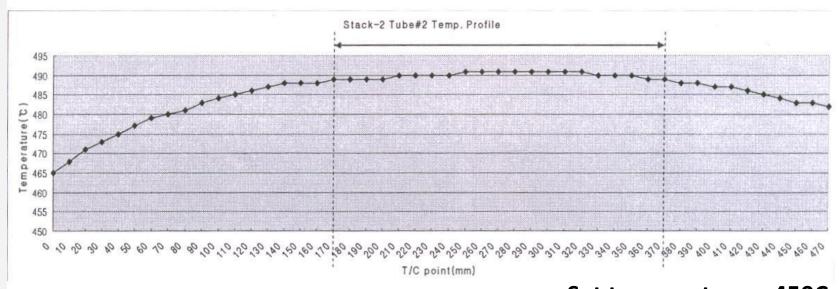
Horizontal Furnaces (2)



Zone 1

Zone 2

Zone 3

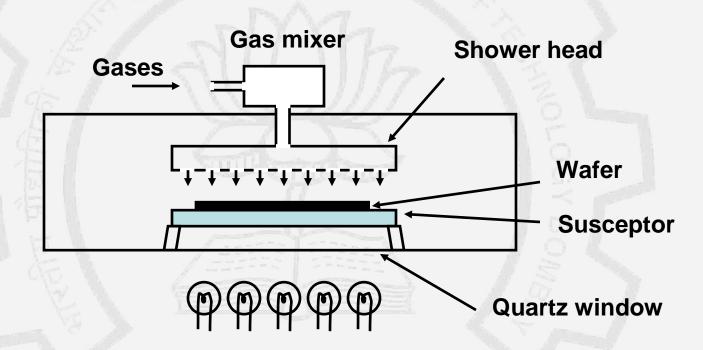


Set temperature = 450C

Suresh Ch., CEN

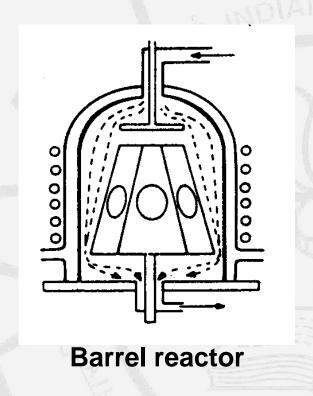
Thermal CVD Reactor Designs (2)

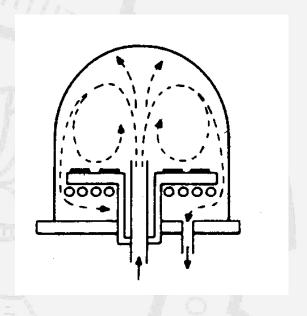
Single wafer, cold wall RT - CVD reactor



- Typical of 300mm CVD reactors
- For non-RTCVD, the heating may be using induction or resistive heating
- No deposition on the chamber walls, less particle contamination concerns

Thermal CVD Reactor Designs (3)





Pancake reactor

EPI, poly-Si

S. Sivaram, "Chemical Vapor Deposition", Van Nostrand Reinhold, 1995

Turbulence in Thermal CVD Reactors

Turbulence

- Leads to nonuniform film growth
- Gas phase reactions
- Laminar flow (smooth layer by layer flow) is desired
- Flow regime determined by Reynolds number

$$R_e = \frac{\rho u d}{\mu}$$

 ρ : Volume density of the gas in kg/m³

u: Mean fluid velocity in m/sec

d: Tube diameter in m

 μ : Viscosity in Pa. sec

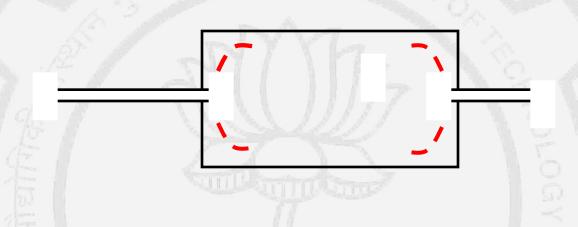
Turbulence in Thermal CVD Reactors (2)

