Chemical Vapour Deposition: CVD

Reference: Jaeger Chapter 6 & Ruska: Chapter 8

- CVD - Chemical Vapour Deposition
- React chemicals to create a thin film layer at the surface
- Eg Silicon compound + oxygen to create glass
- Typically gas phase reactions
- Liquid phase reactions used but seldom in Si microfab (most common for III-V semiconductors)
- CVD also used for nanofilm processes eg Carbon Nanotubes

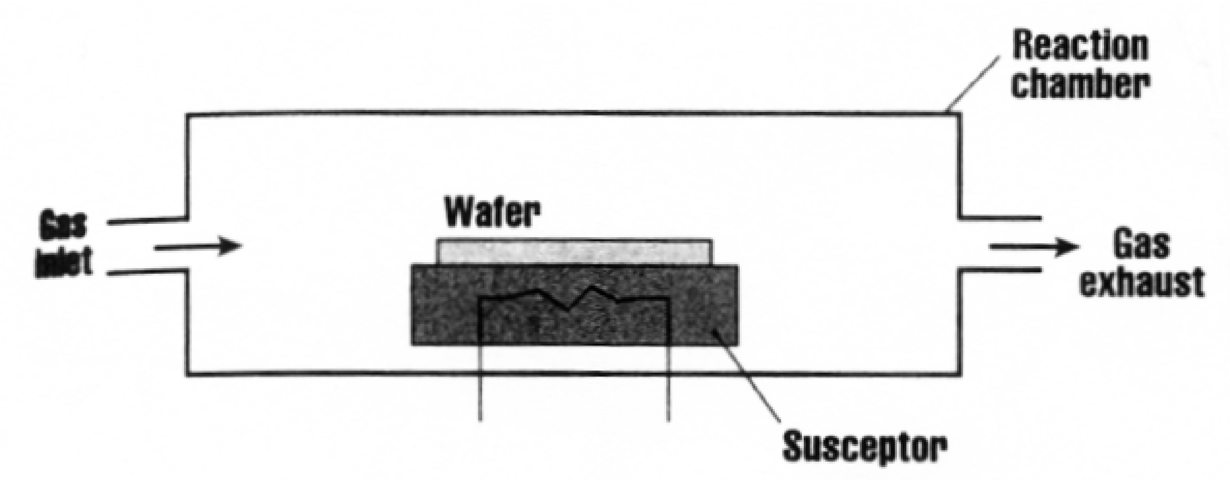
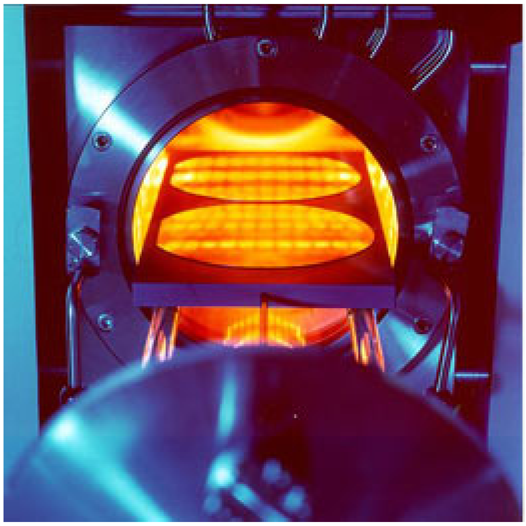
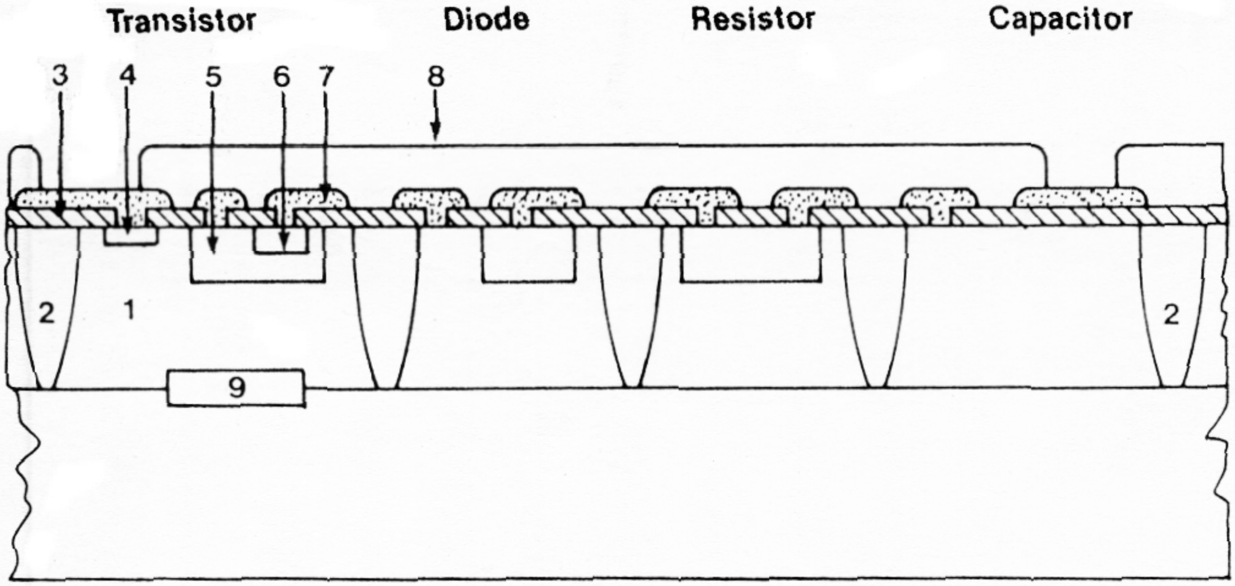


Figure 13-1 A simple prototype thermal CVD reactor.



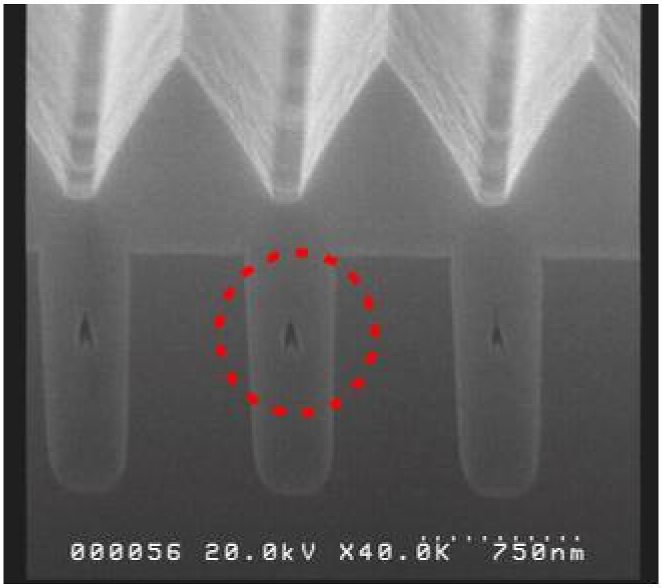
CVD Applications

- Depositing thin insulating films
  Intermetal glass, Silicon Nitride
- Polysilicon (gates/conductors)
- Epitaxial silicon (single crystal on wafer)
- Silicide materials
- III-V compounds



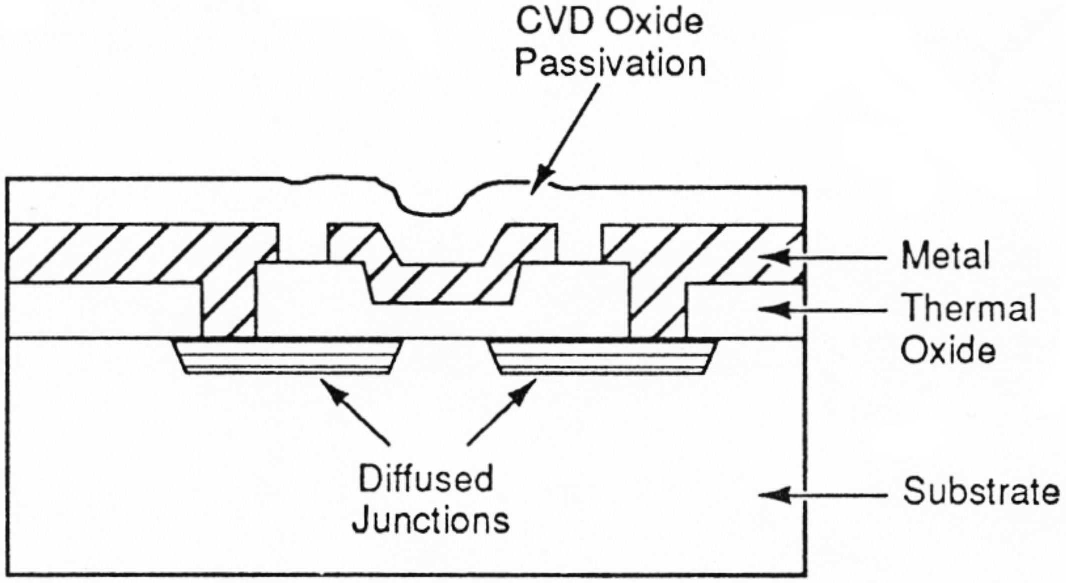
1. EPI and Collector
2. Isolation
3. Surface Oxide
4. Collector Contact
5. Base
6. Emitter
7. Metalization
8. Passivation Layer
9. Buried Layer

Figure 12.1 Cross section of bipolar circuit showing epitaxial layer and isolation.

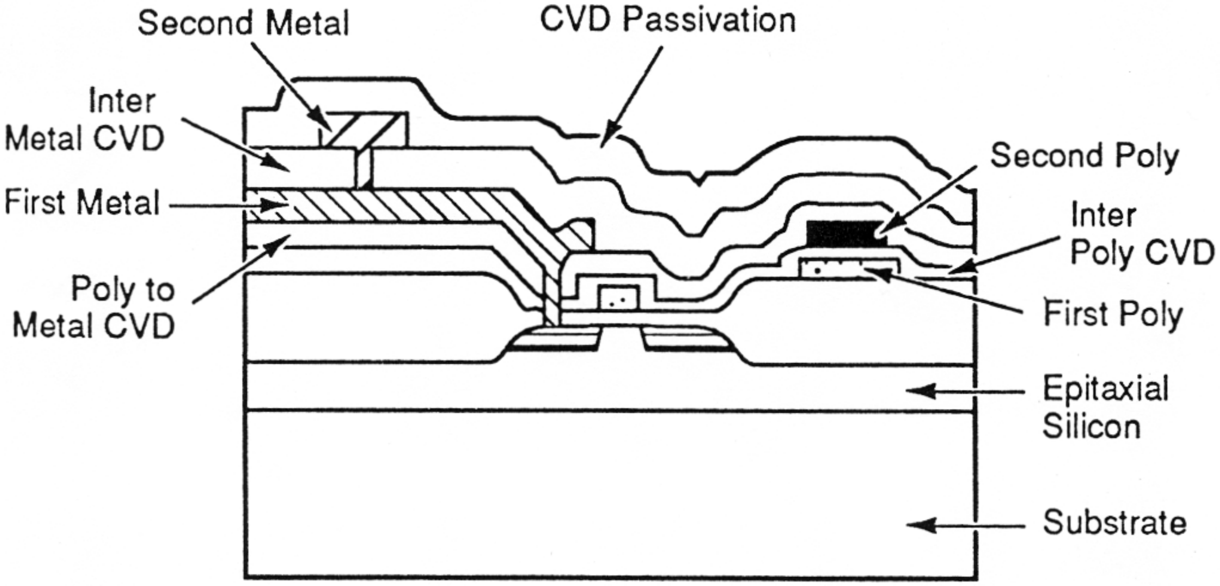


CVD and Evolution of MOS technology

- Initially used metal gates in FETS
- Now double poly processes, double metal as minimum
- Poly Si layers form gate and first/second level conductors
- More important – allows self-aligned gate process
- Often 6-8 metal layers + same insulator layers



“Old” MOS



“Modern” MOS

Figure 12.2 Evolution of MOS layers.

