CHAPTER 7

Chemical Vapor Deposition

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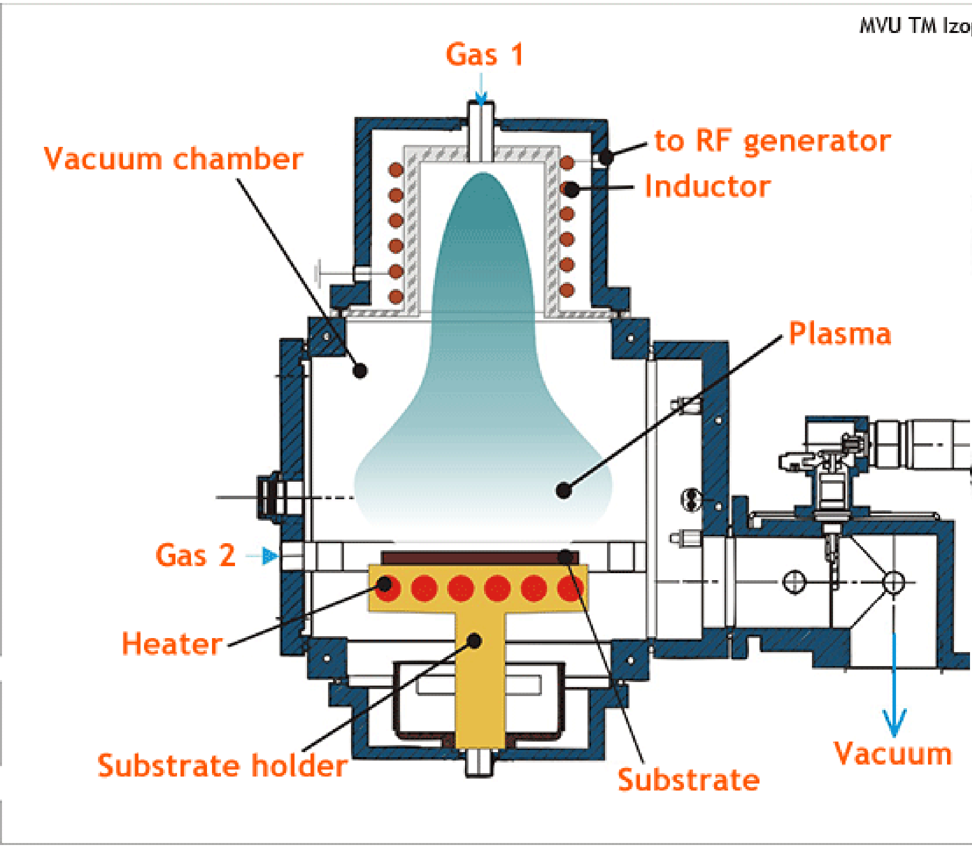
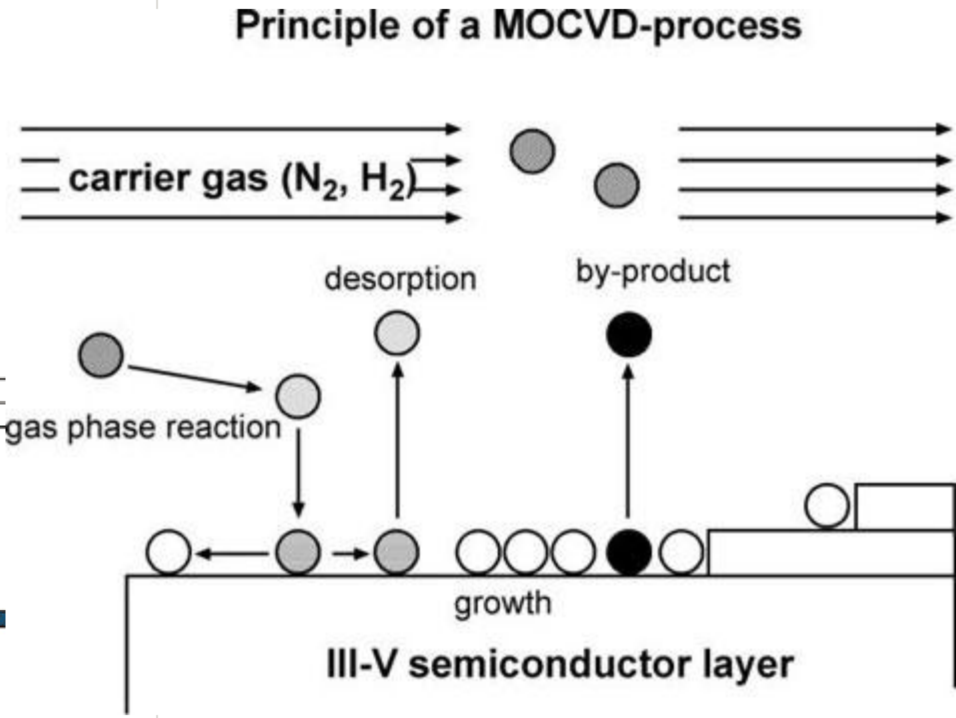
Introduction

- Solid material is deposited from a vapor by chemical reaction occurring on or in the vicinity of substrate
- Uniform thickness and Low porosity because of excellent throwing power
- A variety of films can be grown by

  substrate material, substrate temperature, composition of the reaction gas mixture, total pressure gas flow