When the Reynolds number > 2000: turbulent flow

When the Reynolds number < 1000: laminar flow

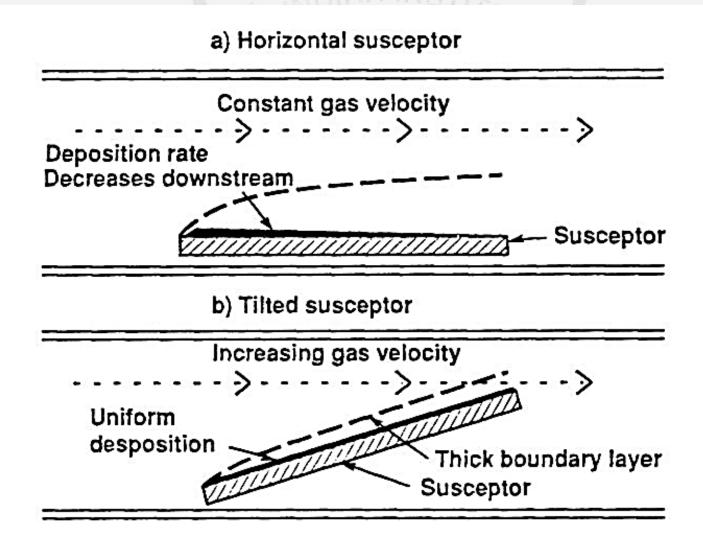
$$R_e = \frac{\rho u d}{\mu}$$

Dead Zones in Thermal CVD Reactors

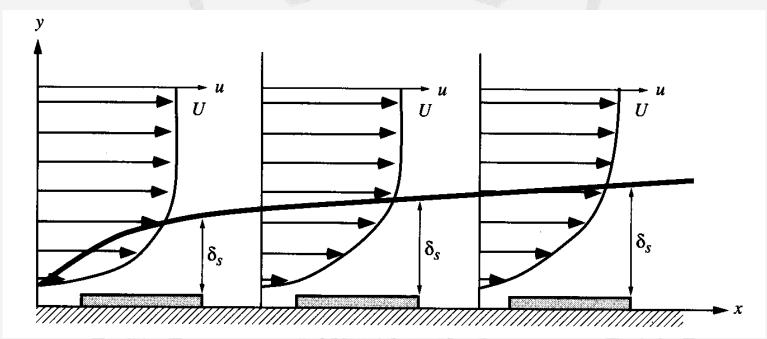


- The wafers should not be placed in dead zones
 - since there is no flow in deadzones, controlled depositions are not feasible
- Creates particulate problems

Boundary Layer in Thermal CVD Reactors



Boundary Layer in Thermal CVD Reactors



$$\delta_{S}(x) = \left(\frac{\mu x}{\rho U}\right)^{1/2}$$

Where all the parameters are as defined on slide 25. U is the velocity of the gas in the main flow above the boundary layer.

Plummer et al., "Silicon VLSI Technology", Prentice Hall, 2000

 μ = viscosity ρ = volume density

Boundary Layer in Thermal CVD Reactors

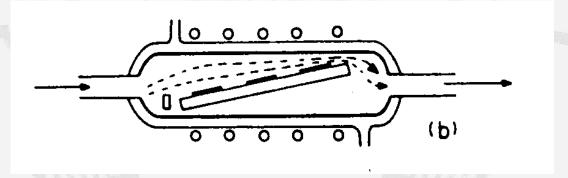
- The boundary layer plays an important role in determining the layer growth kinetics
- In laminar flow regime, the reactants are transported from the main flow by diffusion to the wafer surface through the boundary layer
- Reaction byproducts are transported from the wafer surface to the flow through the boundary layer
- ➤ Thicker the boundary layer, longer it takes for the reactants to diffuse to the wafer surface → lower reactant flux arriving on the wafer surface → slower film growth rate if the growth is limited by availability of reactants

Boundary Layer in Thermal CVD Reactors (3)