Four main CVD Reactions

- Pyrolysis: heat driven break down of source
- Reduction: usually react with Hydrogen
- Oxidation: react with oxygen to form oxides
- Nitradation: create nitrides with nitrogen compounds

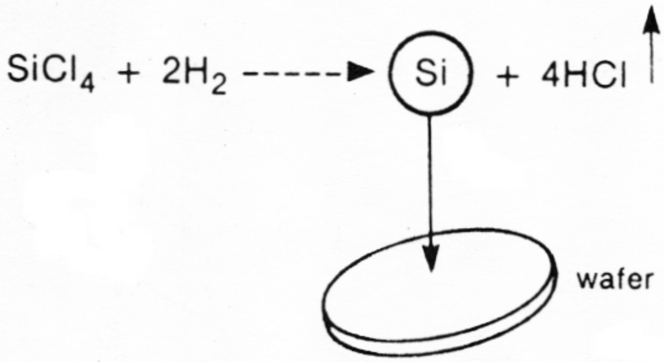
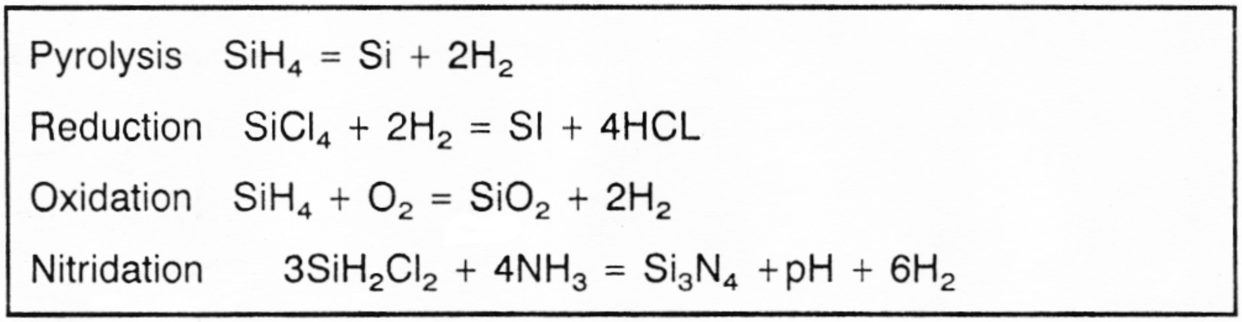


Figure 12.4 Chemical vapor deposition of silicon from silicon tetrachloride.



Pyrolysis $SiH_4 = Si + 2H_2$

Reduction $SiCl_4 + 2H_2 = SI + 4HCL$

Oxidation $SiH_4 + O_2 = SiO_2 + 2H_2$

Nitridation $3SiH_2Cl_2 + 4NH_3 = Si_3N_4 + pH + 6H_2$

Figure 12.5 Examples of CVD reactions.

Major CVD Processes

- All CVD have 4 main process steps controlling the reaction
- Reactants diffuse to surface
- Reaction at surface creates the film
- Film reformed at surface (eg crystal size grows)
- Products Desorbed and diffuse from surface
- Reaction rate may be limited by any of these steps
- Similar issues in wet etching and furnace oxidation
- For CVD fluid flow processes control some of these steps

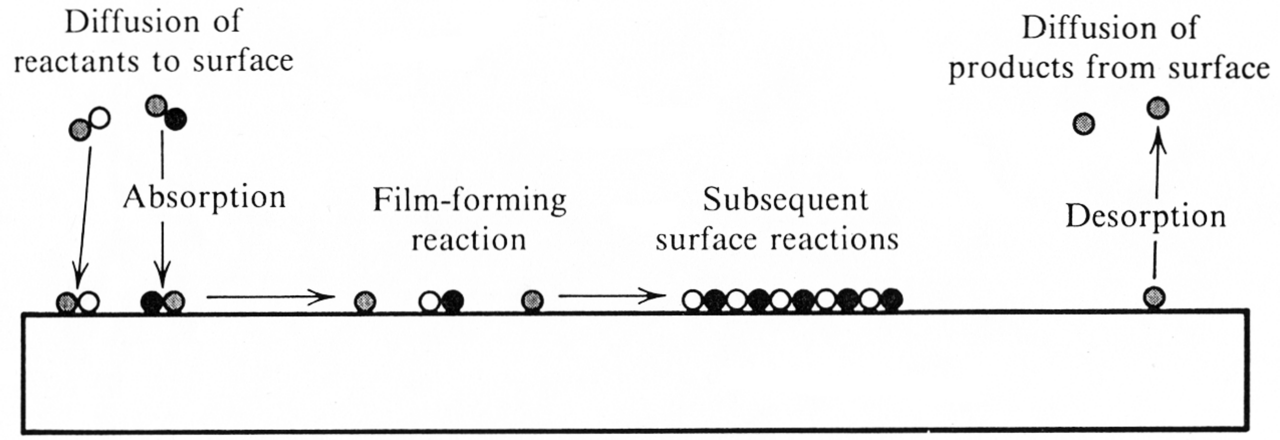
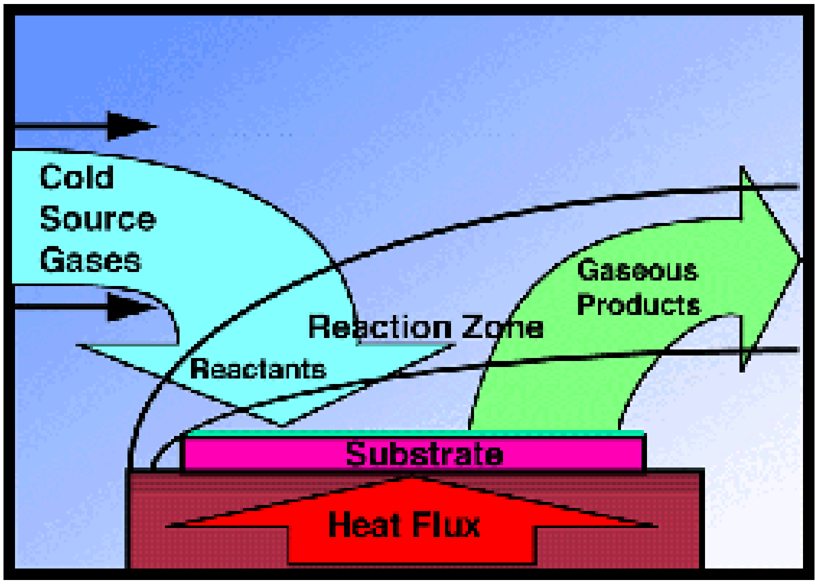


Figure 8-1 The sequence of reaction steps in a CVD reaction.



Fluid Flow

- For gas or liquid process these follow Fluid Flow equations
- Assume "laminar flow" ie smooth flow with no turbulence
- Near surface fluid velocity decreases due to drag of surface
- Force F on the fluid:

$$F = \mu \frac{dv}{dz}$$

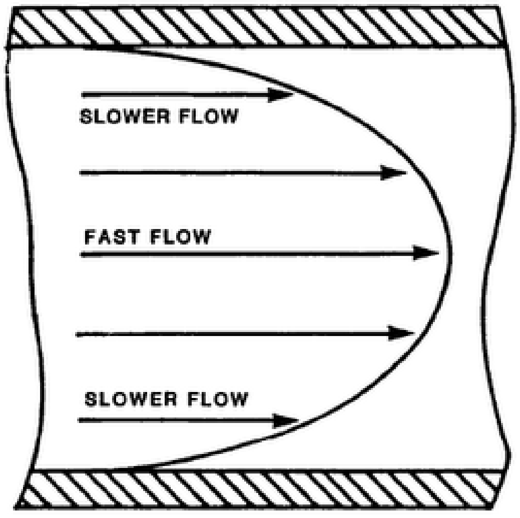
Where: v = velocity of fluid
z = distance from the surface
μ= viscosity of fluid

- Fluid flow is often measured by Reynolds number Re

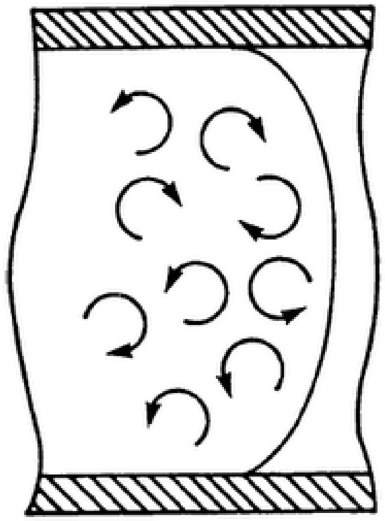
$$\mathrm{Re} = \frac{dv\rho}{\mu}$$

Where: d = length of system (diameter of pipe)
ρ = density of fluid
v = velocity

- Reynolds number for CVD system ~ 100
- When Re >2000 tend to get turbulent flow



LAMINAR (STREAMLINE) FLOW



TURBULENT FLOW

Boundary Layers and Flow

- Boundary Layer: slow moving layer near surface
- Thickness δ goes from full fluid velocity point to the surface
- Laminar Boundary thickness varies as distance from flow start

$$\delta = \frac{l}{\sqrt{\mathrm{Re}}}$$

l = distance from the front edge of object flowed around

- Equation varies with object shape

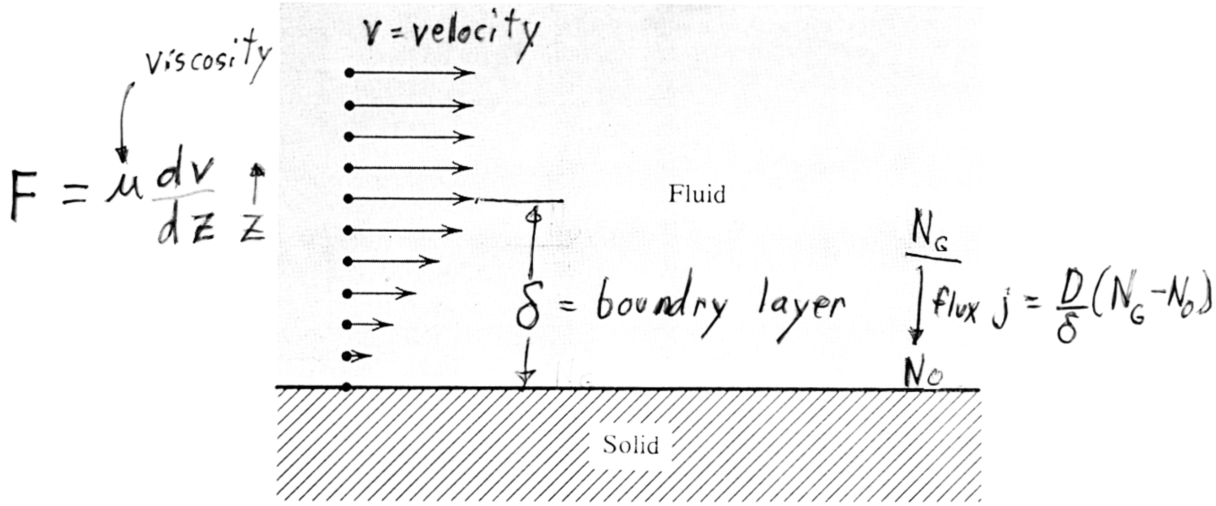


Figure 8-2 Movement of a fluid past a solid surface, illustrating the formation of a boundary layer.