MVU TM Izophase CVD ICP



Applied in

Dielectrics

Conductors

Passivation layers

Oxidation barriers

Conductive oxides

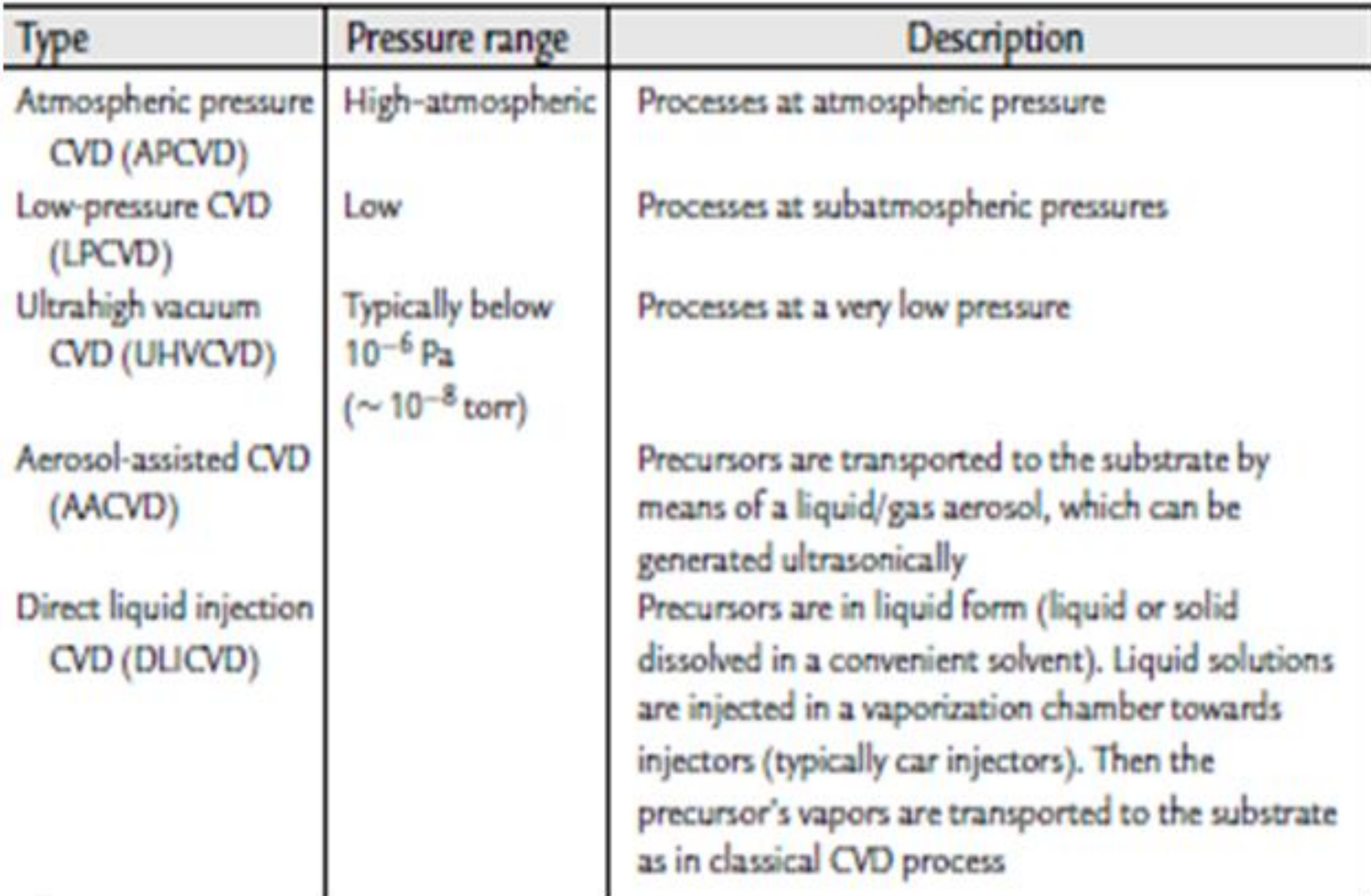
Corrosion-resistant coatings

Heat-resistant coatings

Preparation of high temp. materials

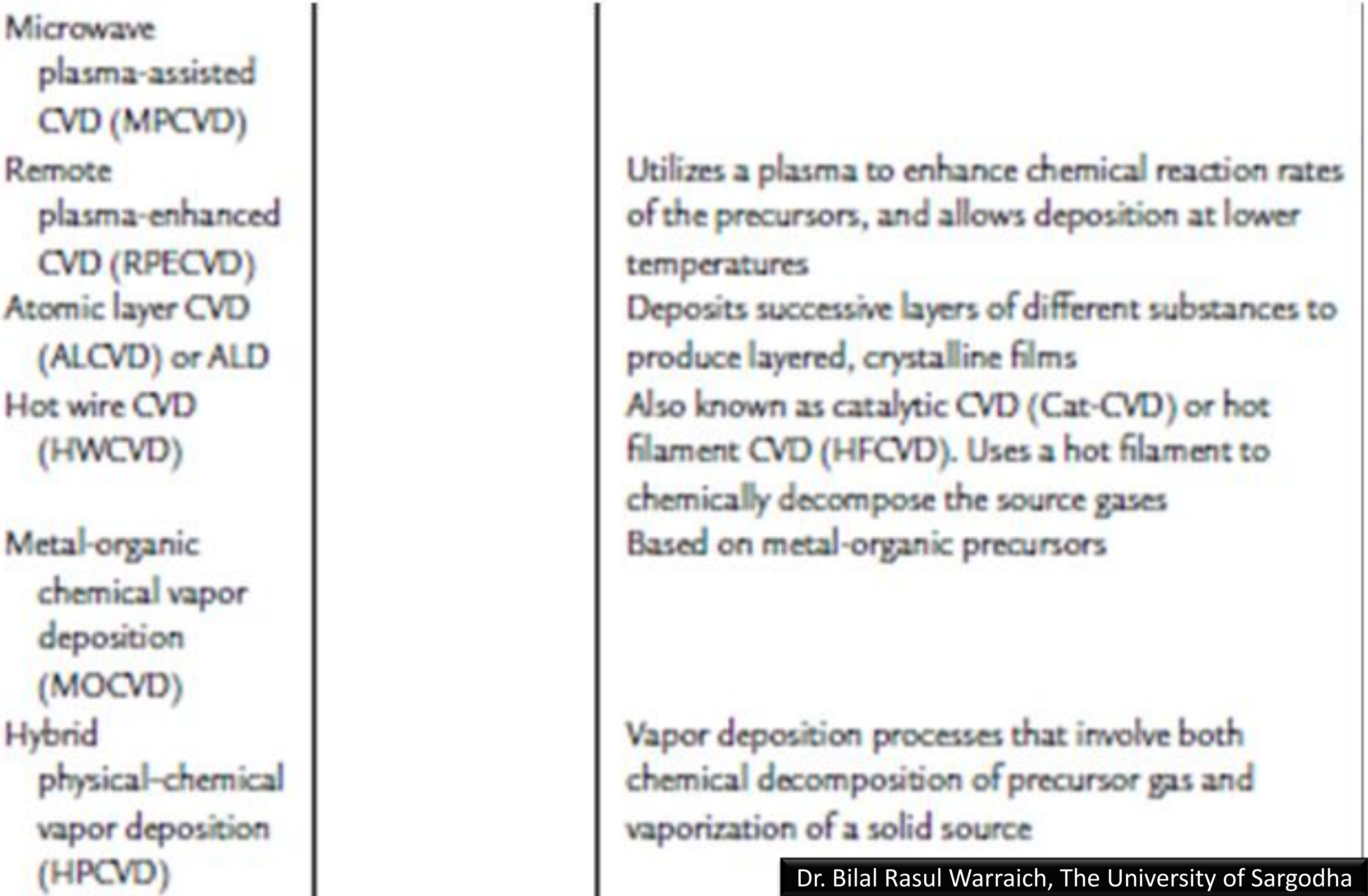
Solar cells

Summary of CVD process family



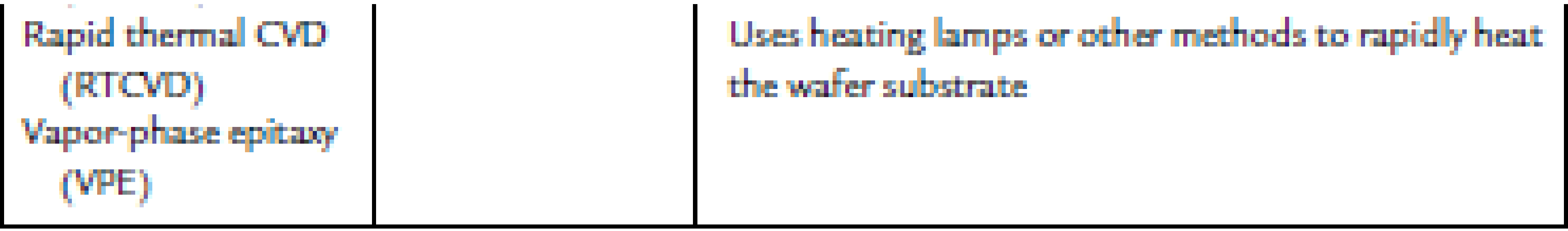
Type	Pressure range	Description
Atmospheric pressure CVD (APCVD)	High-atmospheric	Processes at atmospheric pressure
Low-pressure CVD (LPCVD)	Low	Processes at subatmospheric pressures
Ultrahigh vacuum CVD (UHVCVD)	Typically below 10^{-6} Pa ($\sim 10^{-8}$ torr)	Processes at a very low pressure
Aerosol-assisted CVD (AACVD)		Precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically
Direct liquid injection CVD (DLICVD)		Precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursor's vapors are transported to the substrate as in classical CVD process

Summary of CVD process family



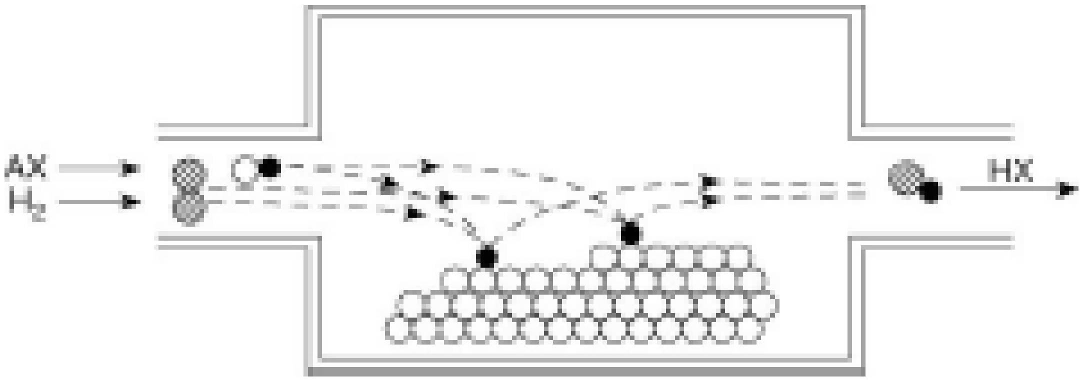
Microwave plasma-assisted CVD (MPCVD)		
Remote plasma-enhanced CVD (RPECVD)		Utilizes a plasma to enhance chemical reaction rates of the precursors, and allows deposition at lower temperatures
Atomic layer CVD (ALCVD) or ALD		Deposits successive layers of different substances to produce layered, crystalline films
Hot wire CVD (HWCVD)		Also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). Uses a hot filament to chemically decompose the source gases
Metal-organic chemical vapor deposition (MOCVD)		Based on metal-organic precursors
Hybrid physical-chemical vapor deposition (HPCVD)		Vapor deposition processes that involve both chemical decomposition of precursor gas and vaporization of a solid source