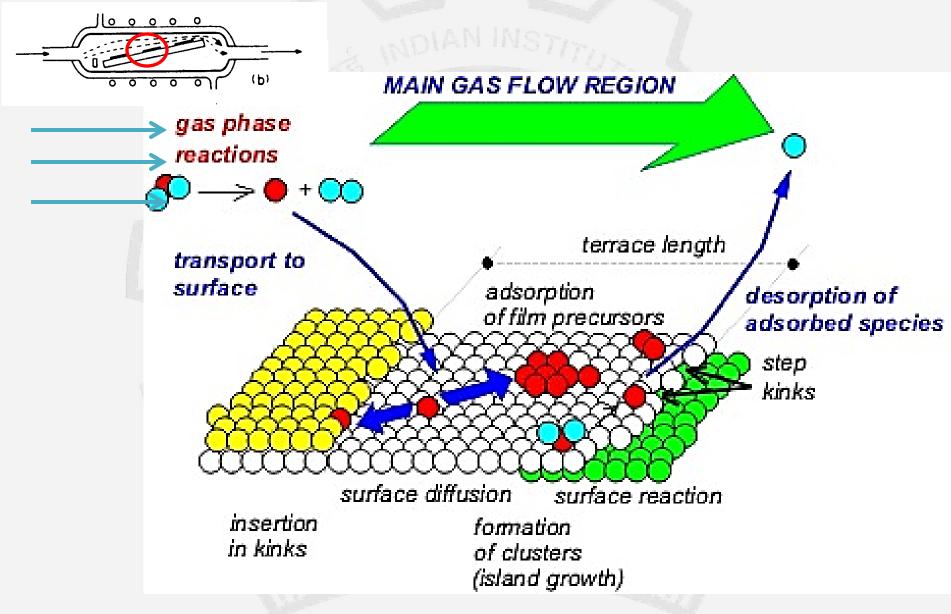
 Qualitatively it is possible to maintain a constant boundary layer by increasing the velocity along the furnace tube

$$\delta_{S}(x) = \left(\frac{\mu x}{\rho U}\right)^{1/2}$$

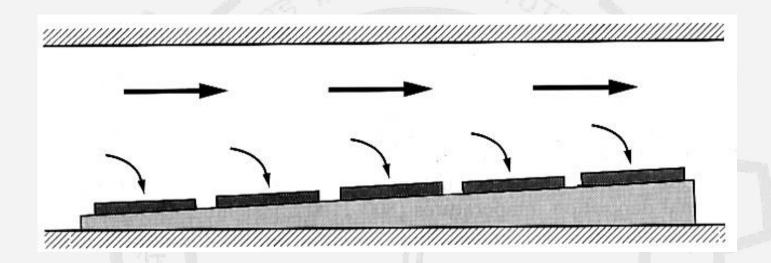
 The velocity can be increased as a function of x by using a tilted susceptor



Deposition Process

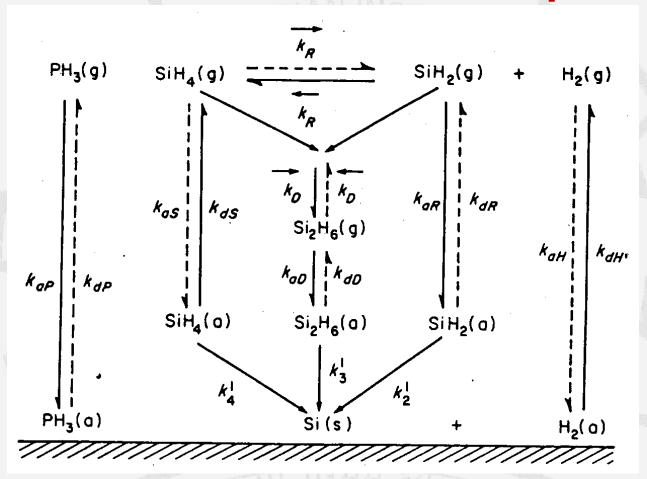


Tilted CVD susceptor



The susceptor in a horizontal epitaxial reactor is tilted so that the cross-sectional area of the chamber is decreased, increasing the gas velocity along the susceptor. This compensates for both the boundary layer and depletion effects.

Deposition Process: Reaction pathways



Si deposition by thermal decomposition (pyrolysis) of SiH₄

Hitchman and Jensen, Chapter 1 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993

Deposition Process: Reaction pathways

□ Pyrolysis of SiH₄ is one of the best understood CVD process:

27 contributing reactions out of the 120 possible elementary reactions

- **→** Complex to analyze
 - Gas phase chemical reactions
 - Adsorption rates
 - Surface reactions
 - Desorption rates

An easier approach for the study of deposition rates is to consider the overall reaction as one of the rate limiting steps. Such an analysis has its own limitations

Hitchman and Jensen, Chapter 1 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993