Fluid Flow - Transport of Reactants to Surface

- Transport flux of reactant through the boundary layer

$$j = \frac{D}{\delta}\left(N_g - N_0\right)$$

where D = the diffusion coefficient

N_g = concentration at top of boundary layer

N_0 = concentration at surface

- Gas phase diffusion coefficients D vary less with temperature
- Common formula Hammond's

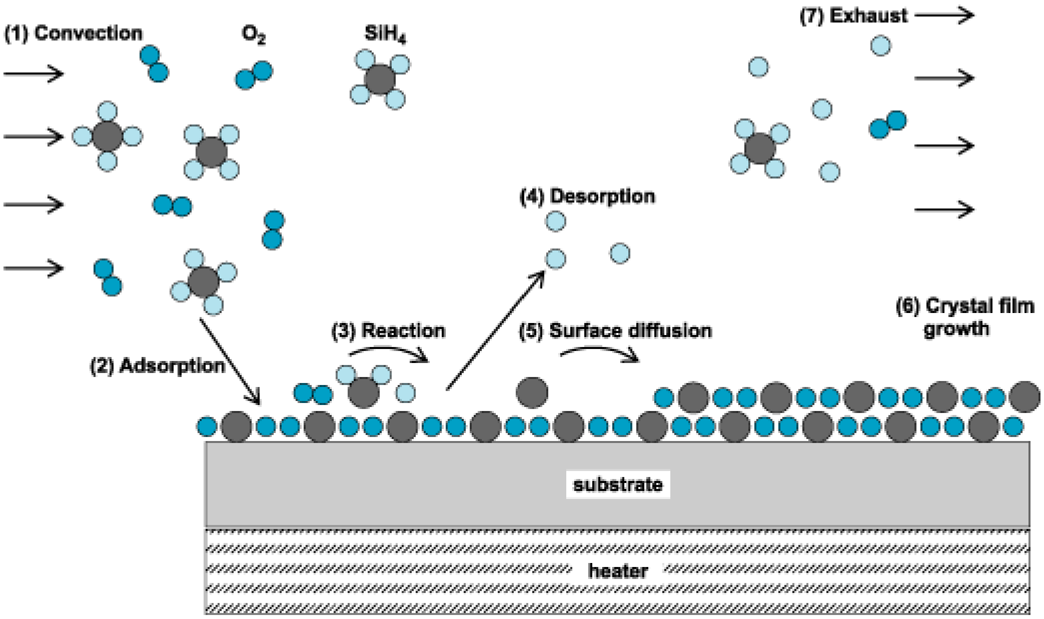
$$D \propto T^{3/2}\frac{P_s}{P}$$

where T = Temperature (K)

P_s = partial pressure of diffusing species

P = total pressure

- Diffusion of reactant to the surface must be determined



Reaction at Substrate Surface

- Flux at surface controlled by reaction

$$j = k_s N_g$$

where k_s = surface reaction rate

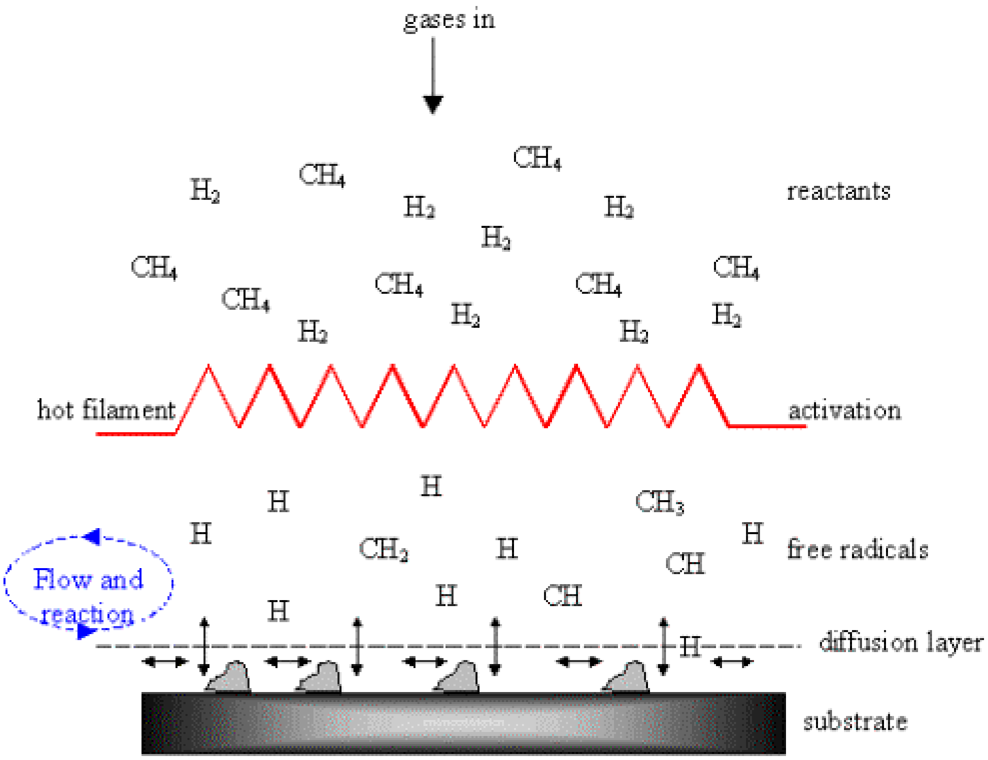
- Reaction rate flows an Arrhenius law

$$k_s = k' \exp\left(\frac{-E_A}{KT}\right)$$

where k' = reaction constant
    E_A = Activation energy of the reaction
    KT = thermal energy (eV)

- Thus the Reaction Flux at the surface

$$j = \frac{D N_g k_s}{D + \delta k_s}$$



Reaction at Substrate Surface

- Thus the reaction rate r:

$$r = \frac{j}{\gamma} = \frac{DN_g k_s}{\gamma(D + \delta k_s)}$$

where γ = the number of atoms per unit volume of reactant

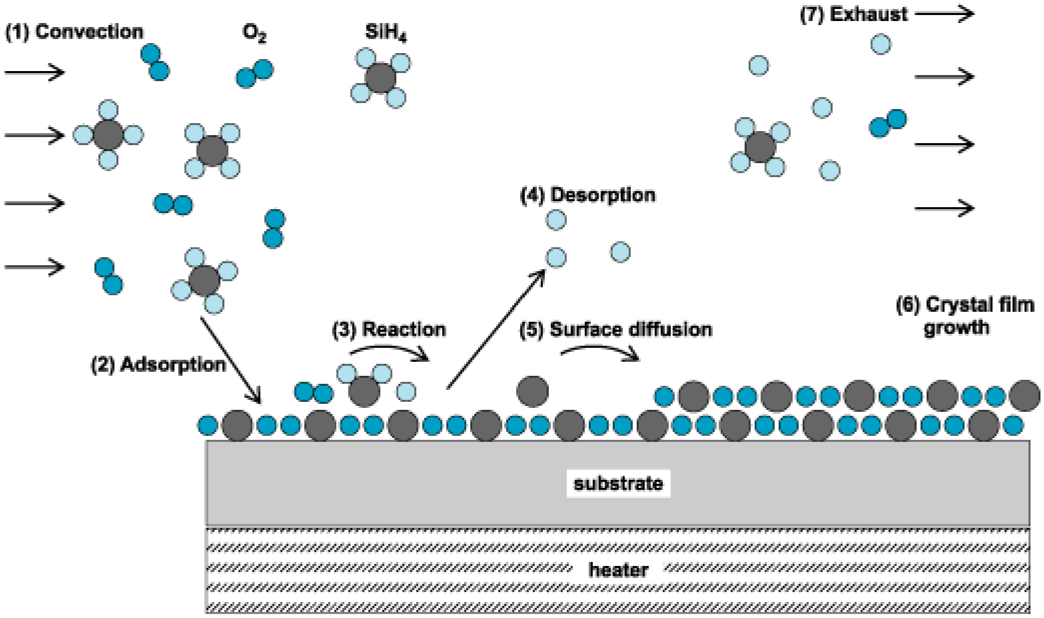
- At high temperatures: **Mass transport limited**:

$$r \approx \frac{DN_g}{\gamma\delta} \qquad \delta k_s >> D$$

- Here surface reaction >> than diffusion
- Hence diffusion of reactants limits the process
- At low temperatures: **Reaction rate limited**:

$$r \approx \frac{N_g k_s}{\gamma} \qquad D >> \delta k_s$$

- Surface reaction << than diffusion rate
- Thus surface reaction limits the process



CVD Film Growth versus Reaction Rate Plot

Mass Transport limited

- Occurs at high temperatures:
- Little change in deposition with temperature
- Rate dominated by transport effects (eg flow rate)

Reaction Rate Limited

- Occurs at low temperatures:
- Deposition rate changes rapidly with temperature
- at Room Temp: 20% change every 10°C

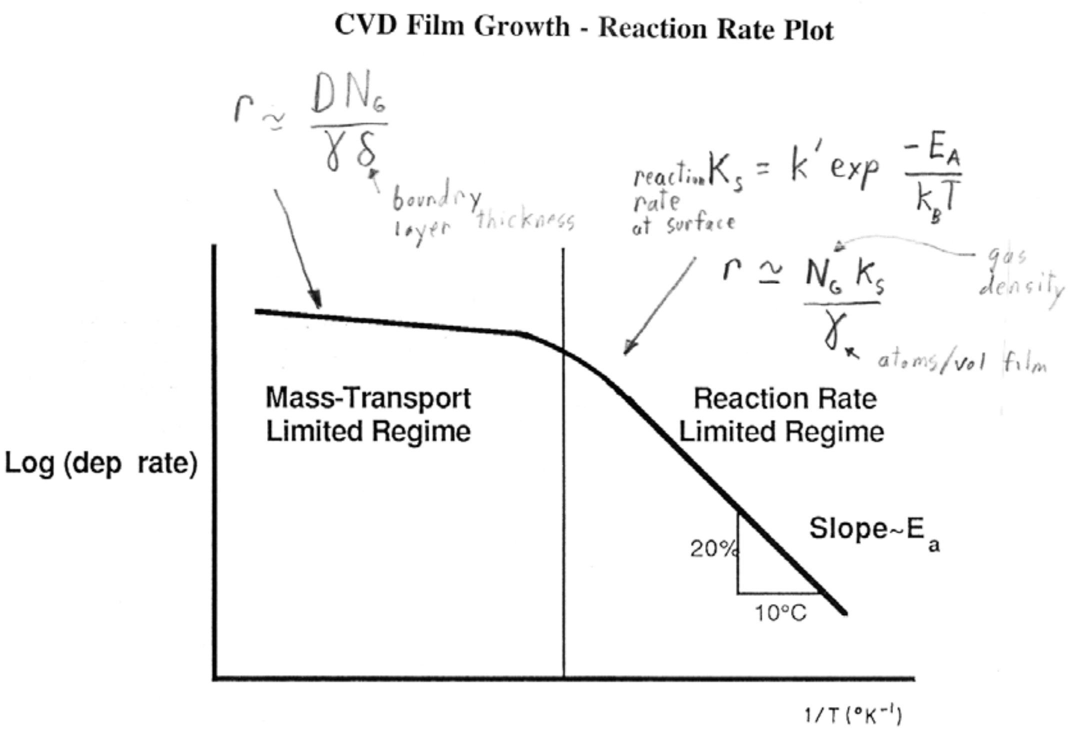
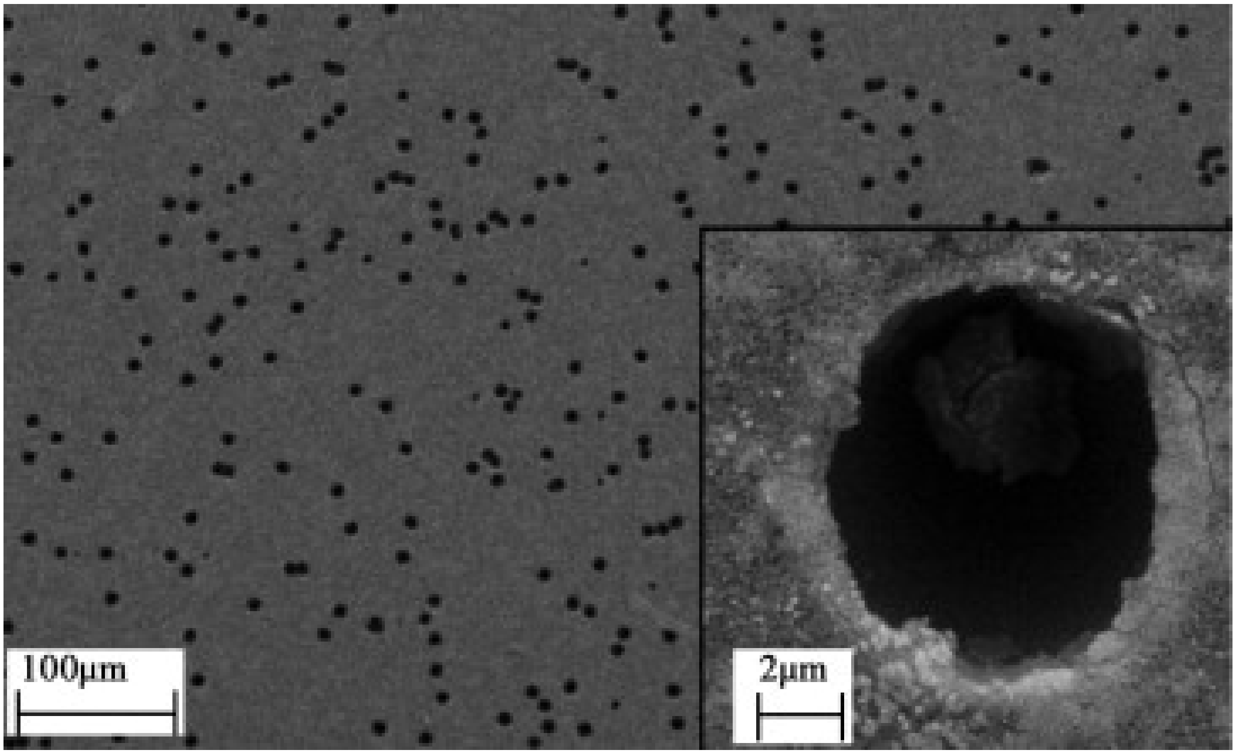


Fig. 1 Temperature dependence of growth rate for CVD films.

