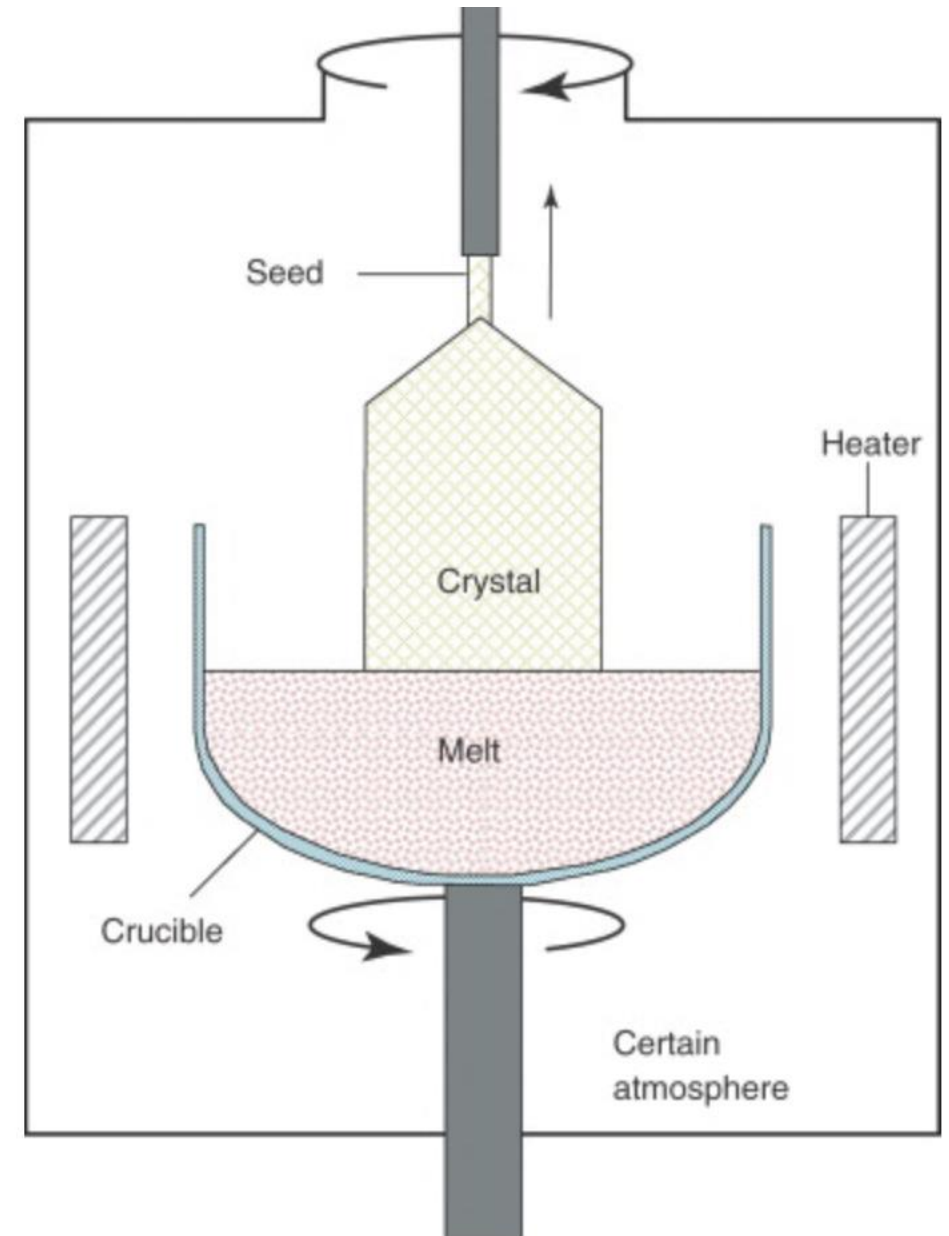
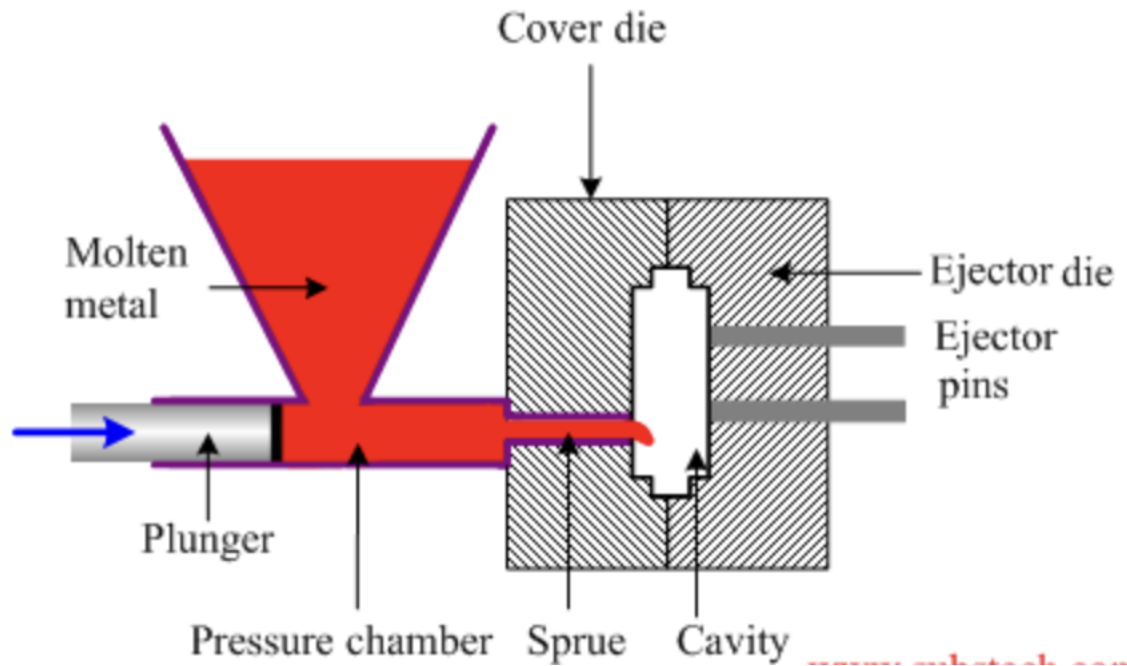
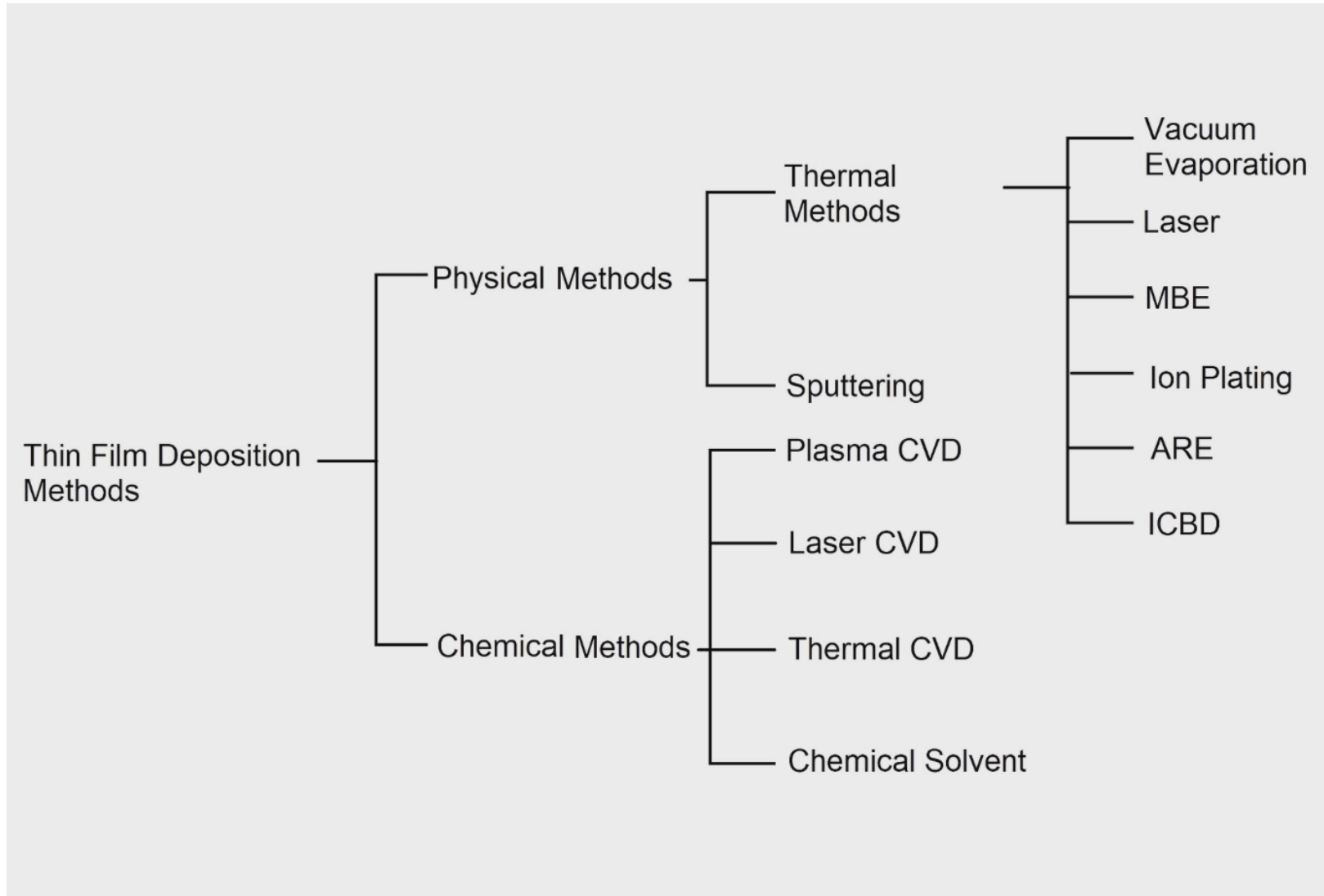