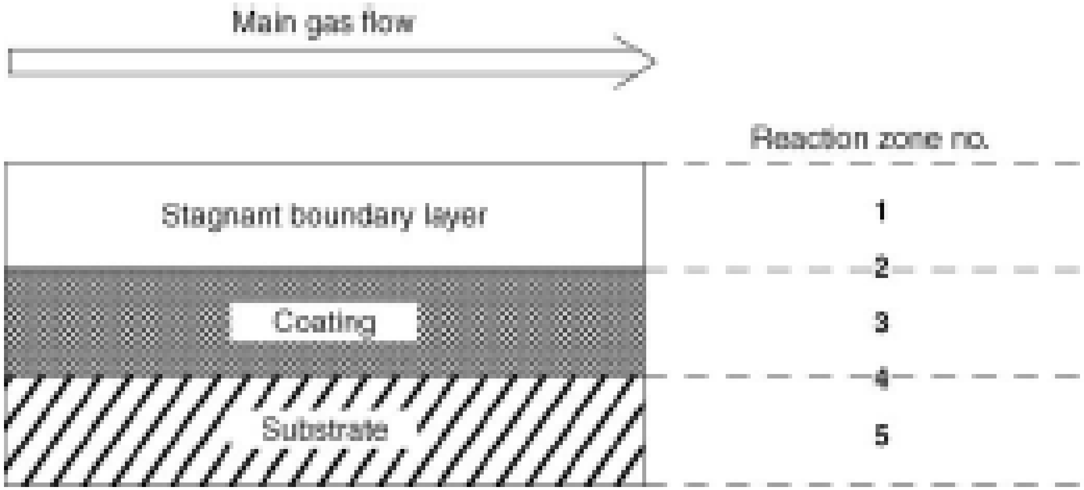
Summary of CVD process family



Rapid thermal CVD (RTCVD)		Uses heating lamps or other methods to rapidly heat the wafer substrate
Vapor-phase epitaxy (VPE)		

Important Reaction Zones





- In Zone 1 and main gas stream, homogeneous reactions may occur in vapor resulting nucleation i.e. non-adherent coating
- Zone 2: reactions determine deposition rate and properties of coating
- Zone 4: diffusion zone defines adhesion of coating

Design of CVD Experiments

- Classification
  - Thermal Decomposition Reactions
    - $AX(g) \longrightarrow A(s) + X(g)$
    - $SiH_4(g) \longrightarrow Si(s) + 2H_2(g)$
    - $B_2H_6(g) \longrightarrow B(s) + 3H_2(g)$ etc.
    - Carburizing and Nitriding
    - $CH_4(g) \longrightarrow C(s) + 2H_2(g)$
  - Reduction Reactions
    - $2AX(g) + H_2(g) \longrightarrow 2A(s) + 2HX(g)$
    - $WF_6(g) + 3H_2(g) \longrightarrow W(s) + 6HF(g)$
    - $SiCl4(g) + 2H2(g) \longrightarrow Si(s) + 4HCl(g)$

Design of CVD Experiments

- Classification
  - Exchange Reactions
    - $AX(g) + E(g) \longrightarrow AE(s) + X(g)$
    - $SiCl_4(g) + CH_4(g) \longrightarrow SiC(s) + 4HCl(g)$
  - Disproportionation Reactions
    - $2AX(g) \longrightarrow A(s) + AX_2(g)$
    - $3AX(g) \longrightarrow 2A(s) + AX_3(g)$
    - $4AX(g) \longrightarrow 3A(s) + AX_4(g)$
    - $2GeI_2(g) \longrightarrow Ge(s) + GeI_4$
  - Coupled Reactions
    - $2AlCl_3(g) + 3CO_2(g) + 3H_2(g) \longrightarrow Al_2O_3(s) + 3CO(g) + 6HCl(g)$
    - $CO_2(g) + H_2 (g) \longrightarrow CO(g) + H_2O (g)$
    - $AlCl_3+3H_2O(g) \longrightarrow Al_2O_3(s) + 6HCl (g)$

The CVD System

- Factors that determine choice of a CVD system
  - Reactants used in the process
  - Maximum acceptable leak rate
  - Purity of the deposit
  - Size and shape of the substrate
  - Temperature (in reactor/on substrate)

The CVD System

1. Gas Dispensing System

- Gases from gas bottles and flow meters
- Liquids and solids by
    1. Boiled or sublimated in separate system
    2. Carrier gas picks up the liquid material and transports it to the reactor
    3. In-situ preparation

  $AlCl_3$ by Al sponge and HCl

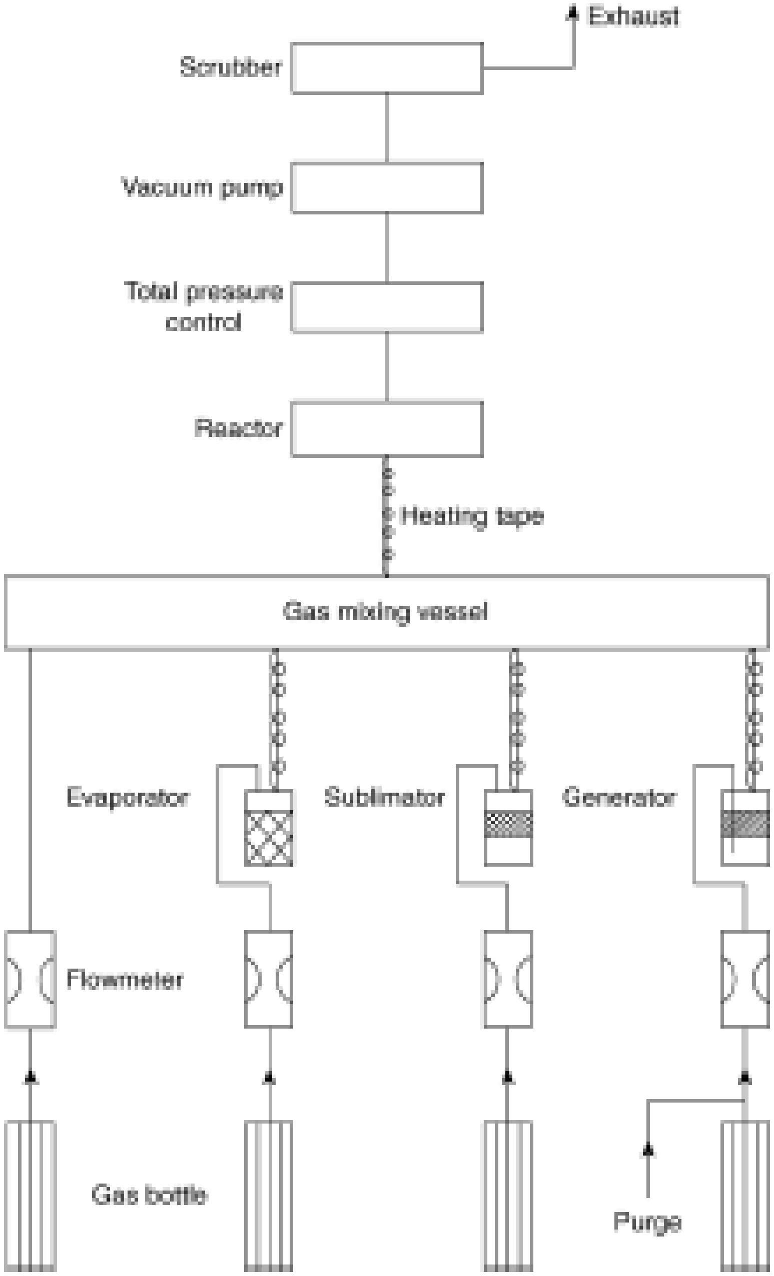


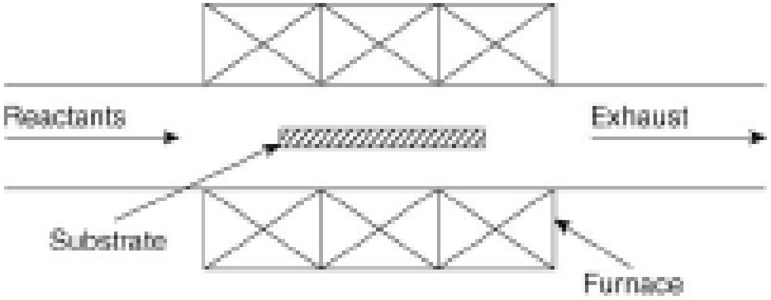
Figure 7.6: Sketch of a CVD system.

The CVD System

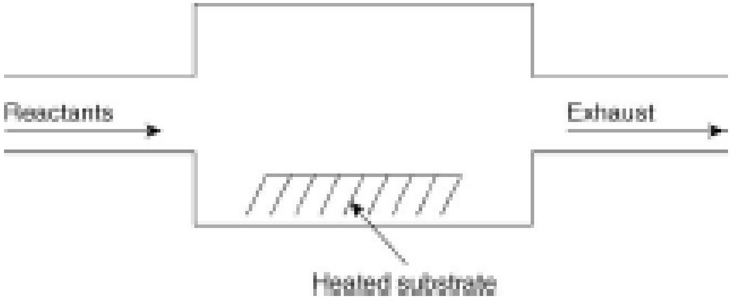
1. Gas Dispensing System
    - Contaminants
        - From reactants themselves
        - From chemical reactions b/w gases and materials in gas dispensing system i.e. tubes, evaporators and sublimators
        - Can be reduced by
            - Purifying the reactants
            - Low leak rate
            - Carrier gas that are non-reactive with materials
            - Materials of tubes etc. that are compatible with gases in use
            - Degassed O-rings as vacuum seals

The CVD System

- Reactor
  - Hot Wall Reactor



    - Film formation on inner walls, may break if thick films
    - Reaction b/w reactor wall and vapor might be a source of contamination
  - Cold Wall Reactor



    - No risk of particles breaking loose from walls
    - Homogenous reactions in vapor phase are suppressed by reactions at the surface
    - Steep gradient of temp. may result non-uniform film thickness
    - High cleanliness, high flexibility, high deposition rates etc.
    - Conductive substrates heated resistively
    - Non-conductive by optical techniques e.g. lasers etc.