CVD Important film parameters

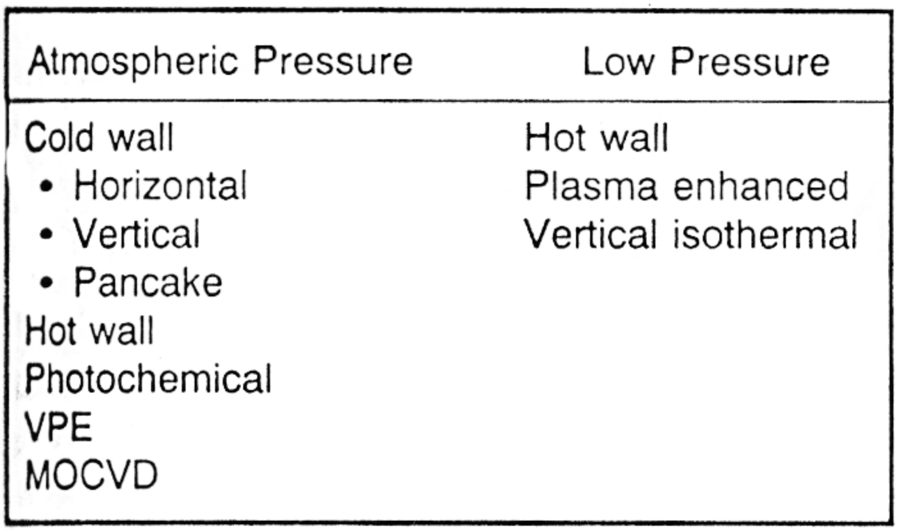
- Stoichiometery: exact composition of film
- Physical parameters: hardness, optical index of refraction
- Electrical parameters:
  dielectric constant, breakdown voltage
- Purity of film: lack of contamination
- Thickness and uniformity
- Conformality and step coverage
- Pin hole (very small holes in film) and particle free
- Adhesion (how well does film stick to surface)
- Test adhesion with the scotch tape test
- Does the film pull off with scotch tape – then poor adhesion



Summary of CVD systems

- Gas Phase: Atmospheric & Low Pressure
- VPE: Vapour Phase Epitaxy (Si single crystal)
- MOCVD: Metal-Organic CVD (metal films)
  used in III-V compounds

Figure 12.2 Evolution of MOS layers.



Atmospheric Pressure	Low Pressure
Cold wall	Hot wall
• Horizontal	Plasma enhanced
• Vertical	Vertical isothermal
• Pancake	
Hot wall	
Photochemical	
VPE	
MOCVD	

Figure 12.3 Overview of CVD systems.

Basic CVD System

- Chemical source (typically gas)
- Flow control for setting film parameters
- Reaction chamber: with energy input
- Energy sources (heat, RF, optical)

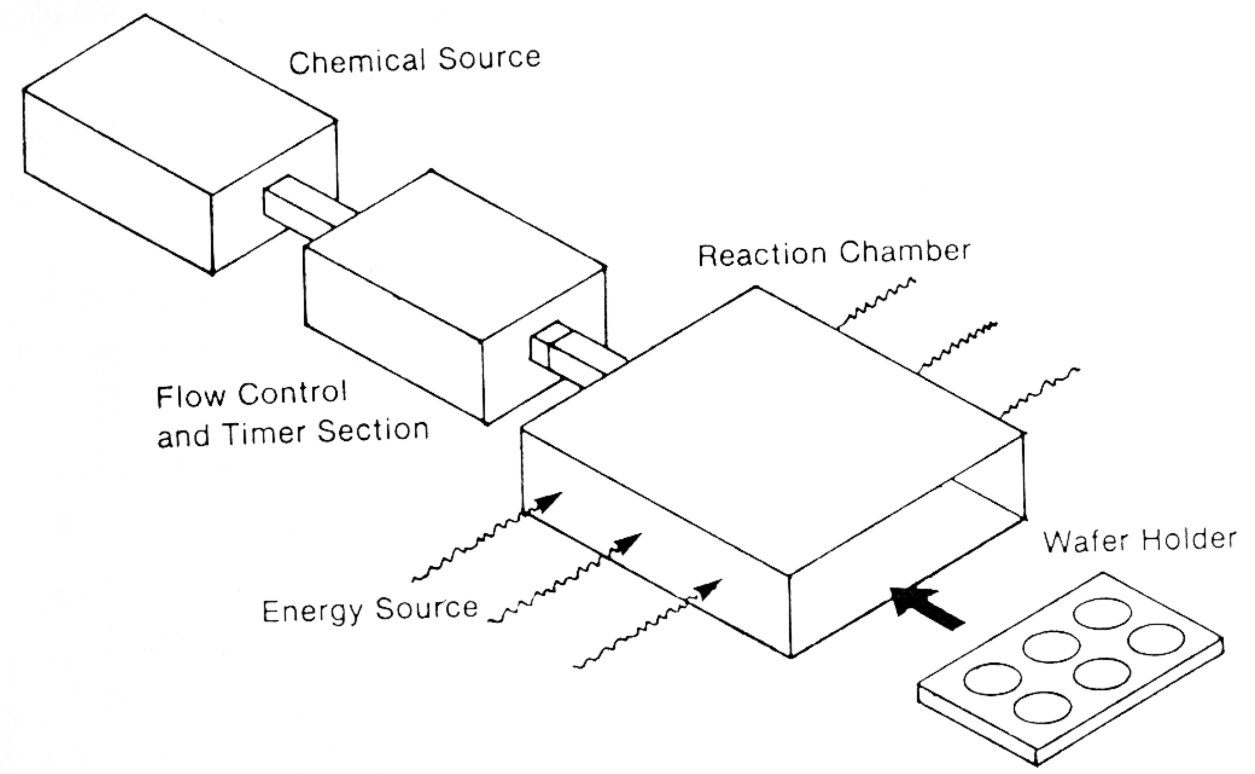
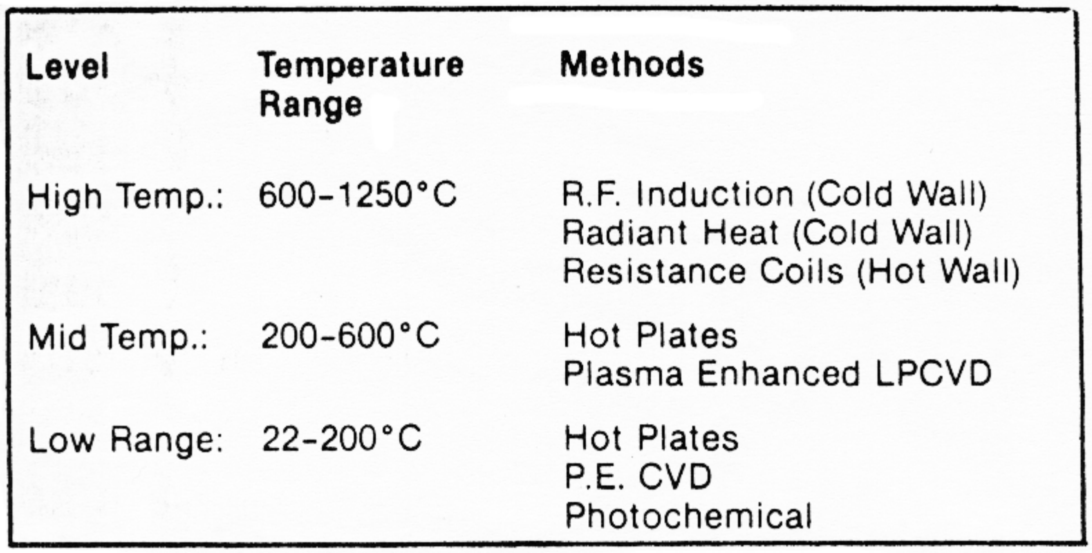


Figure 12.8 Basic CVD subsystems.

Energy sources for CVD Reactions

- Energy used to break up the source material
- Conductive/convective heating
- Inductive RF (Radio Frequency - Microwave)
- Radiant heat (heater strips or lamps)
- RF plasma (Plasma CVD)
- Light (ultraviolet generated recation)



Level	Temperature Range	Methods
High Temp.:	600-1250°C	R.F. Induction (Cold Wall) Radiant Heat (Cold Wall) Resistance Coils (Hot Wall)
Mid Temp.:	200-600°C	Hot Plates Plasma Enhanced LPCVD
Low Range:	22-200°C	Hot Plates P.E. CVD Photochemical

CVD Film Growth Appearance

- Deposition starts at nucleation sites
  - isolated points on surface
- Film grows around nuclei (grains)
- Crystallites collide, forming film
  - grain boundaries
- Grain size set by deposition parameters

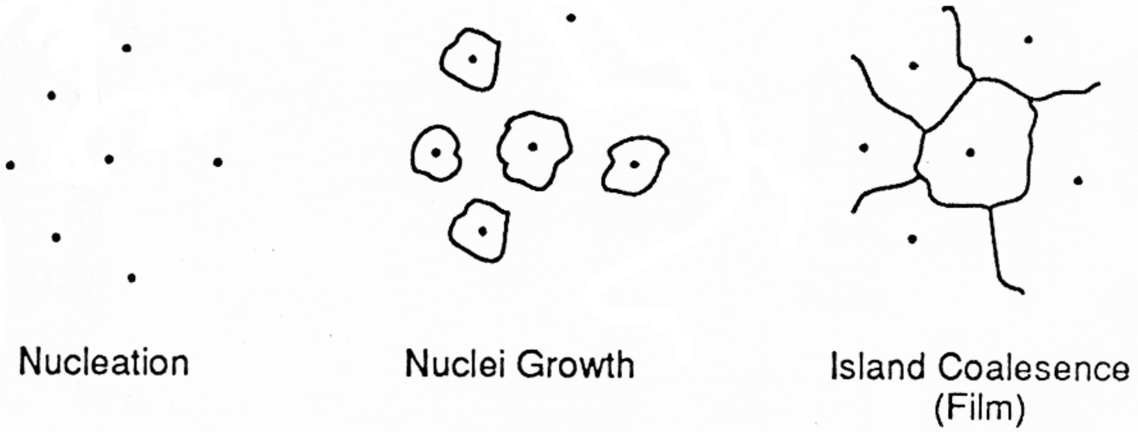
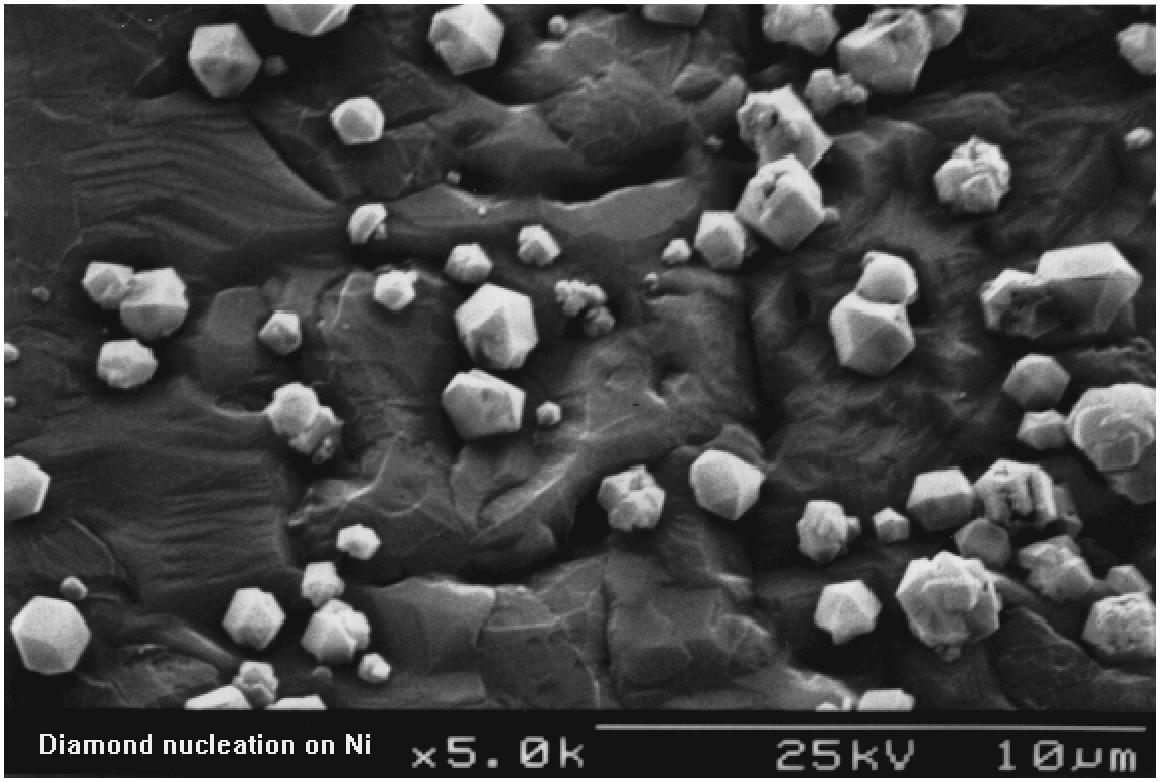


Figure 12.6 CVD film growth steps.