Thin Film Growth Techniques

Bulk growth techniques

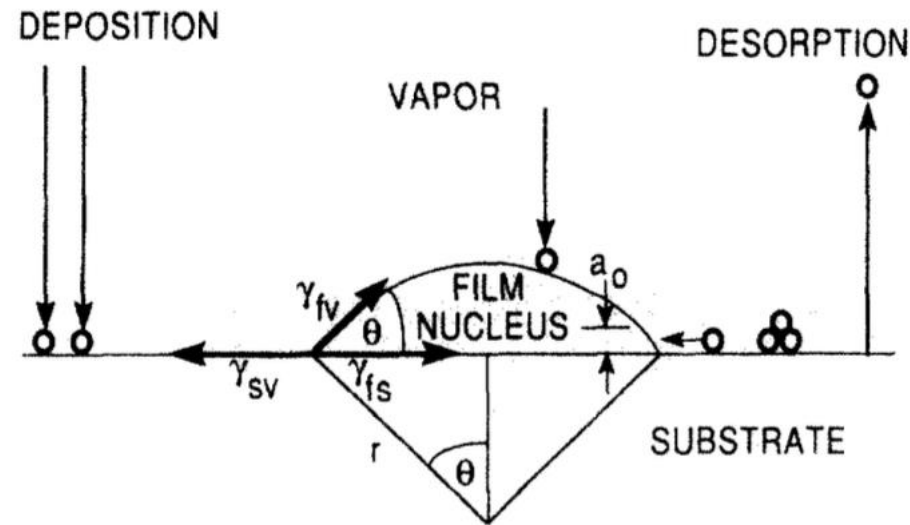
Die casting





Sometimes you don't need bulk films:
Cost effectiveness, functionality

Various processes in a heterogeneous nucleation



$$\Delta G = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{fv} + a_2 r^2 (\gamma_{fs} - \gamma_{sv})$$

Where $a_1 = 2\pi(1 - \cos \theta)$, $a_2 = \pi \sin^2 \theta$ and $a_3 = \frac{\pi}{3}(2 - 3 \cos \theta + \cos^3 \theta)$

Three modes of growth

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta \quad \text{or} \quad \cos \theta = (\gamma_{sv} - \gamma_{fs}) / \gamma_{fv}.$$

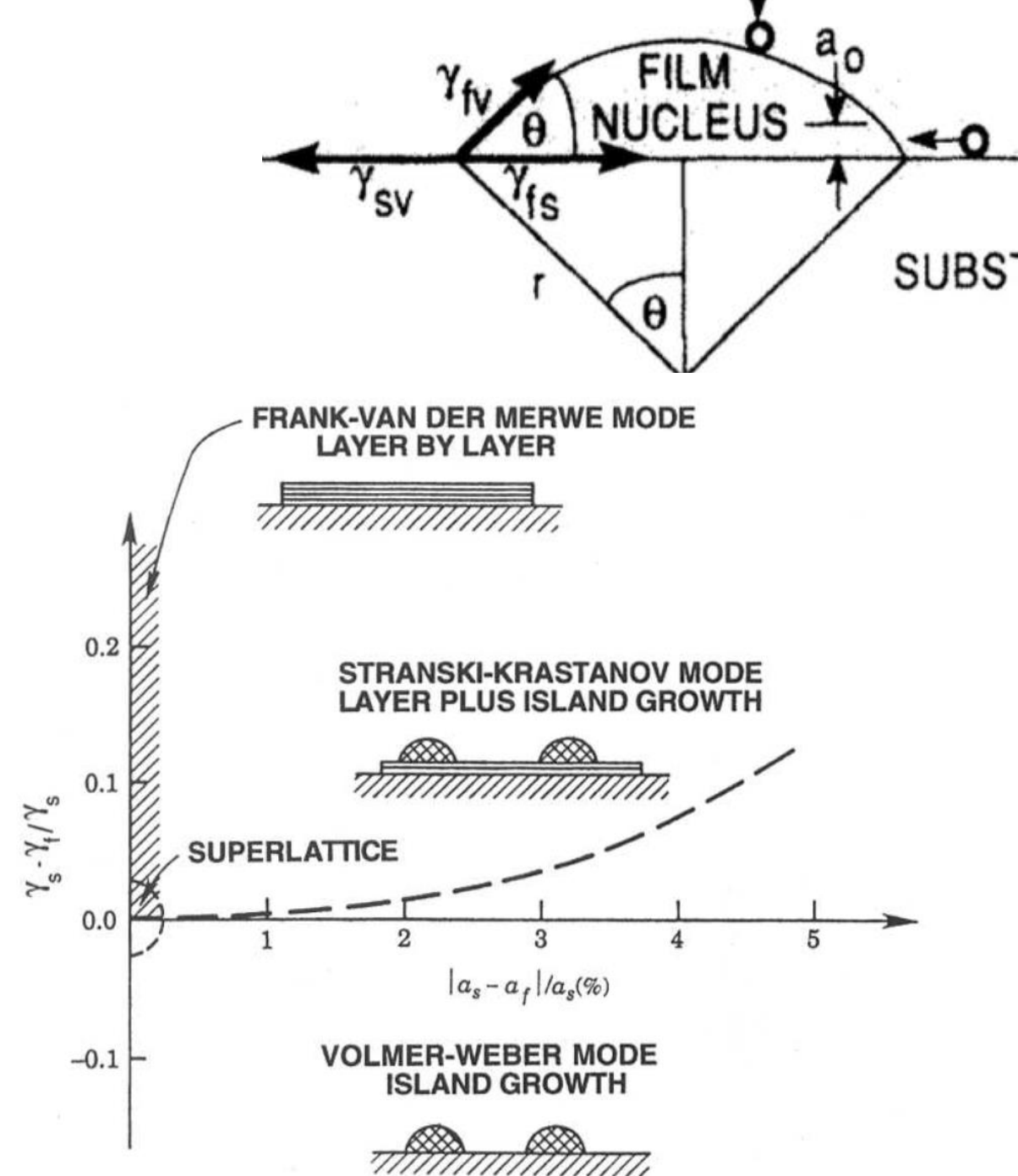
- $\gamma_{sv} < \gamma_{fs}$ Volmer-Weber growth mode