The CVD System

- Exhaust system
- Vacuum pump
- Total pressure controller
- Scrubber
- To remove toxic, explosive

and corrosive gases

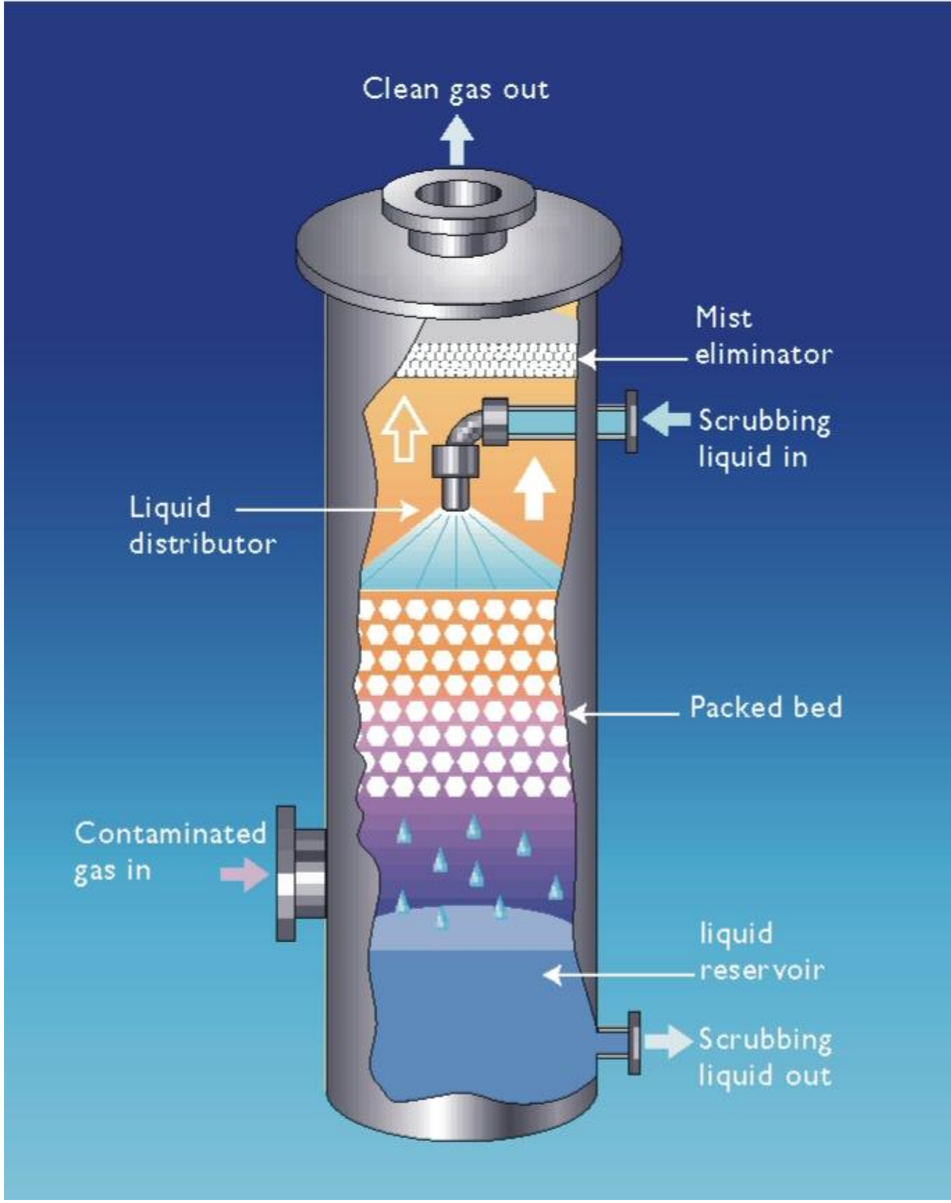
- Halides in water,

CO and H in flame and

arsine is removed by heating reactor

gas in special furnace

- Recycling system (if necessary)



Gas Flow Dynamics

Molecular State

Viscous State (Laminar Flow, Turbulent Flow)

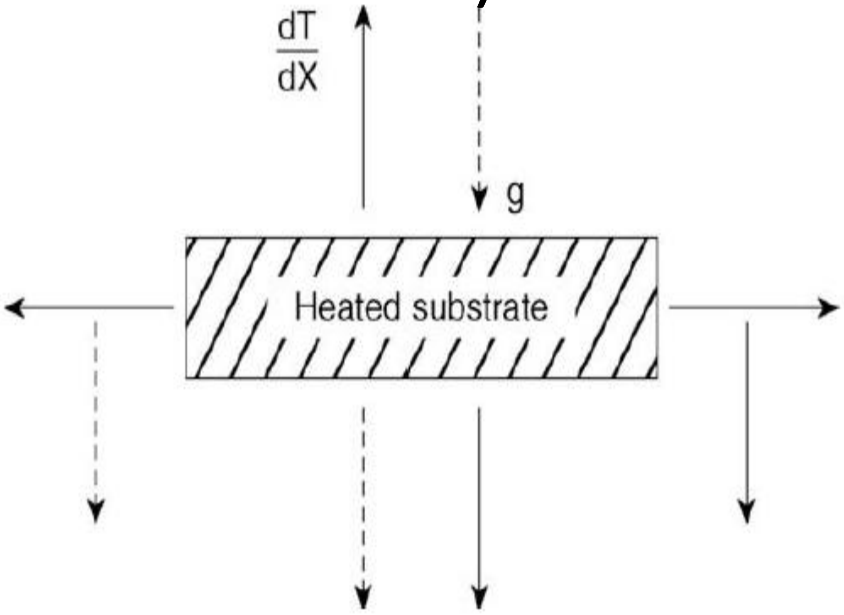
Reynold's Number $R_e = \rho V D / \eta$