CVD Steps

- Pre clean wafer (quality of surface important)
- Deposition
- Post deposition evaluation

Two main Gas CVD types

- APCVD: Atmospheric Pressure CVD
- LPCVD: Low Pressure CVD

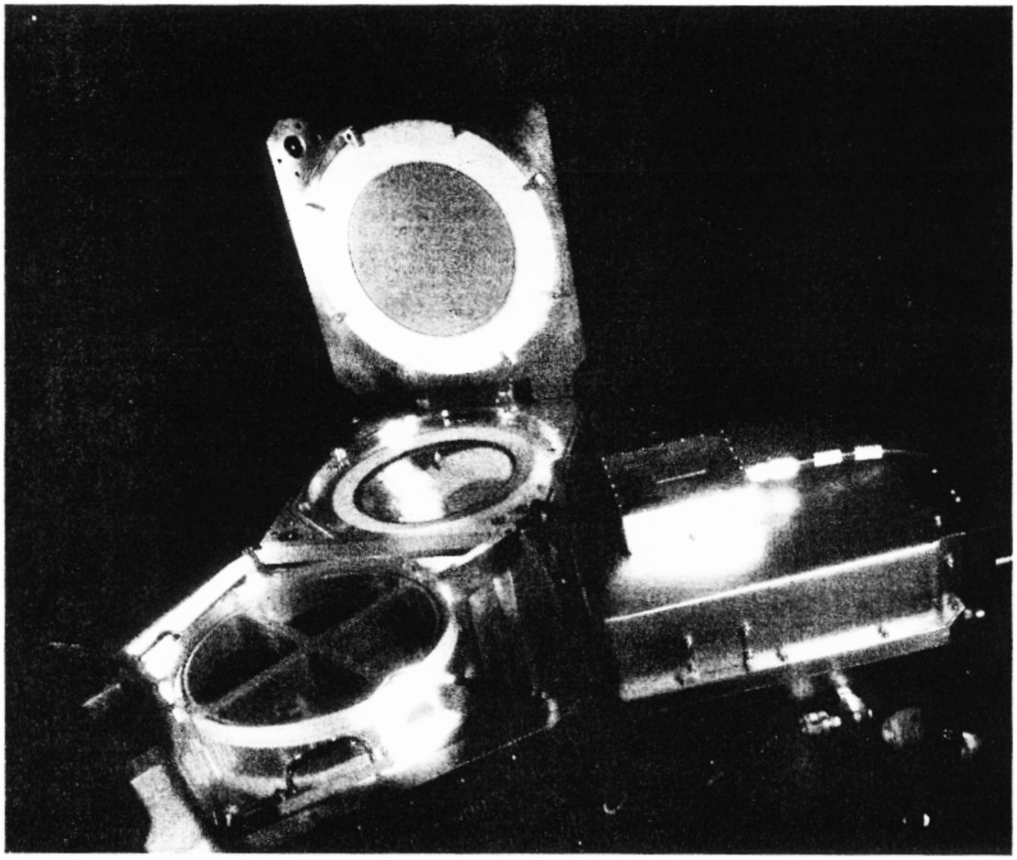


Figure 13-15 A CVD cluster tool showing the central robot and one of the single wafer processing stations *(photo courtesy Applied Materials)*.

CVD Reactor types

- Grouped by pressure: AP & LP
- Then by energy source and chamber
  Hot walls have energy coming from temperature of walls
  Cold wall have other energy sources (eg RF heating)
- Gas distribution method: as second division

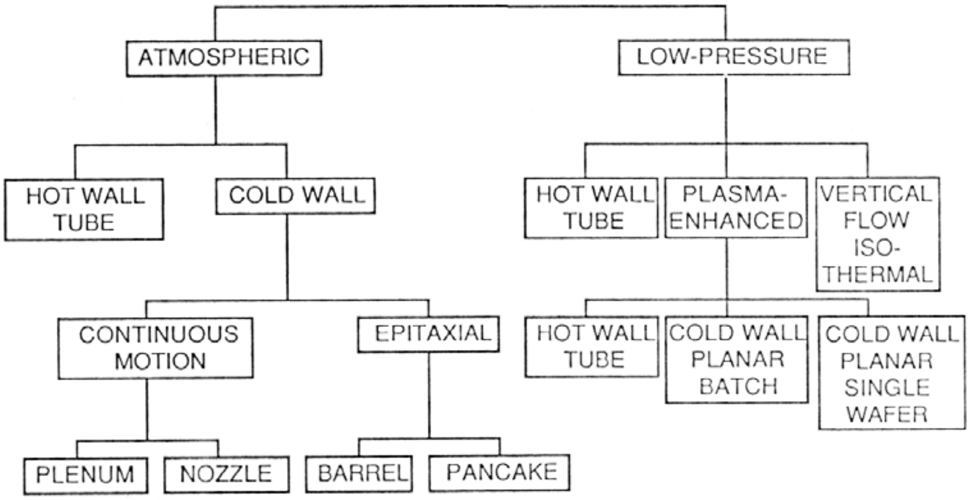
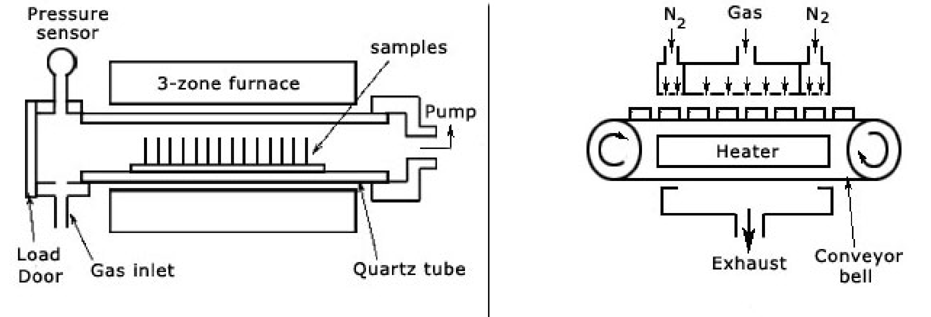


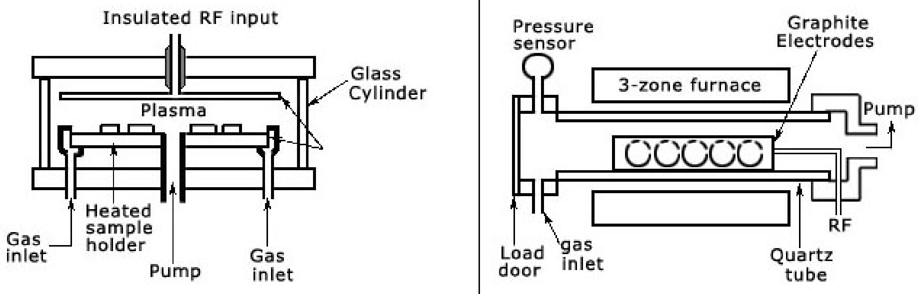
Fig. 4 CVD reactor types.

CVD Reactors



(a) Hot-wall reduced pressure reactor

(b) Coatinuous atmosphene pressure reactor



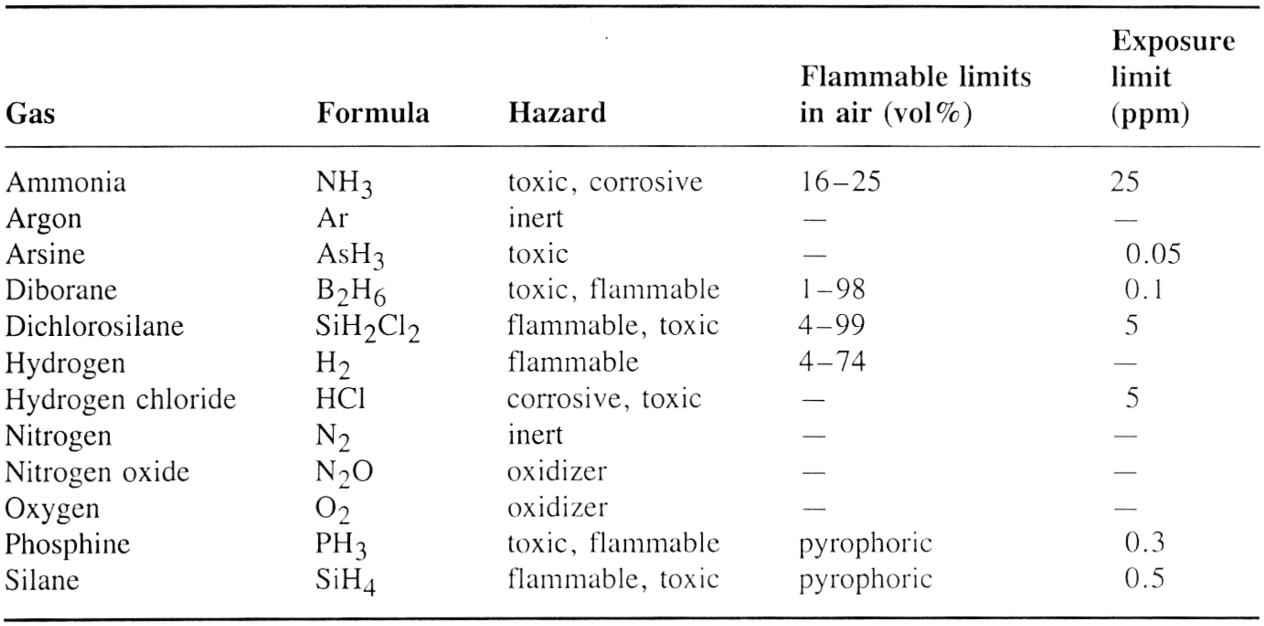
(c) parallel-palte plasma-deposition reactor

(d) hot-wall plasma-deposition reactor

www.CircuitsToday.com

Typical CVD Gases

- Most with important toxic properties
- Must keep sources in gas cabinets (vented to outside
- Piping stainless steel double wall (in case of leak)
- Have gas leak detectors in commercial/large research fabs



Gas	Formula	Hazard	Flammable limits in air (vol%)	Exposure limit (ppm)
Ammonia	NH_3	toxic, corrosive	16–25	25
Argon	Ar	inert	—	—
Arsine	AsH_3	toxic	—	0.05
Diborane	B_2H_6	toxic, flammable	1–98	0.1
Dichlorosilane	SiH_2Cl_2	flammable, toxic	4–99	5
Hydrogen	H_2	flammable	4–74	—
Hydrogen chloride	HCl	corrosive, toxic	—	5
Nitrogen	N_2	inert	—	—
Nitrogen oxide	N_2O	oxidizer	—	—
Oxygen	O_2	oxidizer	—	—
Phosphine	PH_3	toxic, flammable	pyrophoric	0.3
Silane	SiH_4	flammable, toxic	pyrophoric	0.5

Gas Cabinet

Cold Wall CVD

- Induction (RF) heating of graphite plate
- Gas flows over plat – deposits film on substrates
- Issue – up stream wafers get thicker film
- Sometimes tilt plate to reduce this

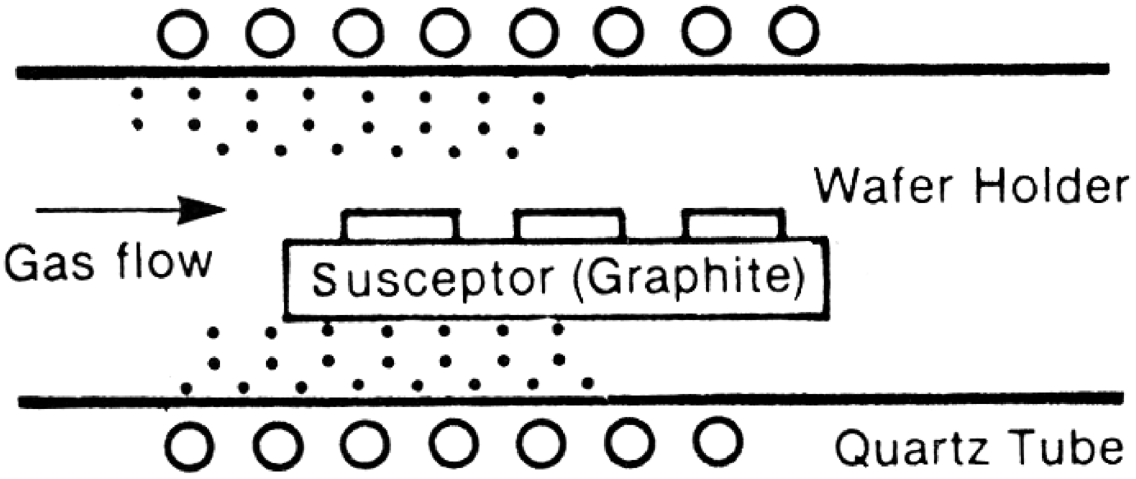


Figure 12.9 Cold-wall induction APCVD with horizontal susceptor.