The nuclei balls up and forms a cluster

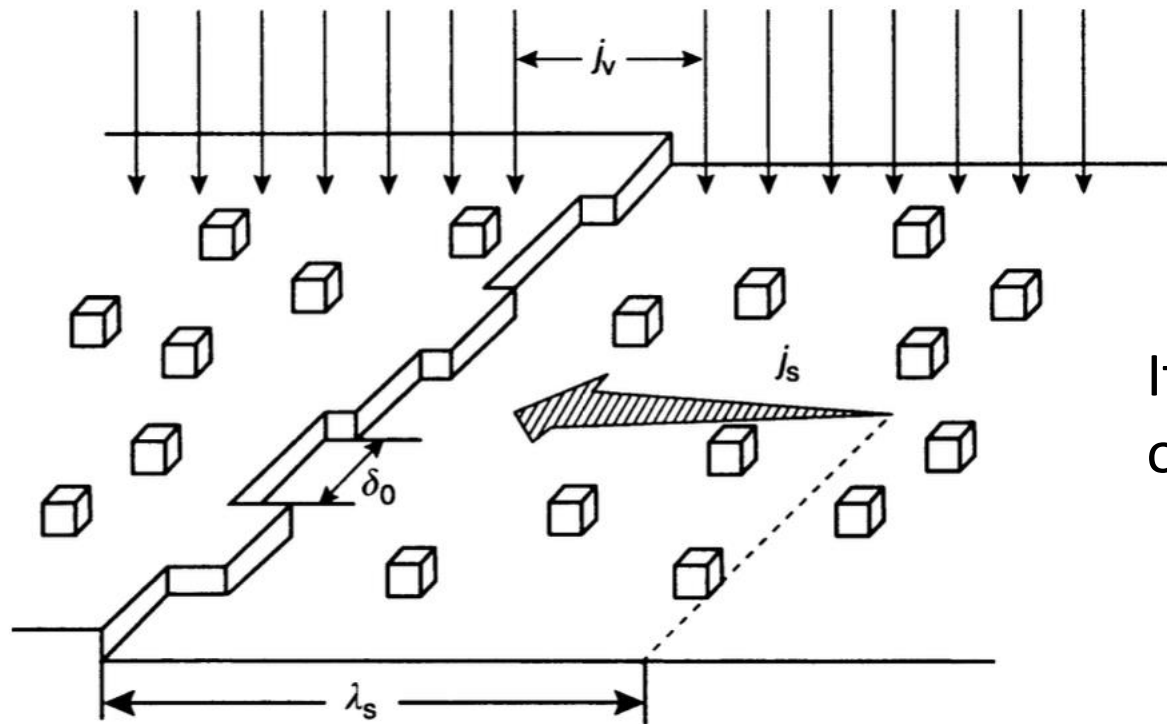
- $\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv}$ Frank-van Der Merwe growth mode

The nuclei completely wets the surface.

- Any intermediate growth (Stranski-Krastanov Mode)



Elementary processes on a surface



1. Adsorption of the adatom on the growth surface

2. Diffusion of the adatom on the surface

3. Incorporation of the adatom at kinks

If τ_s is the mean time of residence of adatom on surface before desorption

$$\tau_s = \frac{1}{\nu_{\perp}} e^{\frac{E^{des}}{KT}}$$

Flux of atoms on the surface

$$R = \frac{P_{\infty}}{\sqrt{2\pi mKT}} \tau_s$$

Distance of diffusion

$$\lambda_s = \sqrt{D_s \tau_s}$$

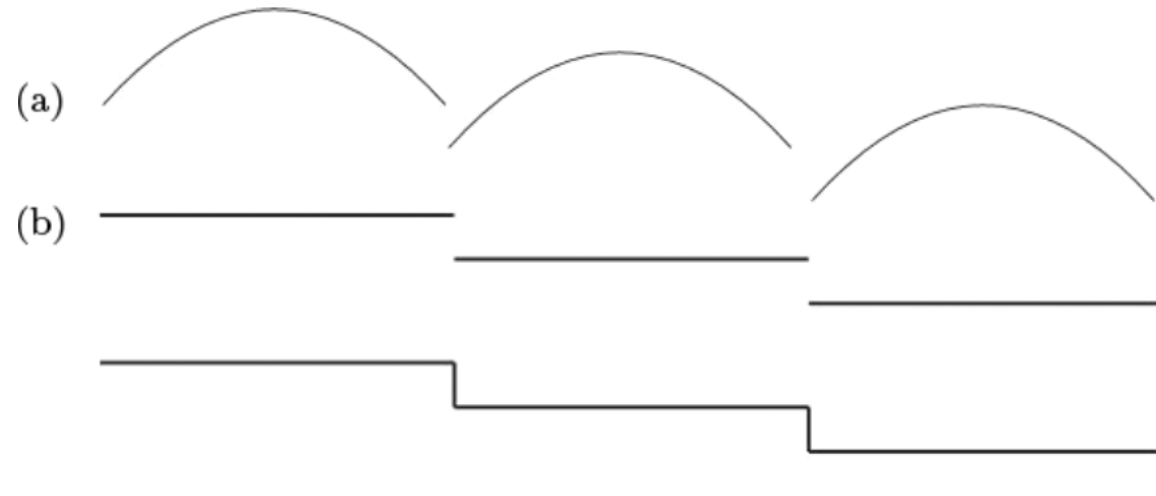
1. Diffusion dominated

$$\text{If } \frac{D_s}{\lambda_s} \ll \beta_{st}$$

The diffusion is so slow, the steps are curved!

2. Kinetic dominated

The adatom adsorption is the slowest! The diffusion is fast. In this case, the adatoms very quickly move to the growing island leading to flat surfaces and terraces.



Introduction of Vacuum systems

Most thin film deposition systems require vacuum systems

In a container containing N molecules of an ideal gas

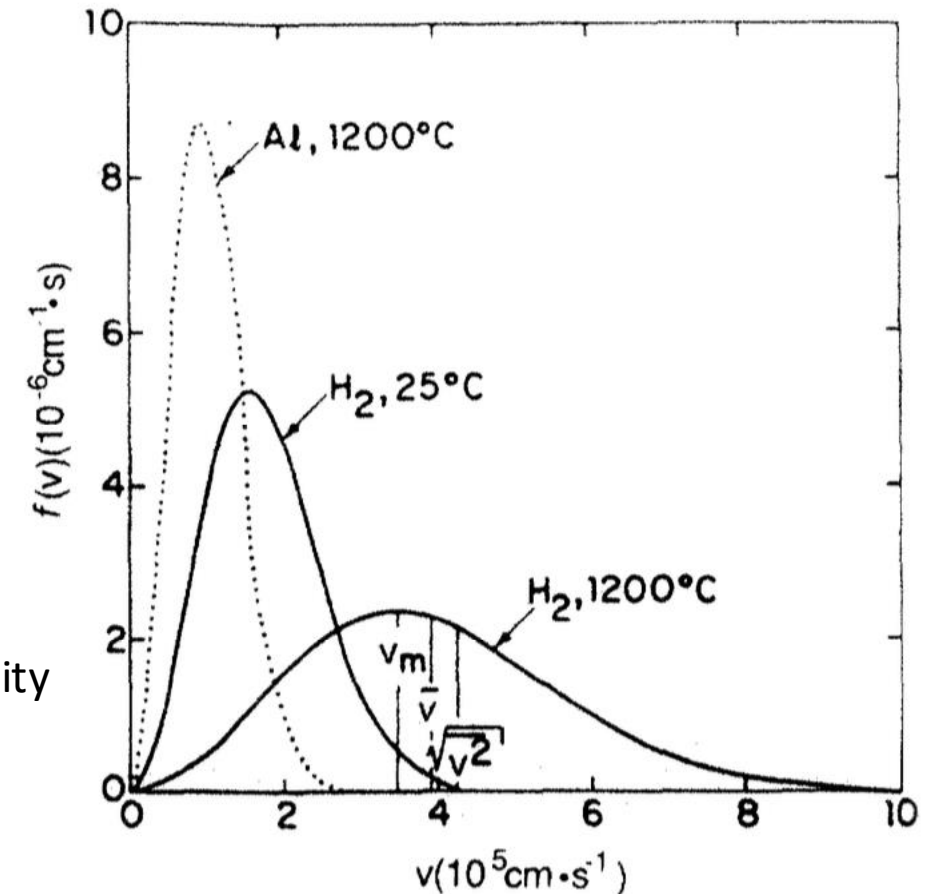
The fraction of molecules with velocity v is : $f(v) = A e^{-\frac{Mv^2}{RT}}$