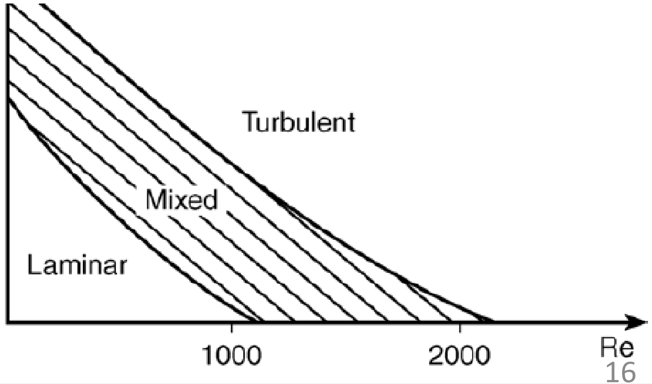
Temperature gradient ***dT/dx***

Rayleigh Number R_a

Grashof Number G_r

Prandtl Number

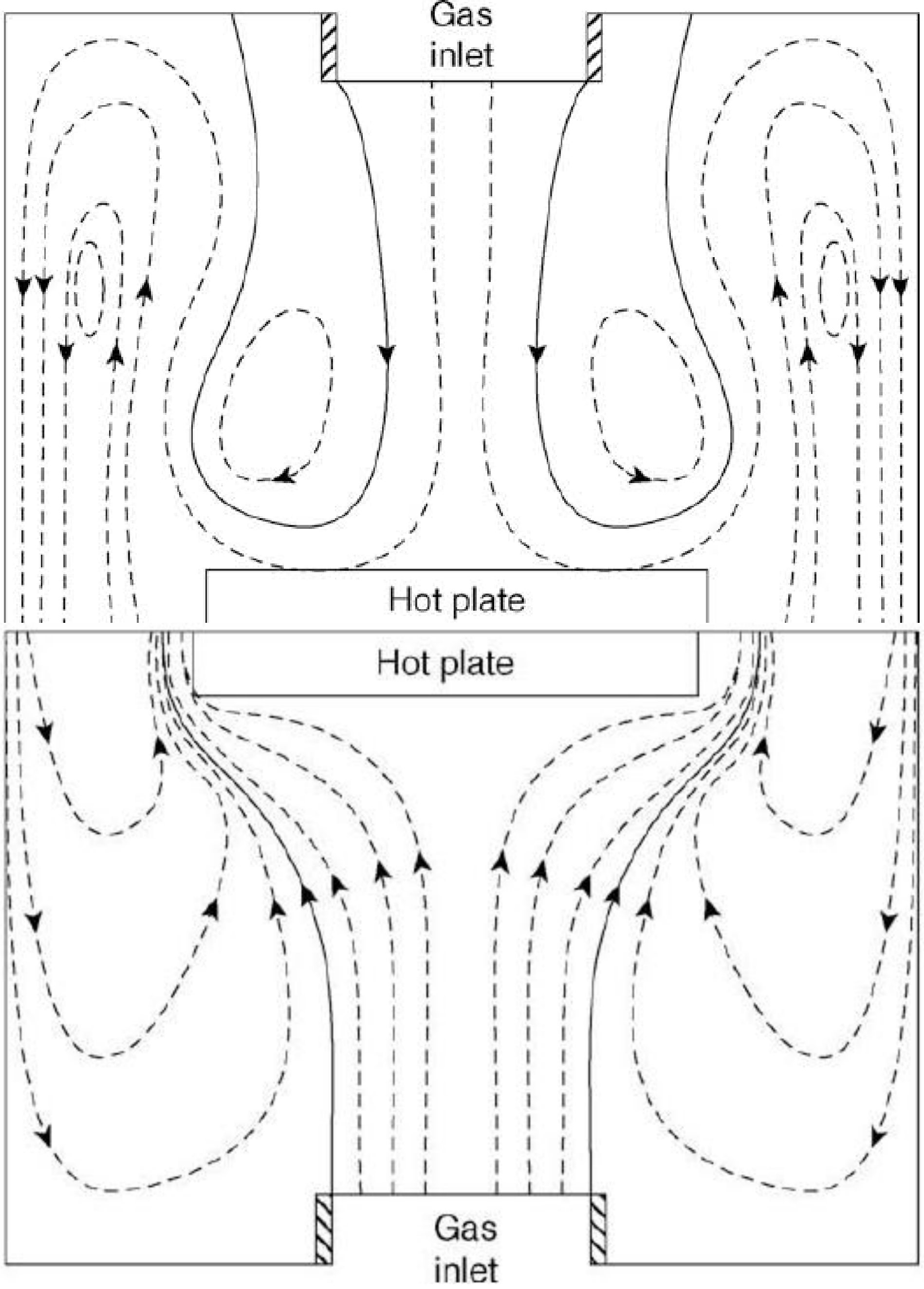




Gas Flow Dynamics

- Gas Flow Patterns
  - Vacuum
  - Pressure difference (forced convection)
  - Gravity (free convection)

Wahl [35]



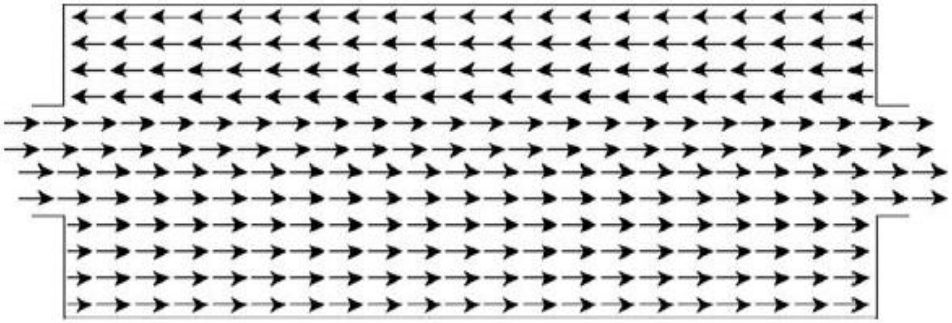
Wahl and Hoffman[36]

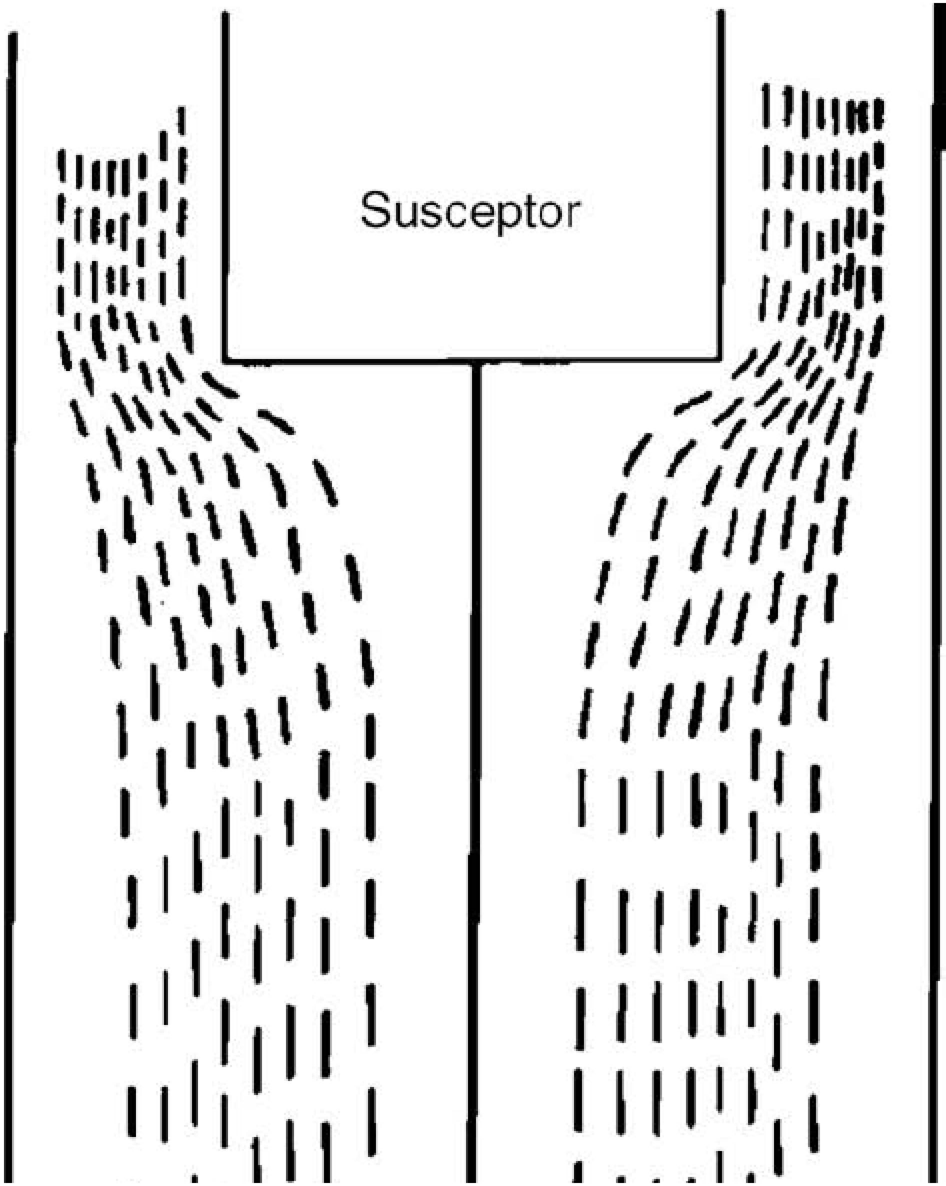
Correction of successive depletion

Westpahl[33]

GaAs by Ga-$AsCl_3$-H_2, for different temp grad, gas flow vel and heights 6K/cm, 2cm/s and 5cm

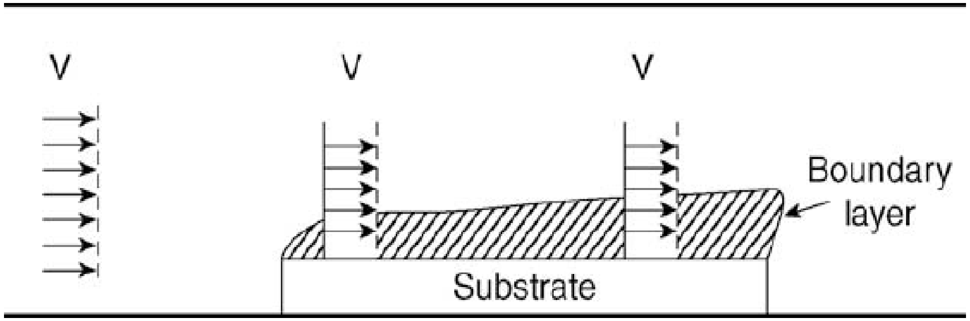
Effect of free convection dec. with dec. temp grad., inc. gas flow vel. and dec. reac. Heights





Gas Flow Dynamics

- Boundary Layers
  - Velocity Boundary Layer
  - Concentration Boundary Layer
  - Thermal Boundary Layer
  - Thickness of B.L