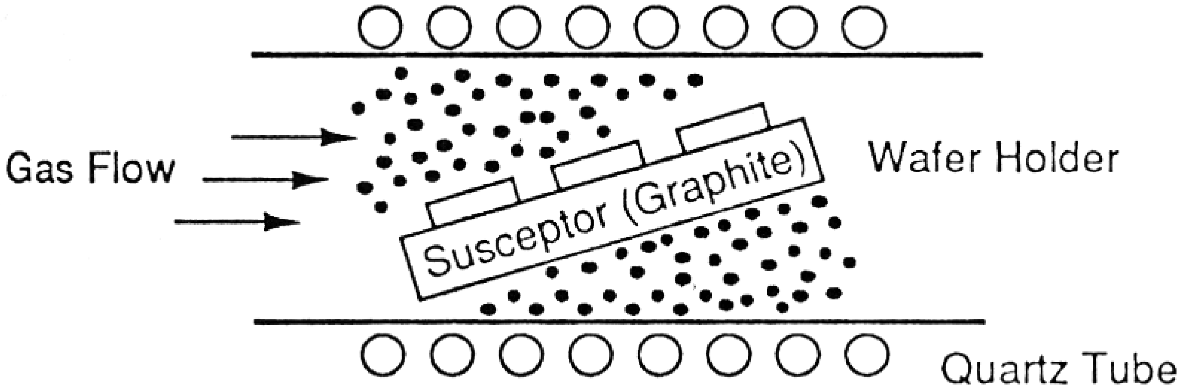
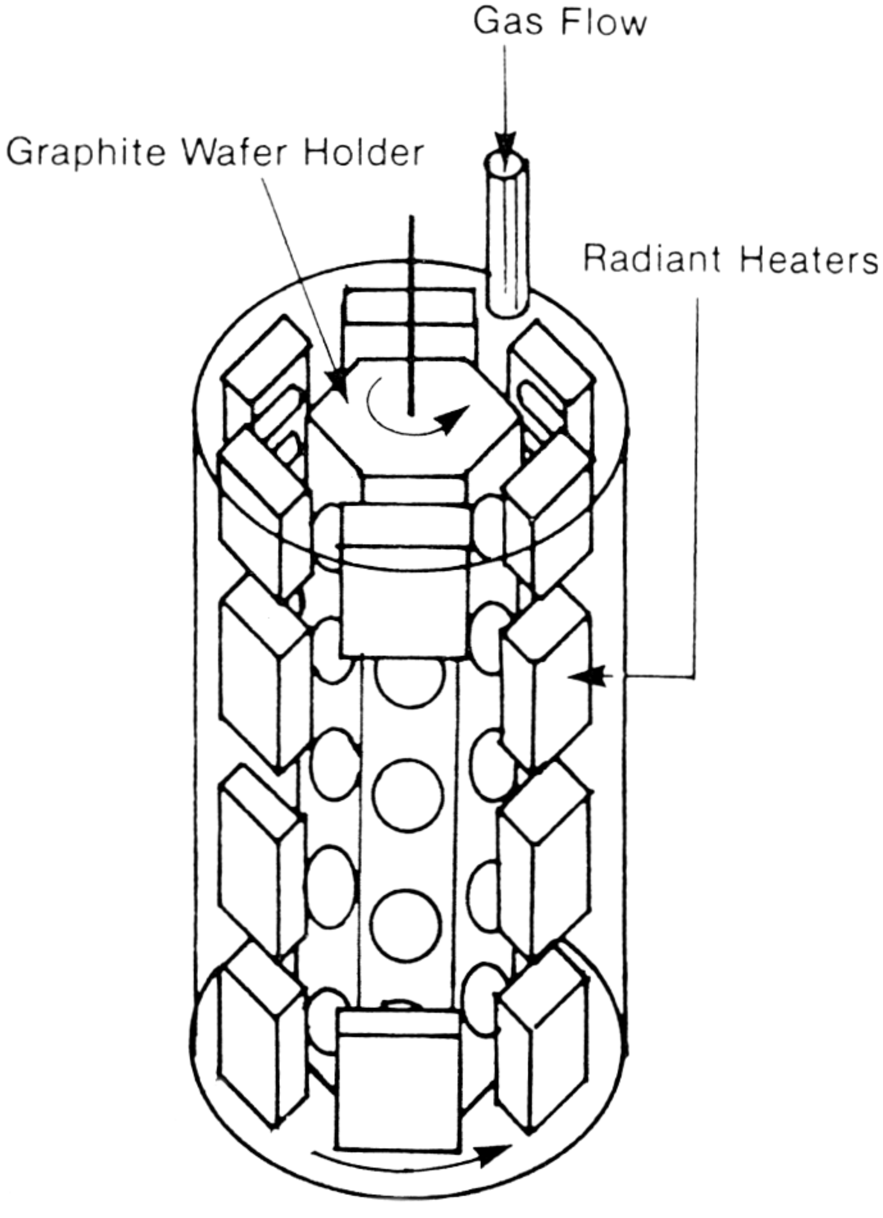


Figure 12.10 Cold-wall induction APCVD with tilted susceptor.

Cylindrical/Barrel CVD Reactor

- Used in large systems
- Wafers mounted on rotating graphite holder
- Heaters on outside



Pancake Air Pressure CVD

- Gas distributed through centre
- Palten rotates to improve uniformity (often a planetary motion)

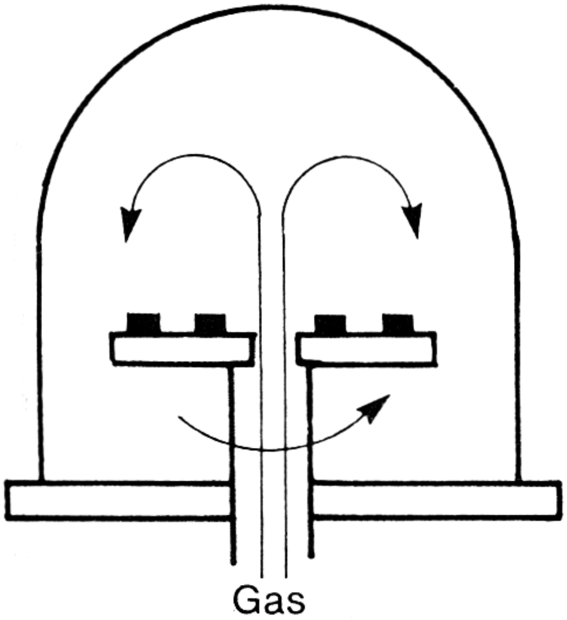


Figure 12.12 Rotating pancake APCVD.

Horizontal Flat Plate CVD

- Plates flat with heaters inside
- Gas flows over plates
- Or Gas distributed with "shower head"

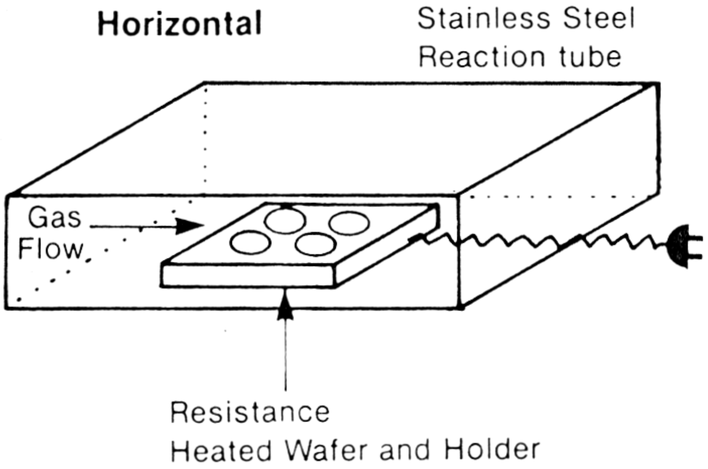
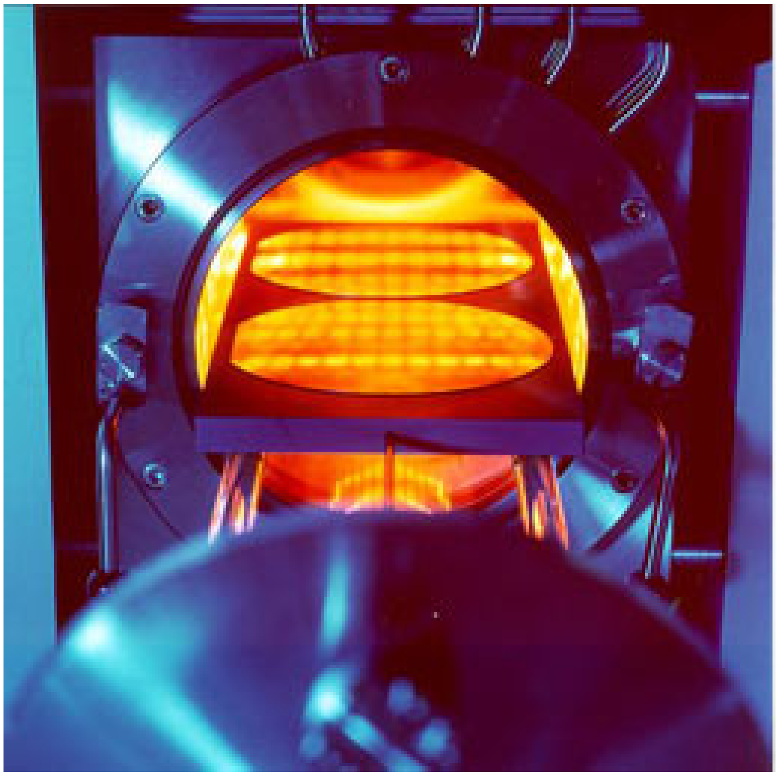


Figure 12.13 Hot-plate APCVD.



Moving Hot Plate Air Pressure CVD

- Move plate for uniform films
- Flat plate moved under shower head
- Continuous belt moved under gas plenum
- Continuous flow of film deposited wafers

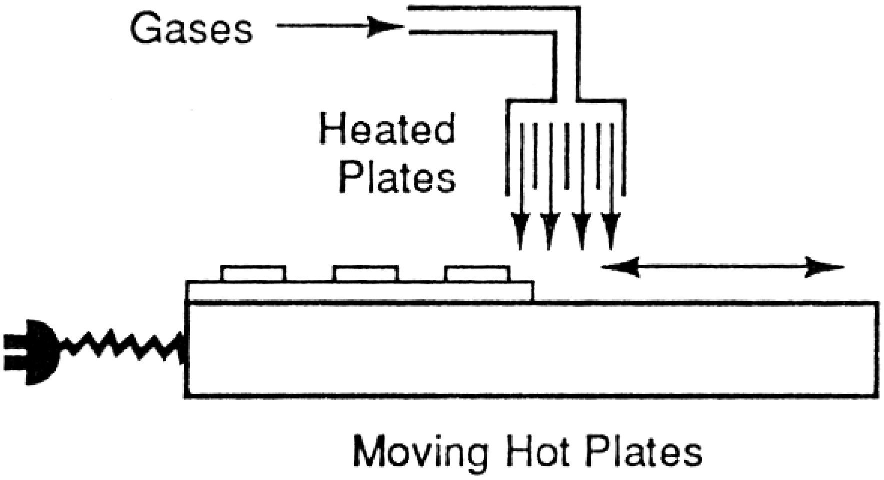
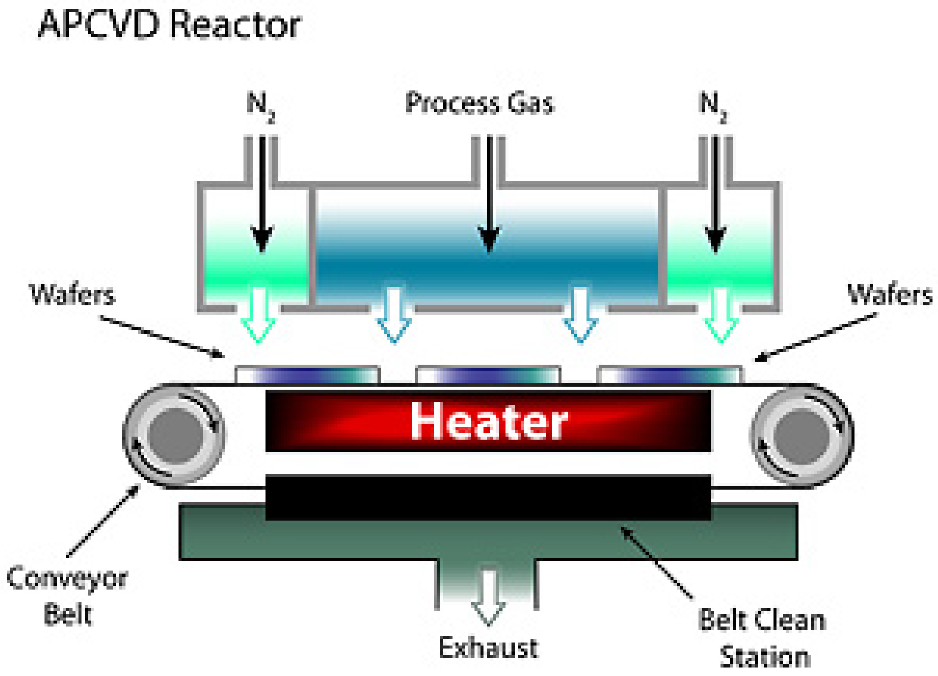


Figure 12.14 Moving hot-plate APCVD with shuttle.