And the constant of proportionality: $A = \frac{4}{\sqrt{\pi}} \left(\frac{M}{2RT} \right)^{\frac{3}{2}}$

The root mean square of velocities turns out to be $\sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}}$

The system pressure (force applied on the walls) depends on mean sq. velocity

$$P = \frac{n}{N_A} RT = \frac{n}{N_A} \frac{M \bar{v}^2}{3} \text{ where } \frac{n}{N_A} \text{ is the number of moles}$$



Most crucial parameter:

Take a arbitrary surface, number of molecules that impinge on the surface:

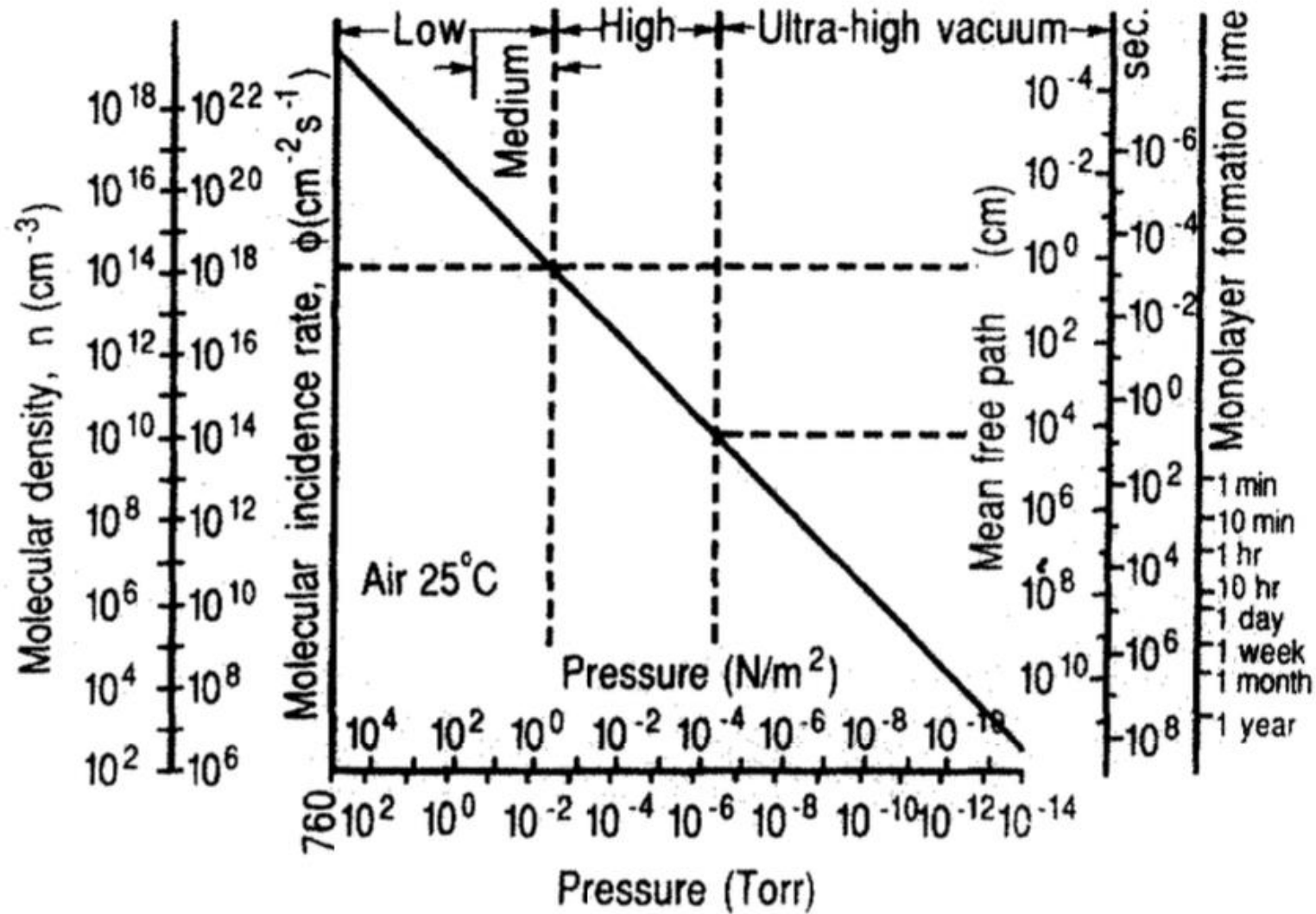
$$\frac{\phi}{N_A} = \int_0^\infty v_x dn_x$$

Assuming a simplified, one dimensional velocity, a wall perpendicular to the x-direction

Flux rate is

$$\frac{\phi}{N_A} = \frac{P}{\sqrt{2\pi MRT}} \text{ moles/cm}^2\text{s.} = 3.51 \times 10^{22} P/(MT)^{1/2} \text{ molecules/cm}^2\text{s}$$