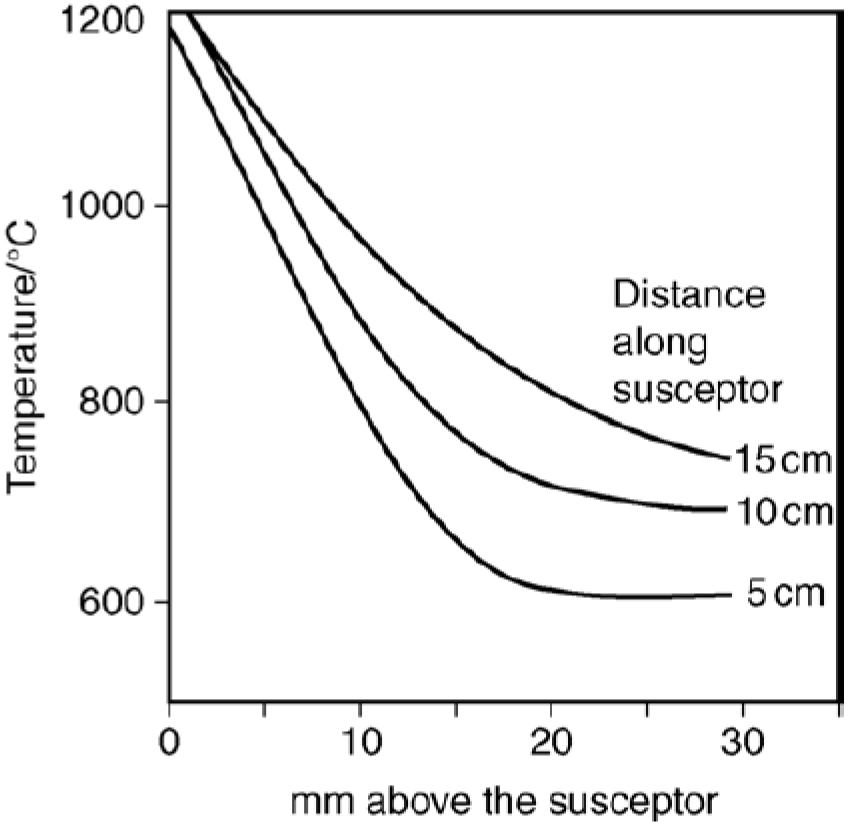
$$\delta = a(\eta X / \rho V)^{1/2}$$

Inc. with inc. temp, inc trans. dist. & dec. total pressure

Eversteijn[38]: smoke from $TiCl_4$-H_2O-Stagnant Layer

Ban[29]:heating in He-temp grad.

concentration profiles-Si CVD by H2/SiCl4



Temperature profile in He. Linear gas flow velocity: 24.9 cm/s

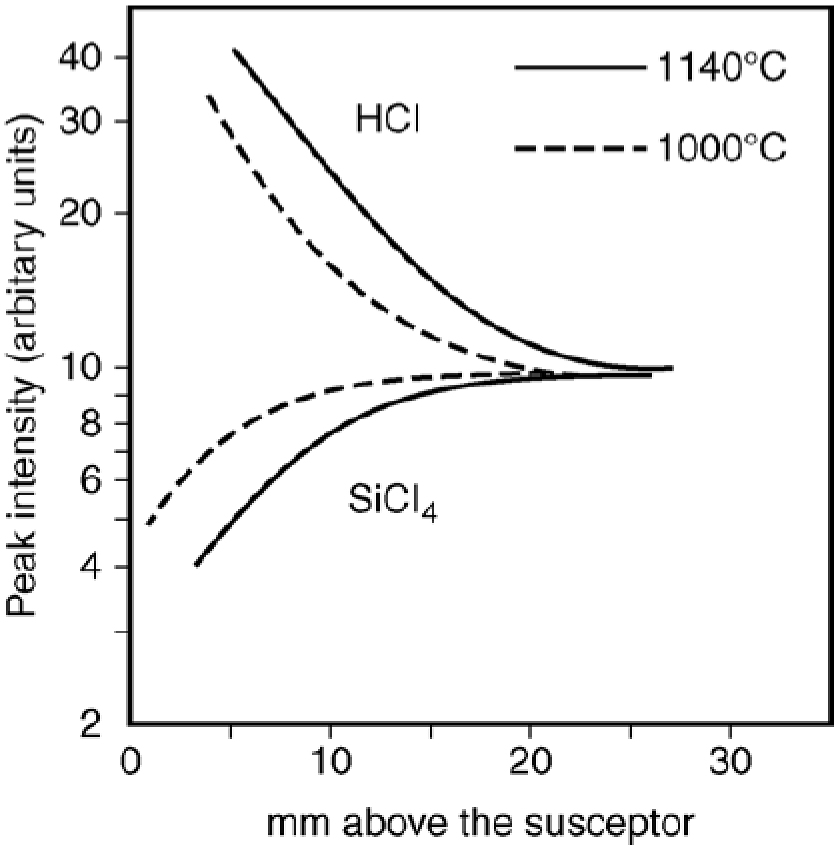


Figure 7.17: Concentration profiles of $SiCl_4$ and HCl in the CVD of silicon from $SiCl_4$ and H_2. Transport distance along the susceptor: 12.5 cm; linear gas flow velocity: 24.9 cm s^{-1}, - - - 1000 °C, – 1140 °C [29].

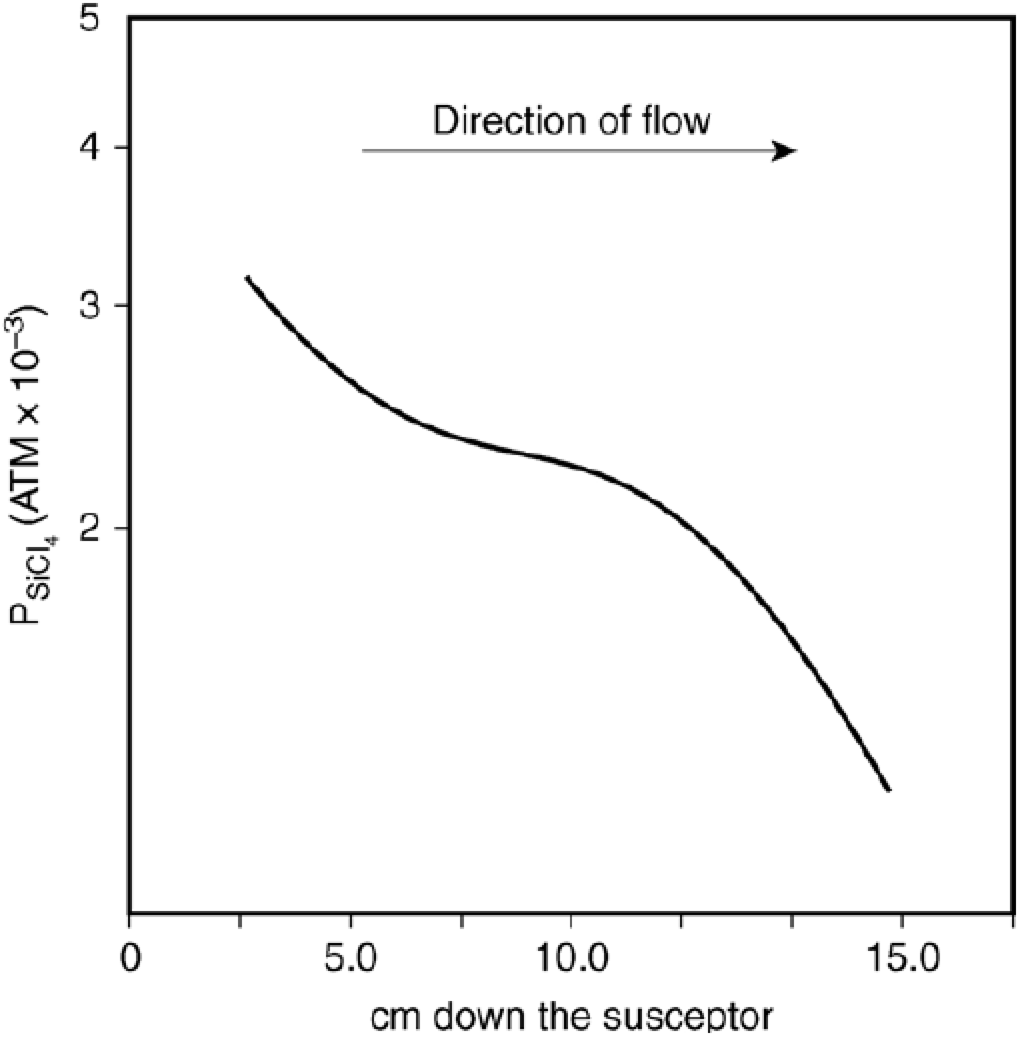


Figure 7.18: Partial pressure profile of $SiCl_4$ as a function of the transport distance along the susceptor at a height of 7 mm above the susceptor [29].