Furnace or Horizontal Tube Low Pressure CVD

- Usually done in furnace tube – hot walled CVD
- Use furnace for temperature
- Must burn and exhaust gases

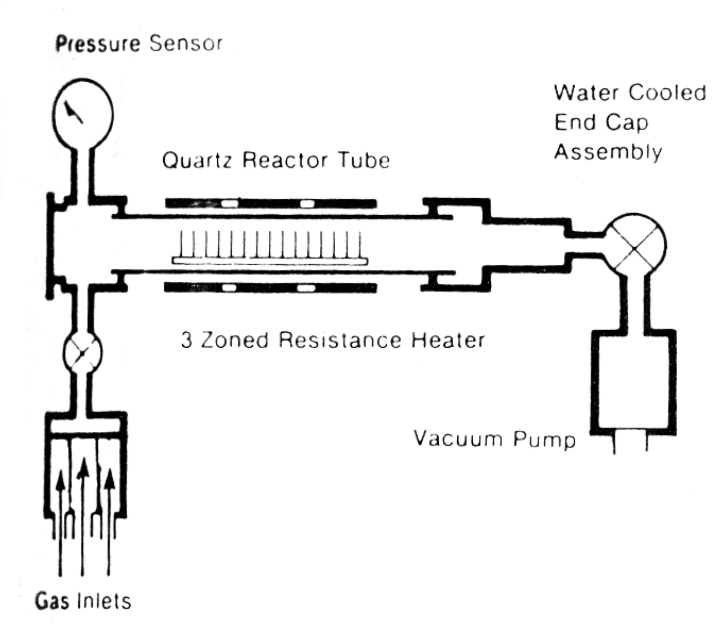
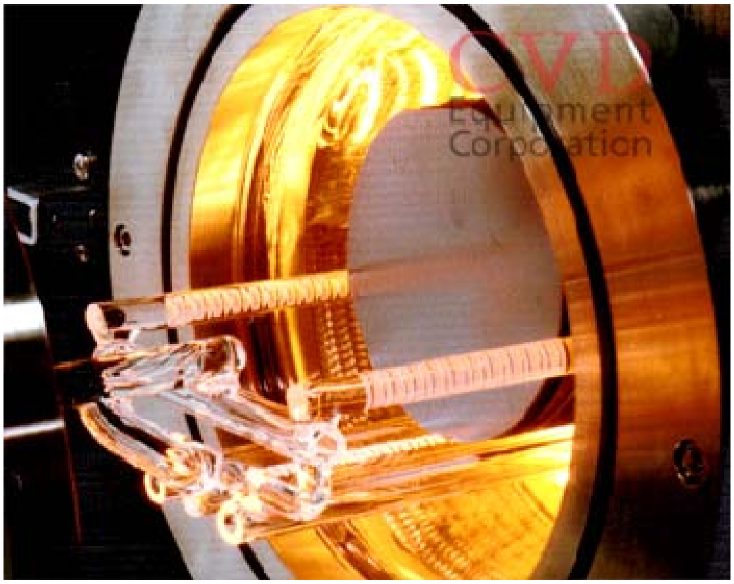


Figure 12.16 Horizontal hot-wall LPCVD system.



Vertical Isothermal CVD

- Use top/bottom heaters for uniformity
- Typically Bell Jar system

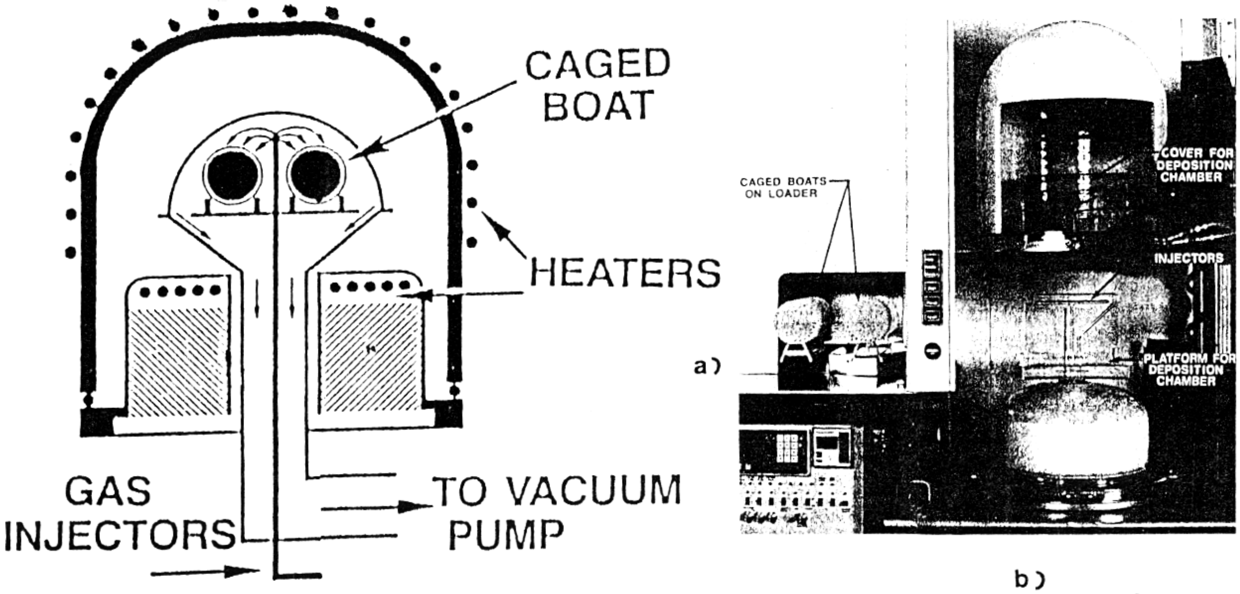


Fig. 7 Vertical isothermal LPCVD reactor. (a) Schematic drawing. (b) Photograph of system. Courtesy of Anicon, Inc.

Large Diameter wafers & Single chamber CVD

- For 150-300 mm wafers go to single chamber
- Hard to make uniform film over such large wafers
- Use single chamger - more control on each wafers

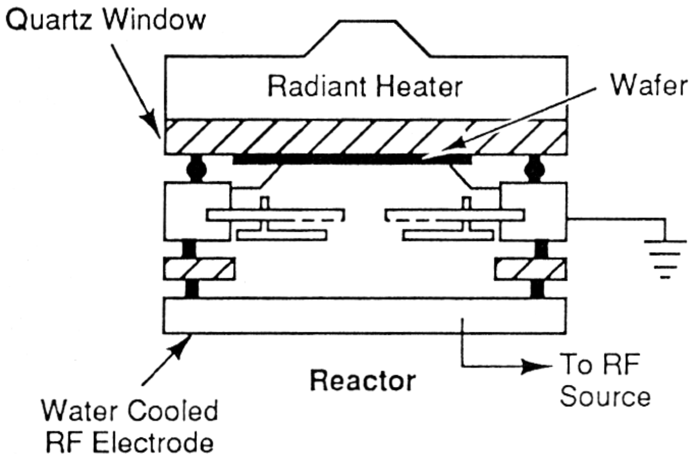


Figure 12.19 Single-chamber planar PECVD.

Plasma Enhanced CVD

- Regular CVD energy (Heat, RF) drives reaction
- At higher energies RF generates plasma in the reactant gas
- Plasma breaks down reactants into ionized gases
- This Plasma Enhanced makes gas much more reactive
- Done at low pressure for plasma (few torr)
- Typical: Vertical Flow pancake (table top) PECVD

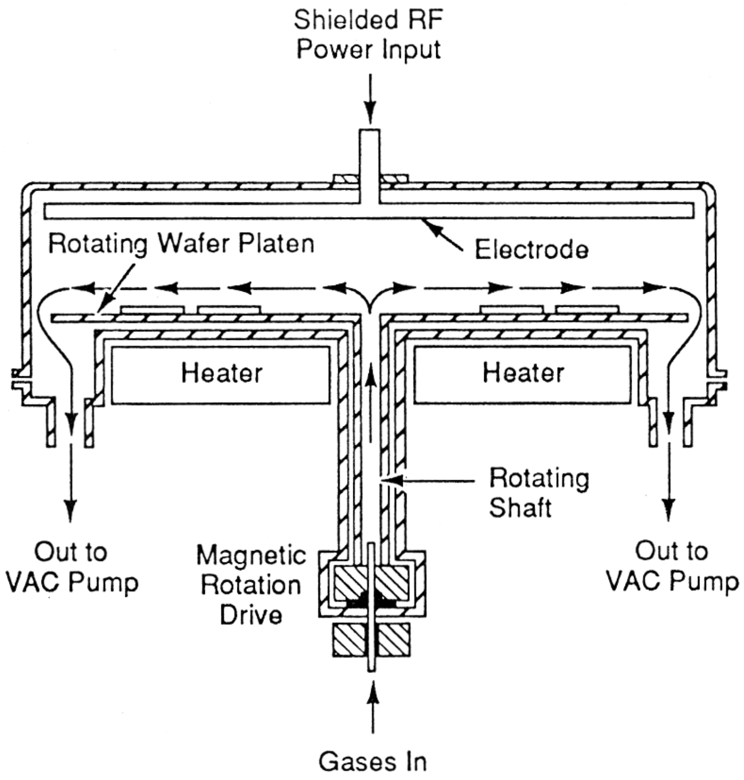
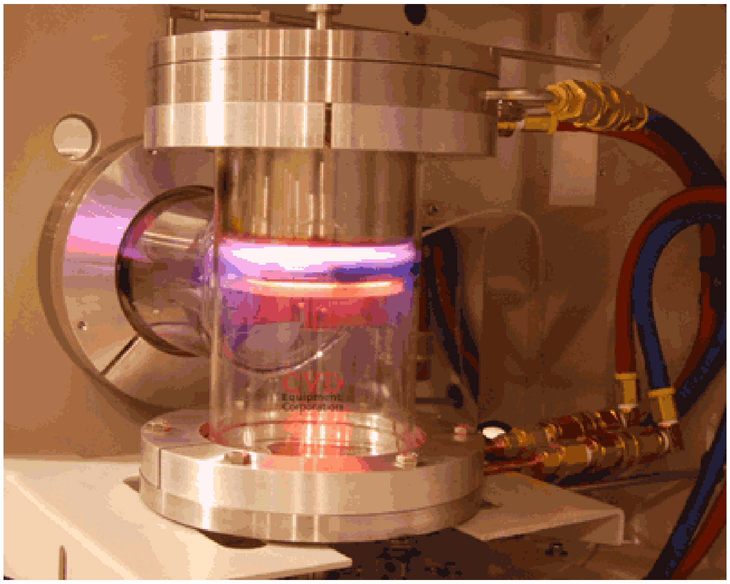


Figure 12.18 Vertical-flow pancake PECVD.