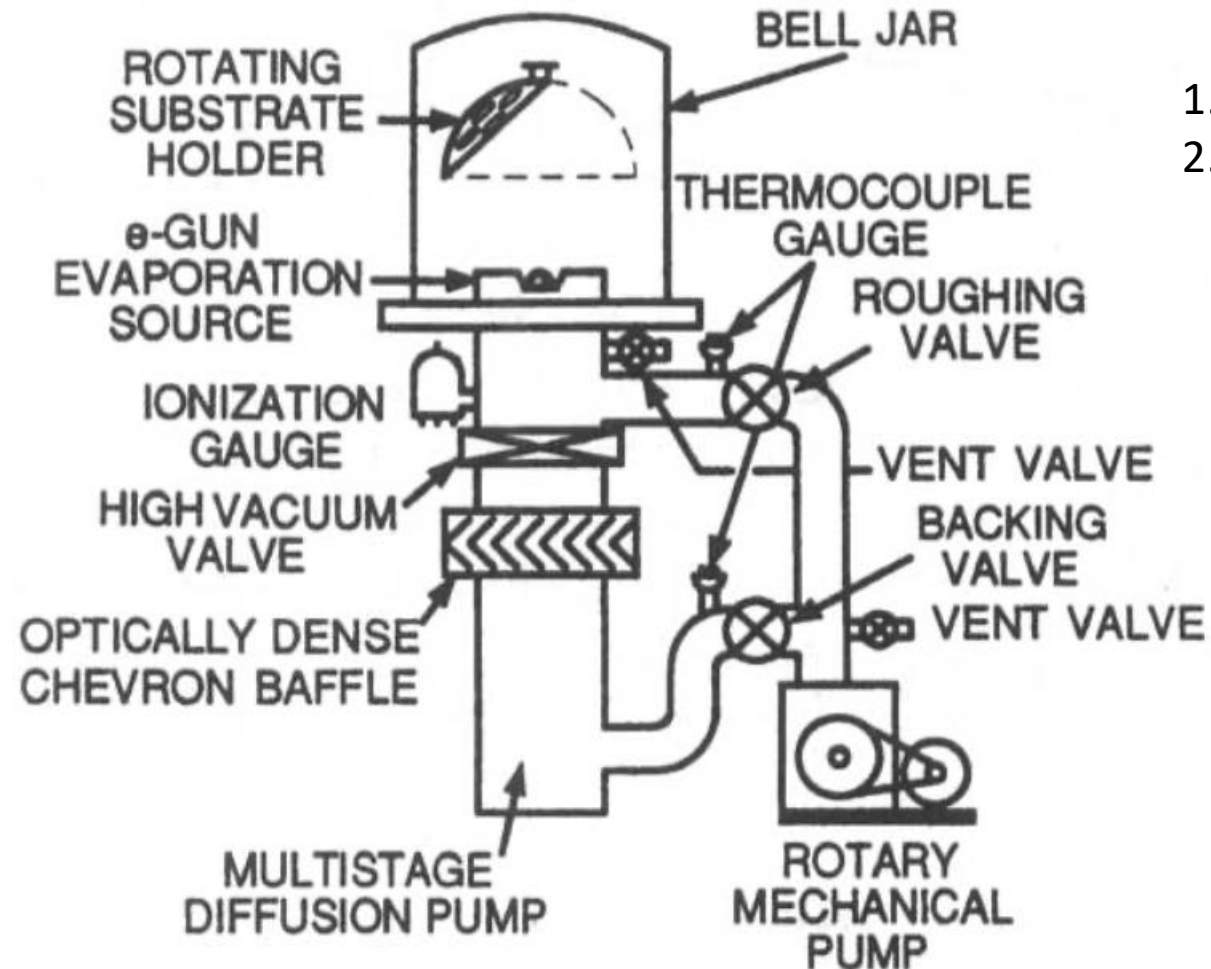
How long does it take to form a monolayer of atoms ?



Typical components of a vacuum deposition system

Steps to develop vacuum:

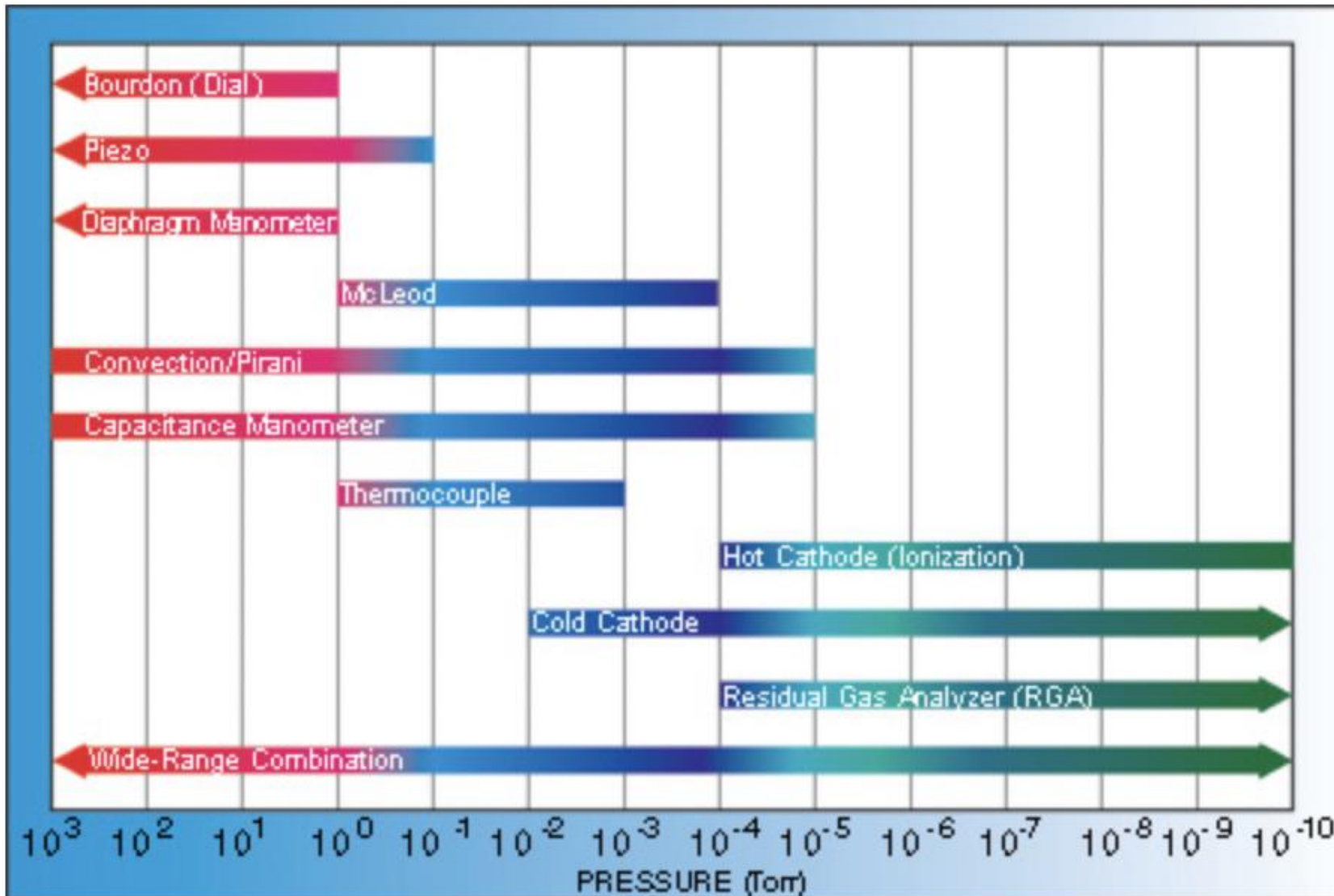
1. Use the rotary pump to generate a 'tolerable' vacuum of < 1 mBar
2. Roughing valve is closed, high vacuum pump is made operational.



Homework: Give a detailed 1 page write up on each of types of vacuum pumps listed below:

1. Rotary vane
2. Diffusion
3. Turbo molecular
4. Sputter Ion pump

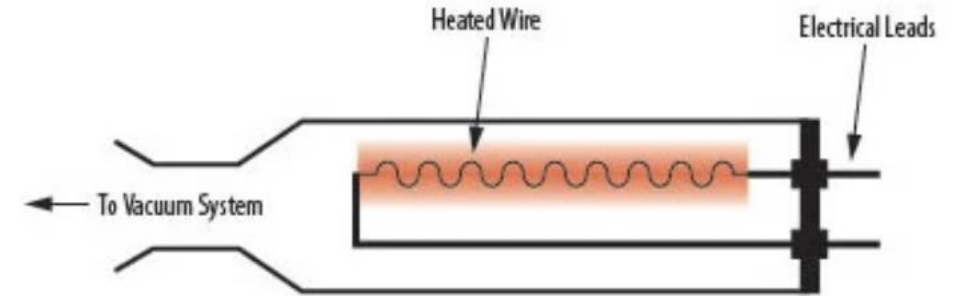
Pressure measurement systems



Indirect measurement (Pirani gauges)

Operational principle:

Convection heat transfer is proportion to pressure of ambient gas



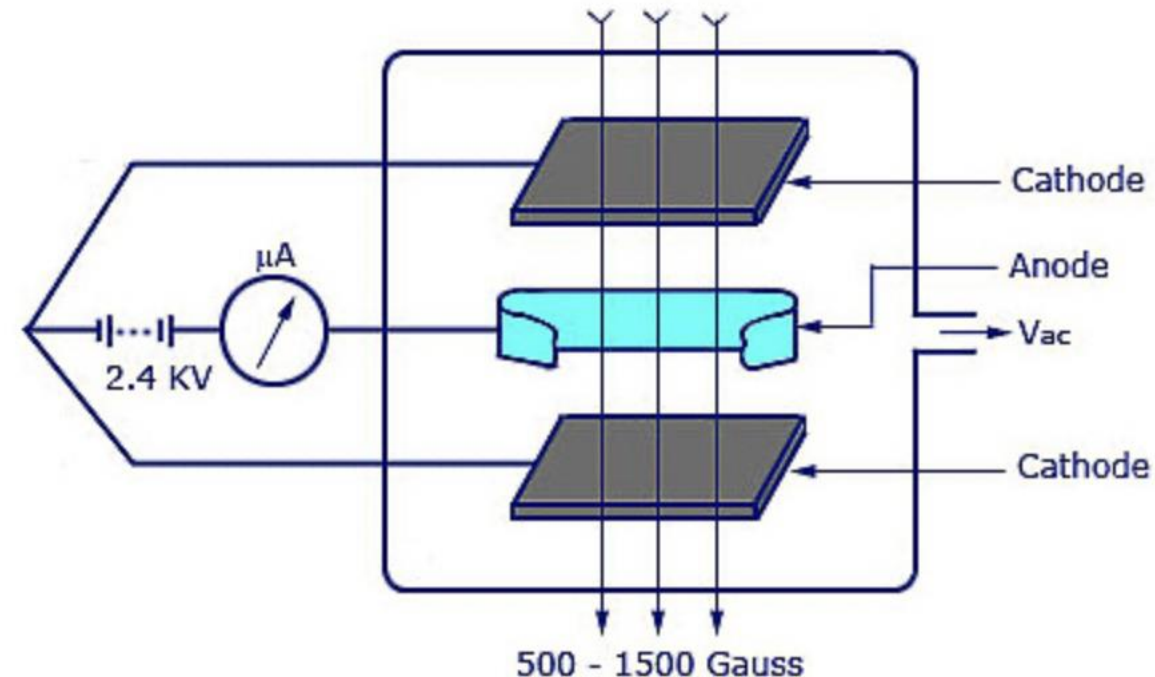
Only limited pressure ranges as the heat conduction at low pressures is not enough to measure any thermal losses

Indirect measurement (Penning gauges) Ion Gauges

A cathode ray is accelerated to anode to ionize.

The ions are then collected by additional cathode.

The ion current is linearly related to pressure of the gas!



Various thin film deposition techniques

- Most commonly employed thin film techniques
 - Evaporation (Thermal and electron beam)
 - Ion beam sputtering
 - Pulsed laser deposition
 - Chemical vapor deposition techniques

Thermodynamic equilibrium of interfaces

- Any interface (Solid-Vapor or Liquid-Vapor)

Clausius-Clapyeron equation: $\frac{dP}{dT} = \frac{\Delta H(T)}{T\Delta V}$

Assumptions:

1. $\Delta V = V_g - V_s \cong V_g$ (solids and liquids have much smaller volume than gas)
2. If we are near the melting temperature