Giling[40]: gas flow patterns and temp profiles

H_2, He: flow vel. > 40 cms^{-1}, cold gas finger

N_2, Ar: flow vel. > 4 cms^{-1} , laminar layer 8 mm near susceptor

Entrance effects: $X= 0.04hR_e$-Schlichting[37]

Coltrin[42]: Mathematical model for Si CVD from Silane

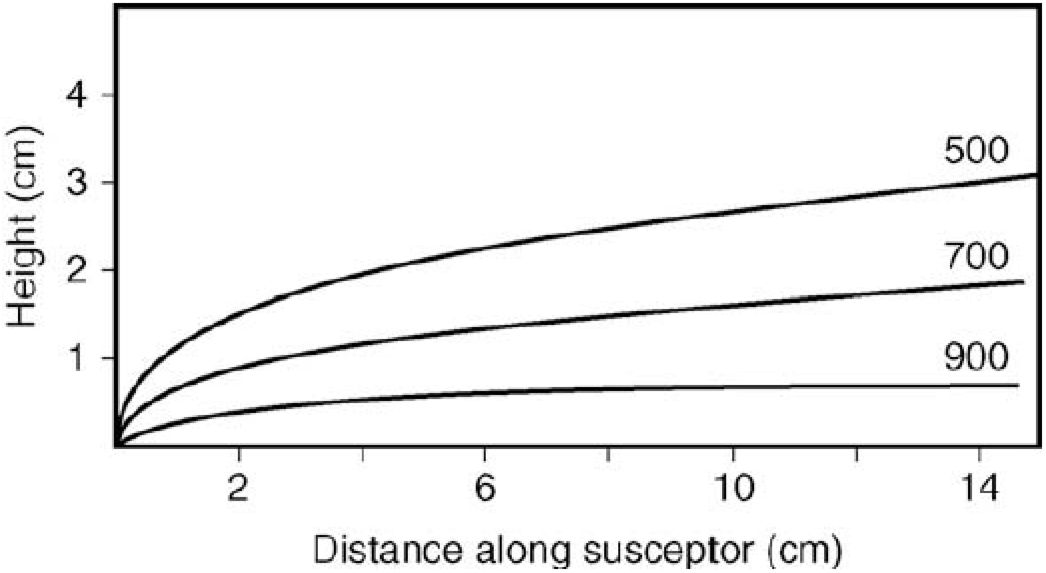


Figure 7.19: Calculated temperature contours for silicon CVD from silane (0.6 torr) and helium as a carrier gas (600 torr). Temperature: 1018 K; gas flow velocity: 15.3 cm s^{-1} [42].

Gas Flow Dynamics

Four mass transport processes across a boundary layer can be distinguished:

- Fickian diffusion occurs from a concentration gradient across the boundary layer.
- Thermal diffusion or Soret diffusion is induced by a temperature gradient in, for example, a cold wall reactor [32]. This type of diffusion is most important in systems having large differences in molecular weights and molecular size between vapor species.
- A concentration gradient leads to a density gradient, resulting in a buoyancy-driven *advective flux* [42].
- In the overall CVD reaction, the number of moles of gas may be changed. This creates flux (Stefan flux) towards or away from the substrate surface. In, for example, the CVD of boron from BCl_3 and H_2 according to the reaction

$$2\,BCl_3(g) + 3\,H_2(g) \rightarrow 2\,B(s) + 6\,HCl(g)$$

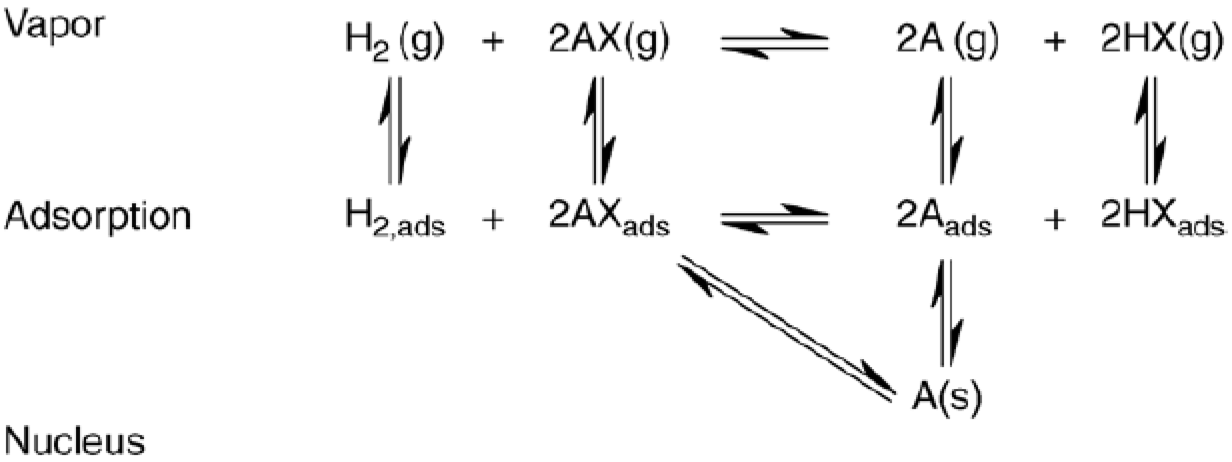
the number of moles in the vapor is changed from 5 to 6, causing a flux from the substrate [43].

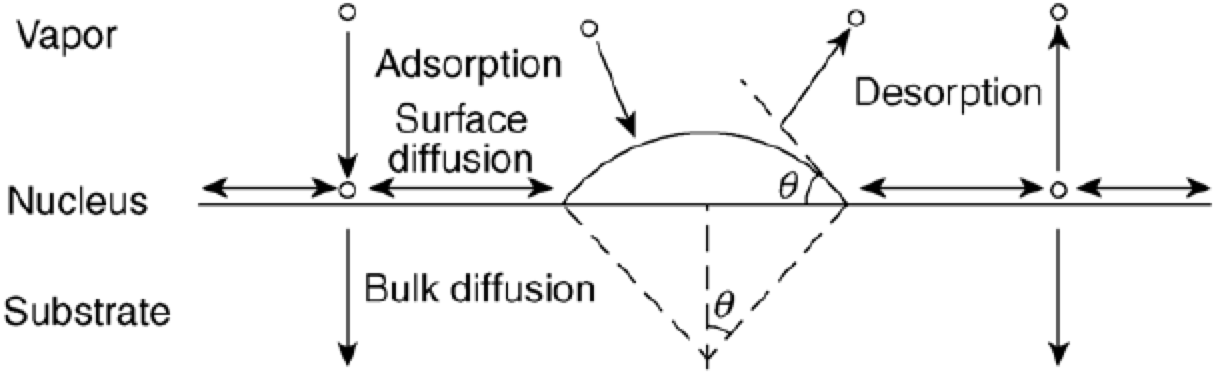
Nucleation

Grain size, defects, inclusions etc. effect properties of deposition

Nucleation on foreign substrate: Adhesion

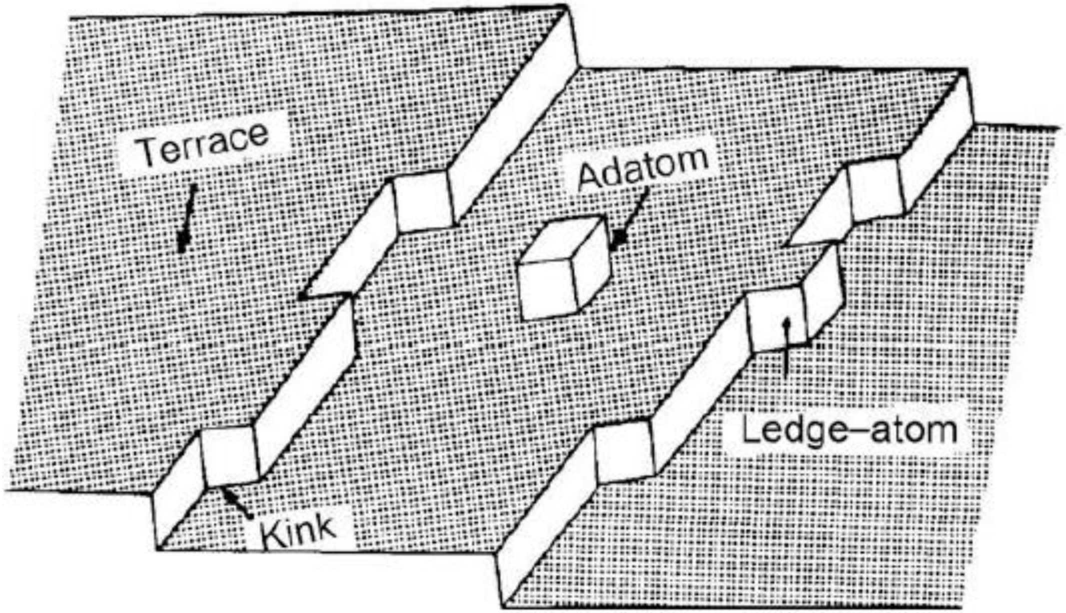
Formation of A, by H_2(g) and AX(g)