Furnace Tube PECVD

- Use graphite substrate as electrodes
- Wafers between RF antenna
- Use furnace as heater assistance

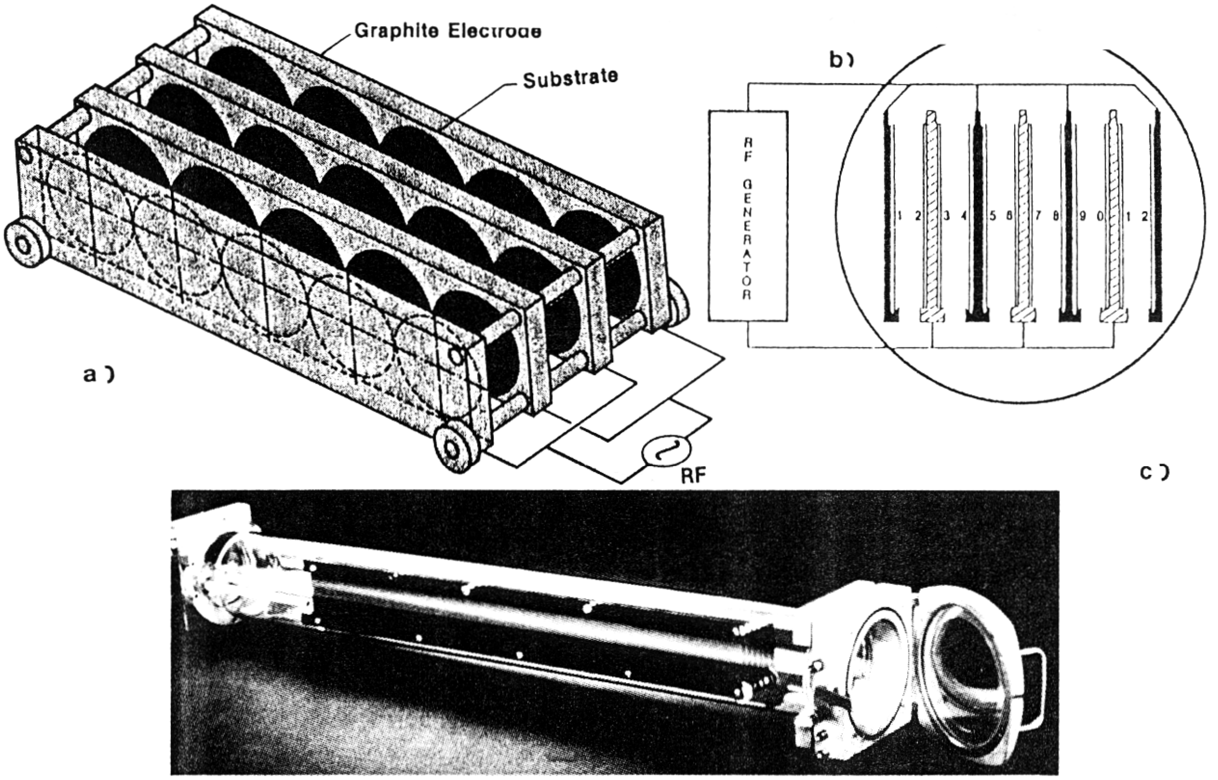
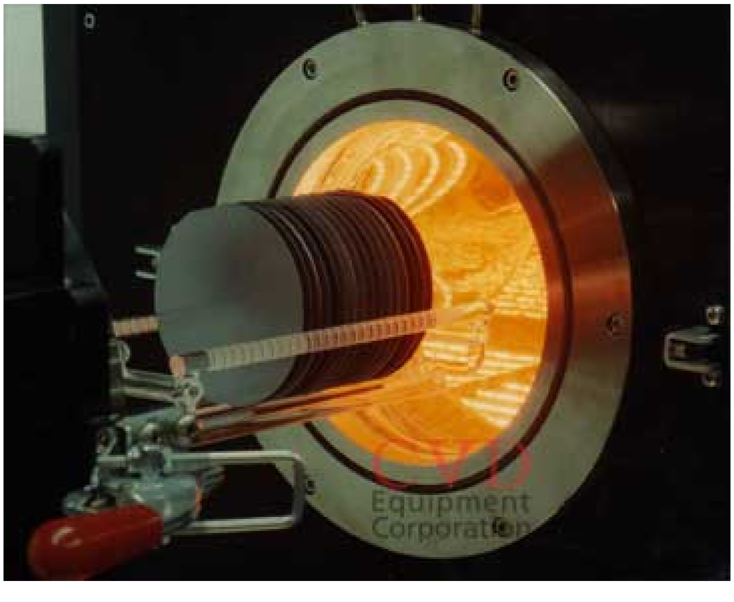


Fig. 9 (a) Long, multiple plate reactor generates plasma between the wafers facing each other on graphite electrodes[14]. (b) Cross section of electrode assembly and wafers shown in (a). Reprinted with permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet. (c) Photograph of tubular PECVD reactor. Courtesy of Pacific Western Systems.



Typical Furnace PECVD system

- Temperature sets crystal size

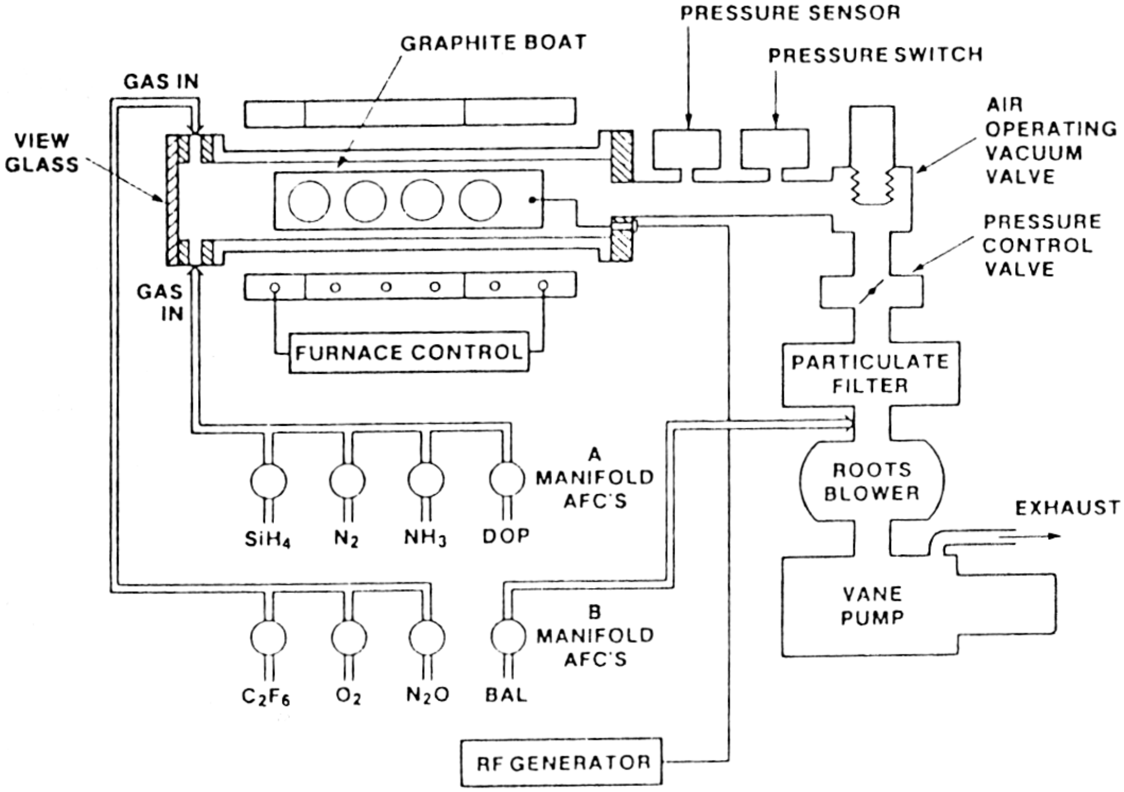


Fig. 2 Diagram of a typical commercial PECVD system. Courtesy of Pacific Western Systems.

Mass Flow Controller

- Need to exactly control gas flow rates – pressure control useless
- Want to control mass of material in gas flow
- Feed back system needed: heats gas, measures temp. change
- Get mass flowing from gas heat capacity

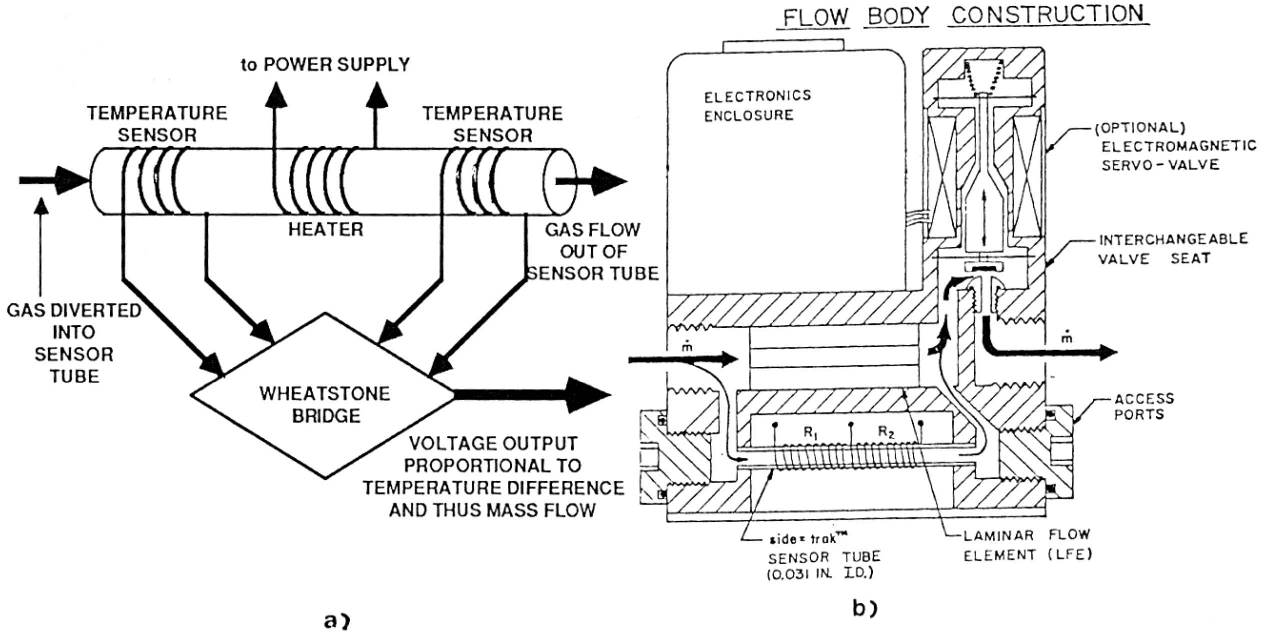


Fig. 3 (a) Operating principle, and (b) cutaway drawing of a mass flow controller. Courtesy of Sierra Instruments.

III-V Compound hot CVD

- III-V device eg LED and laser diodes
- Require many CVD layers of different precise composition
- Use Metal-Organic materials – both hot and cold CVD
- Hot: Use gallium source down stream of substrate
- Flow $AsCl_3$ over Gallium
- Deposit out GaAs
- Laser Quantum Well devices need atomic level thickness control
- Layers only 5 atoms thick

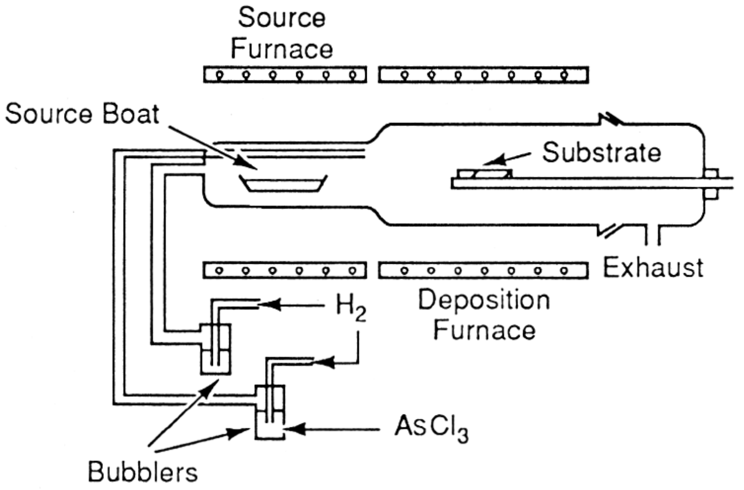


Figure 12.34 Diagram of gallium arsenide VPE deposition system.