$$\Delta H = H_G - H_L = \Delta H_e \text{ (Latent heat of evaporation)}$$

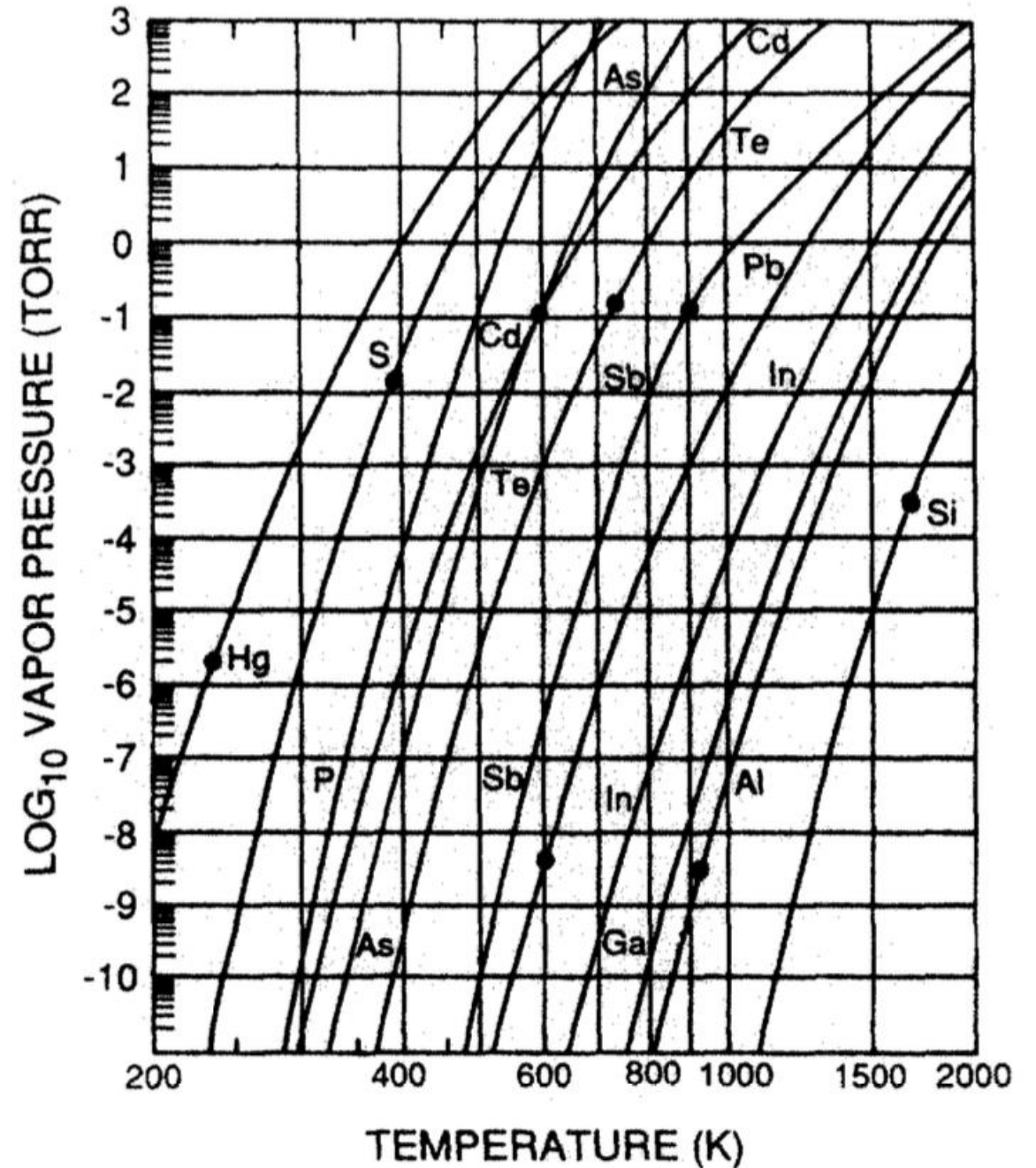
If we assume ideal gases,

$$\frac{dP_G}{dT} = \frac{P_G \Delta H_e}{RT^2}$$

$$V_G = RT/P_G$$

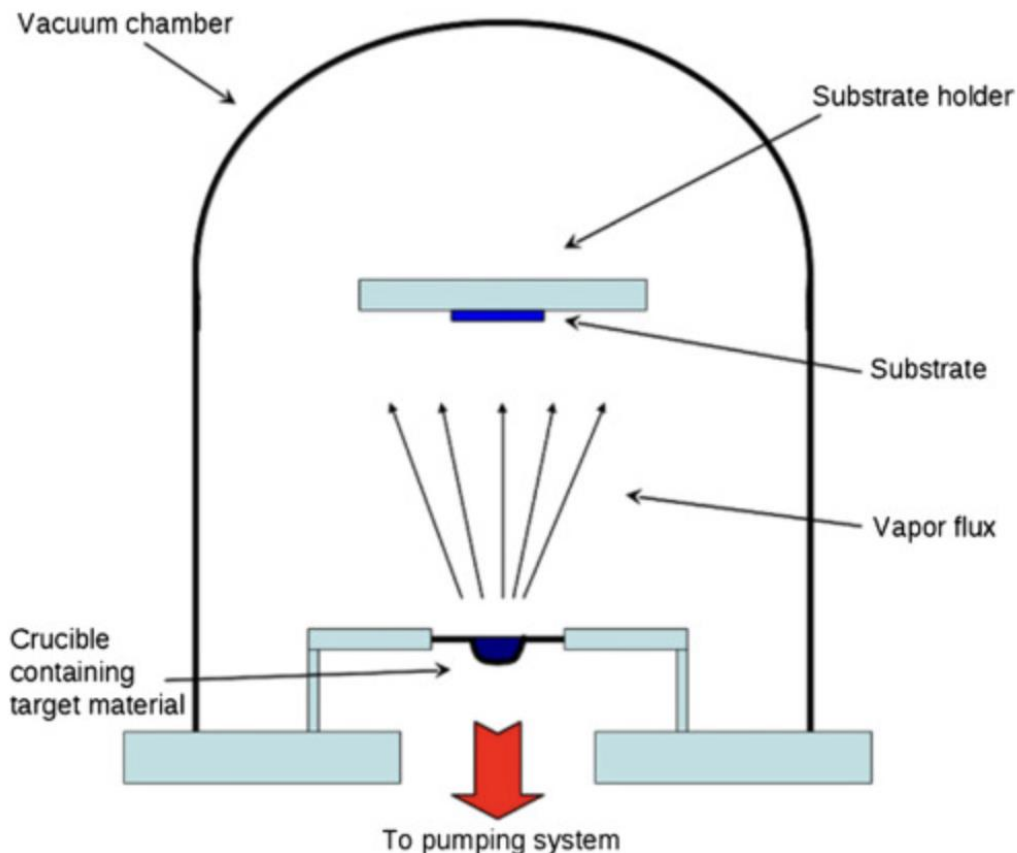
Upon integration

$$P_G = P_0 e^{-\frac{H_e}{RT}}$$



Physical vapor evaporation processes

Thin film deposition by evaporation



Simplest physical deposition process:

Increase vapor pressure of the material (by heating)

1. Thermal evaporation:

Target material heated by resistive heating.

Adv: simplest design.

dis: Crucible contamination, very high temperature required for high melting point materials

2. Electron beam evaporation:

Target material heated by focused electron beam

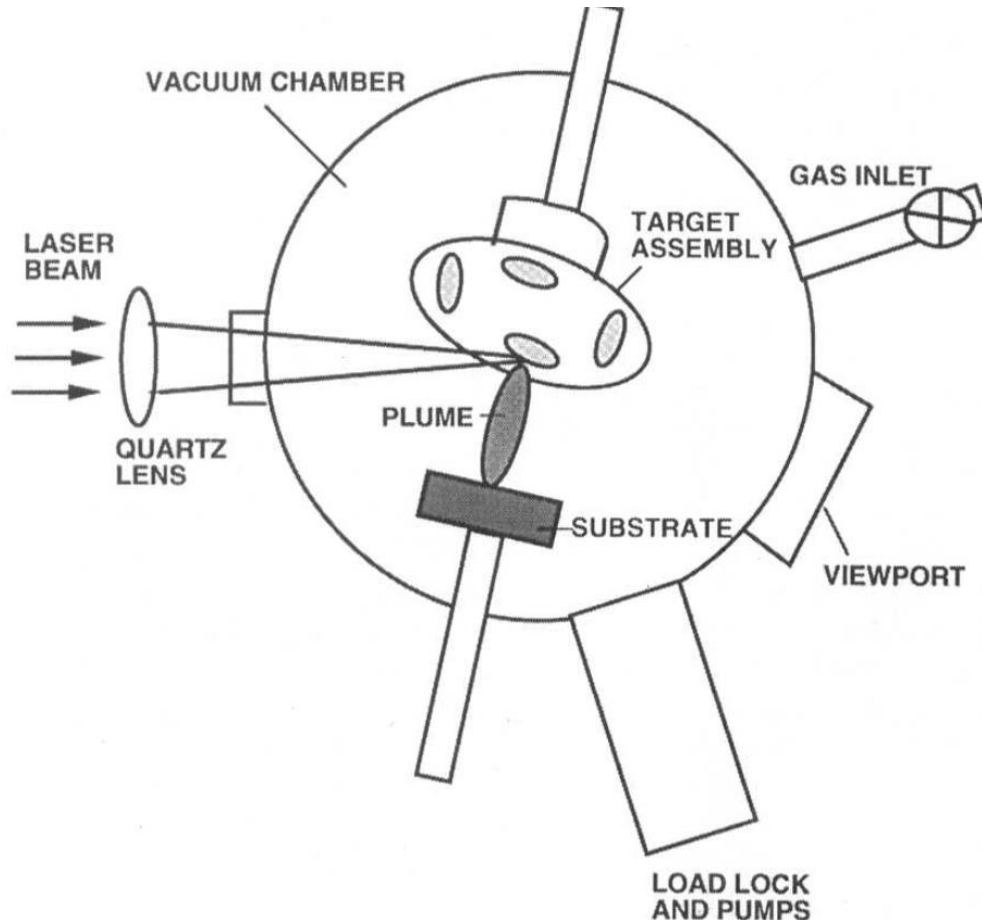
Crucible water cooled.

Adv: Any material can be evaporated.

Only small amount of material is evaporated.

disadvantage: Complex instrumentation, ionization of target material, generation of X-rays that can harm the deposited material

Pulsed laser deposition system



Material is heated by pulsed lasers.

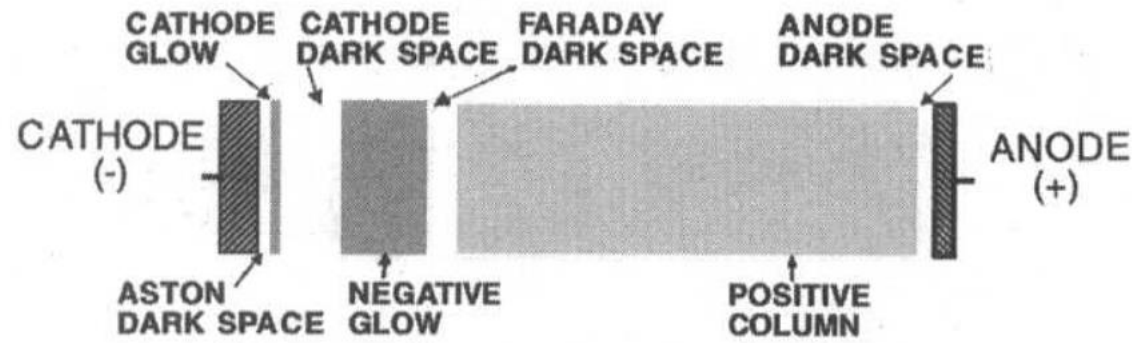
1. UV lasers are employed that most materials absorb.
2. Intense pulsed energies $> \text{J/pulse}$ are delivered to focused spots.
3. Eg: Gas excimer lasers ArF(193 nm), KrF(248 nm)

Evaporated atoms form a plume of energetic neutral atoms, molecules, ions, electrons, molten droplets

Because of high pulse energies of the laser, several unit cells of the target material is evaporated simultaneously.