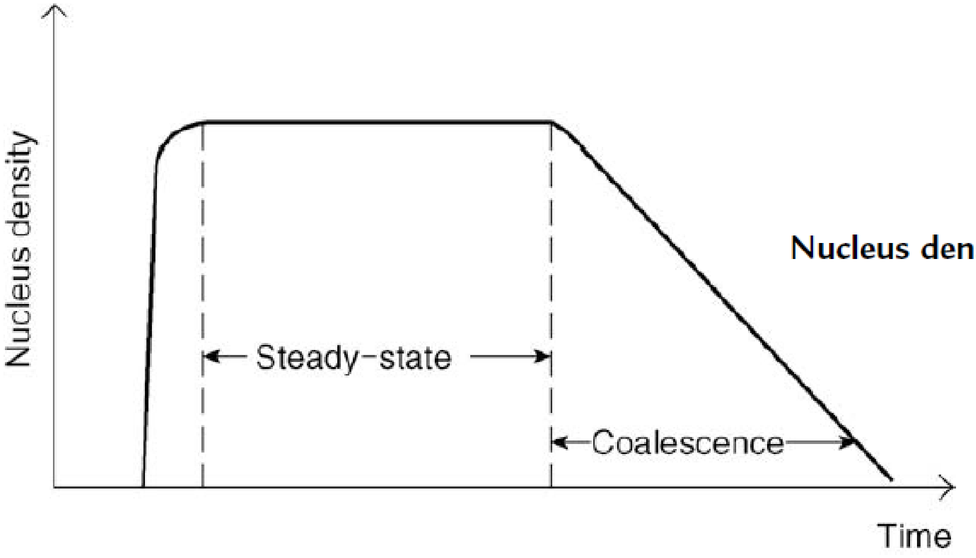
Nucleation

The TLK Model:
Terrace, Ledge, Kink



Growth: positive deviation
Etching: negative deviation

Effects of Temperature and Deposition Rate
Free Surface Sites
are occupied by strongly adsorbed molecules
Si CVD: 99% of surface sites by H & Cl
Layer growth(no nucleation) at only high temp. low dep. rates and low adsorption…required long diffusion distances
Nucleus Density
high nucleation rate ~1010 cm-2s-1
Saturation: when mean diffusion dist. longer than half the mean nucleus distance



Nucleus density as a function of process time.

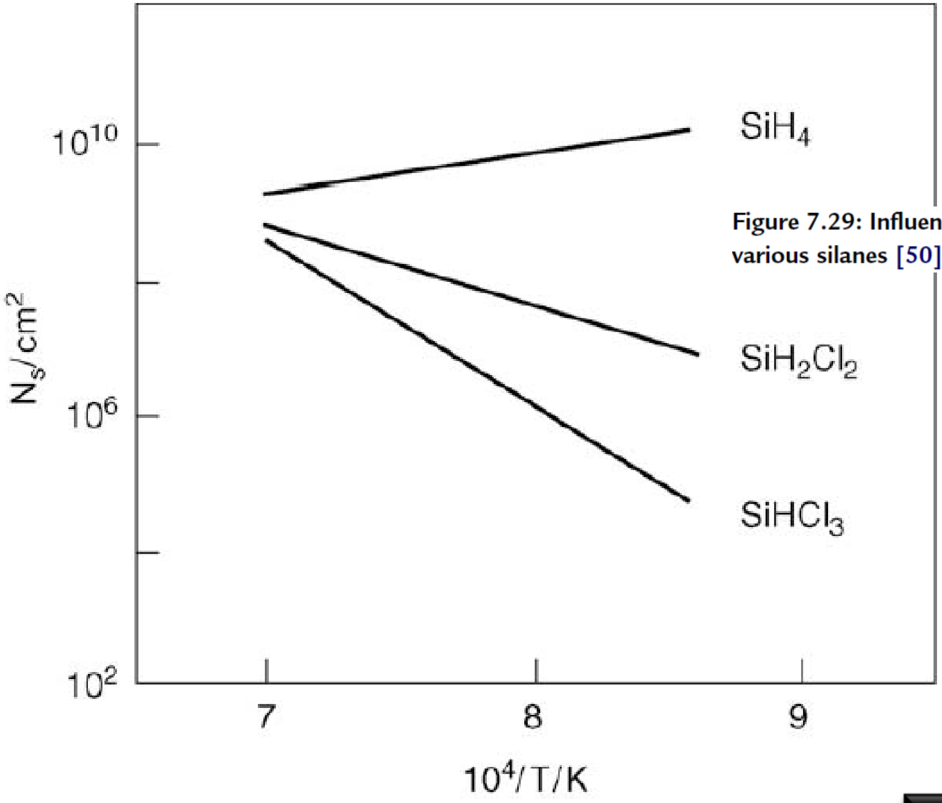
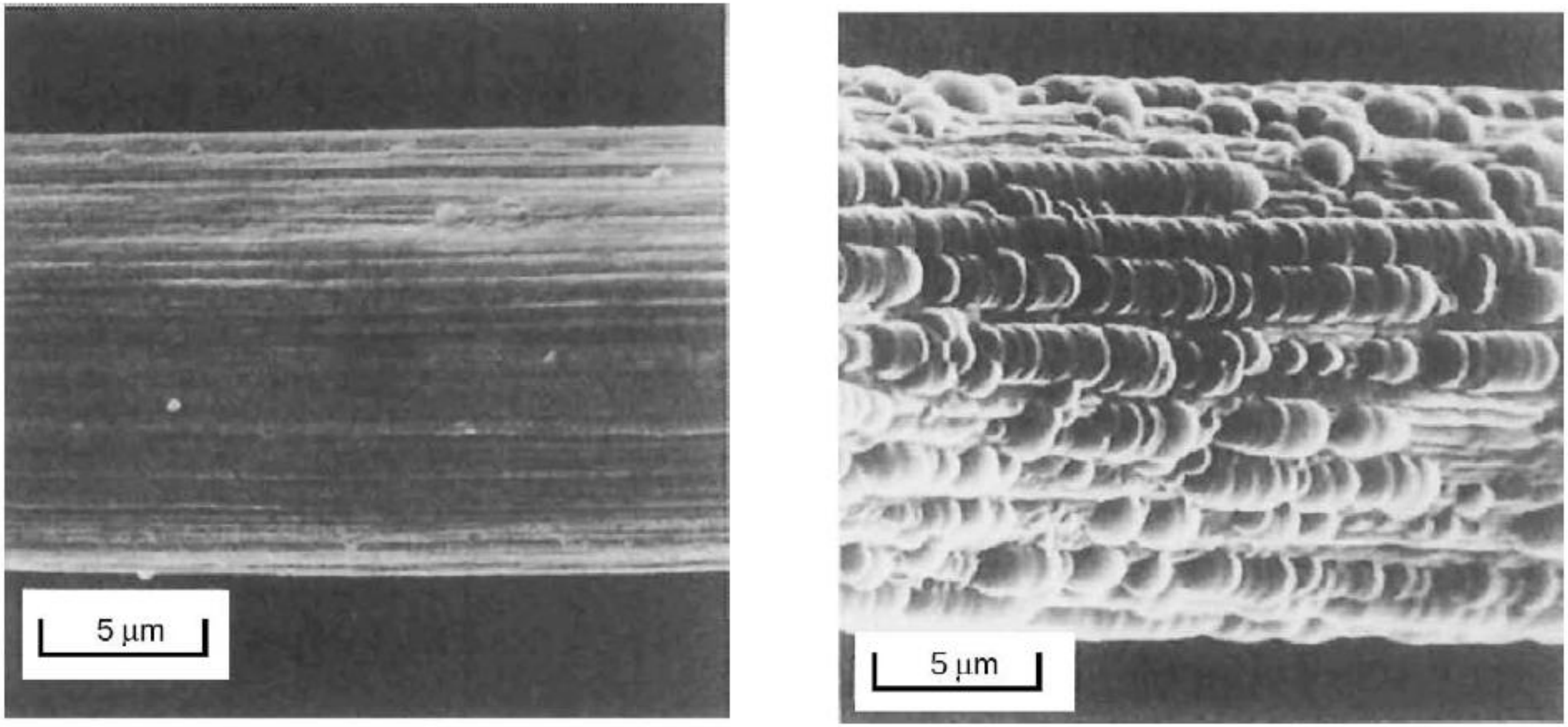


Figure 7.29: Influence of temperature on the saturation nucleus density at silicon CVD from various silanes [50].

Preferential Nucleation



Surface of a tungsten filament, and (b) preferentially nucleated boron on ridges

Applications

- **Microelectronics:** epitaxial layers, films as dielectrics, conductors, diffusion barriers, oxidation barriers etc.
- **SC Lasers:** GaAs…
- **Optical fibers:** Silica tube is coated inside with oxides of Si, Ge or B for correct refractive index
- **Solar energy:** thin film solar cells of silicon and gallium arsenide
- Carbon nanotubes
- Wear-resistant: TiC, TiN and Al_2O_3on cutting tools
- Friction reducing, Corrosion resistant, Erosion resistant, Heat resistant
- Decorative coatings TiN on watches
- Conductive coatings: IC interconnections