This gives stoichiometric deposition of complex ceramics

Plasma based sputtering techniques



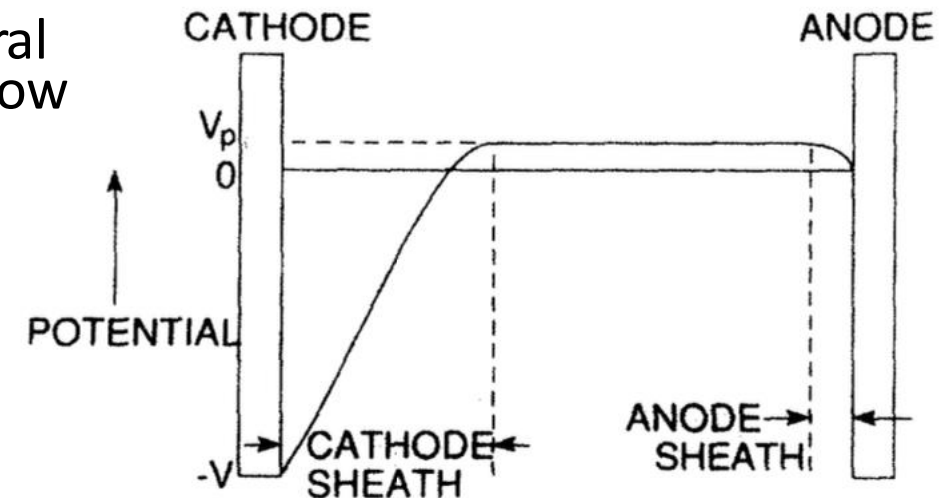
- Basic parts of any plasma system

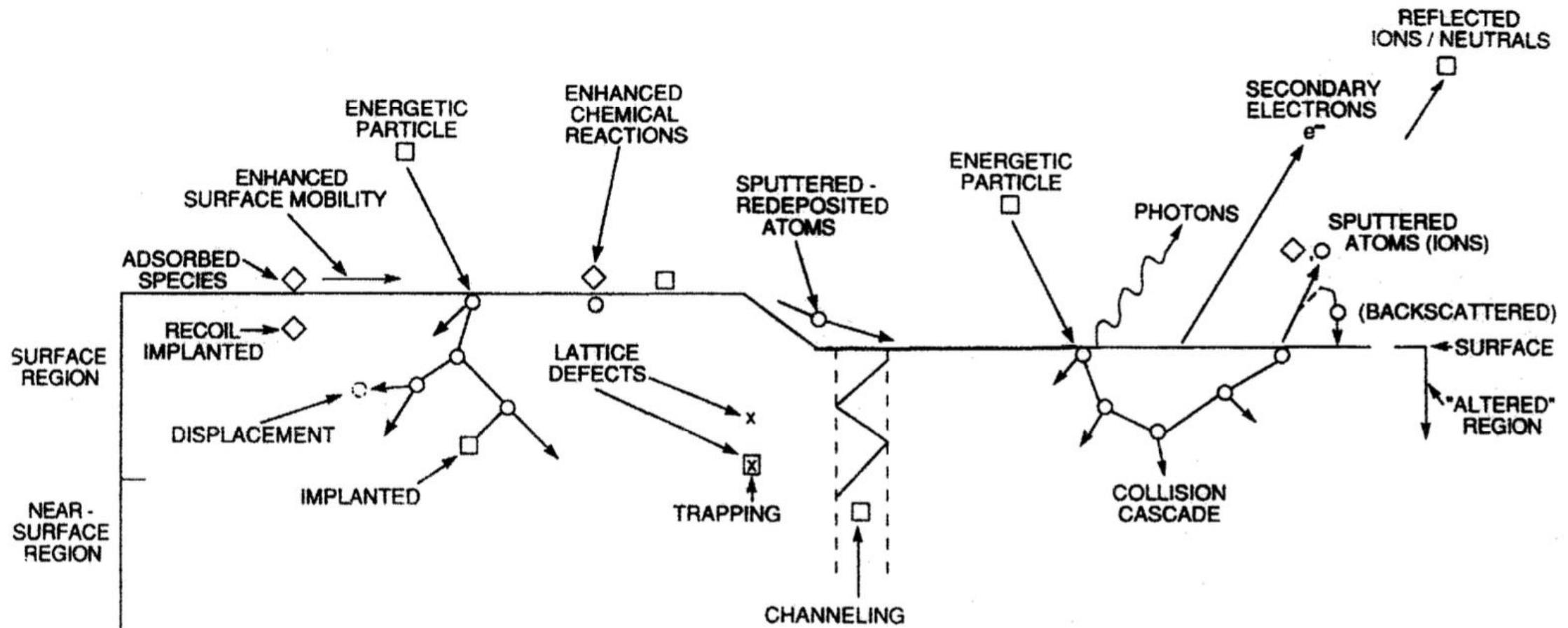
- A strong DC bias, leads to cathode rays (electrons ejected from negative terminal)

- As the electrons gain energy, they start to ionize neutral atoms, which also recombine later on to give you the plasma glow (negative glow)

- The positive ions are accelerated to cathode

- Close to the cathode, they recombine give you the cathode glow.





- Processes in sputtering growth

Ions from plasma incident on the surface

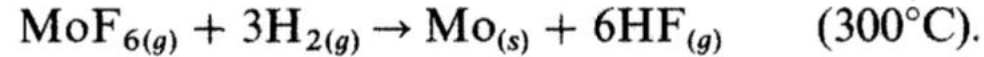
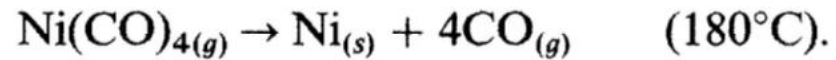
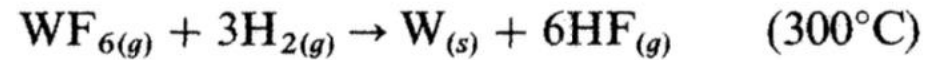
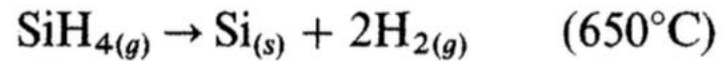
Sticking probability depends on the energy of the ion.

Low energy ions are resputtered back. Very high energy atoms bounce back.

Those atoms that stick, move and form the thin film.

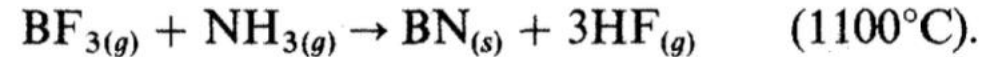
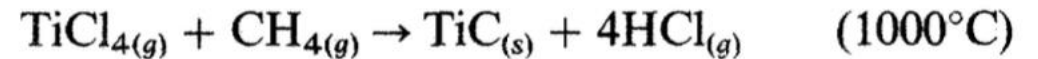
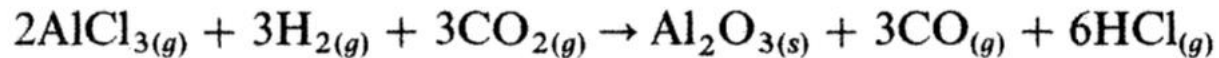
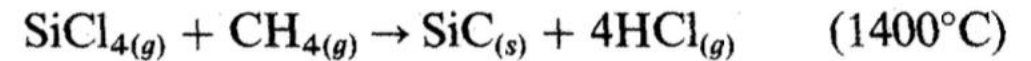
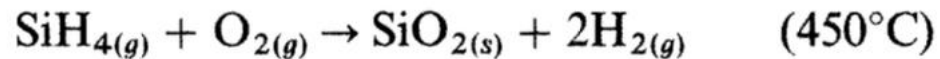
Chemical Vapor Deposition

- Examples of chemical reactions:



Pyrolysis

Reduction

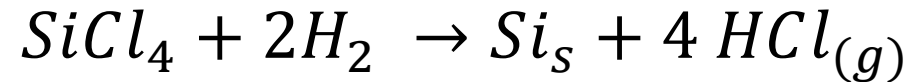


Oxidation

Compound formation

Thermodynamics of Chemical Equations

Say we want to deposit Si using the following equation:



At any temperature : $\Delta G = \Delta G^0 + RT \ln K$

At an elevated temperature, it is known that the $\Delta G^0 = -51\text{kJ/mol}$

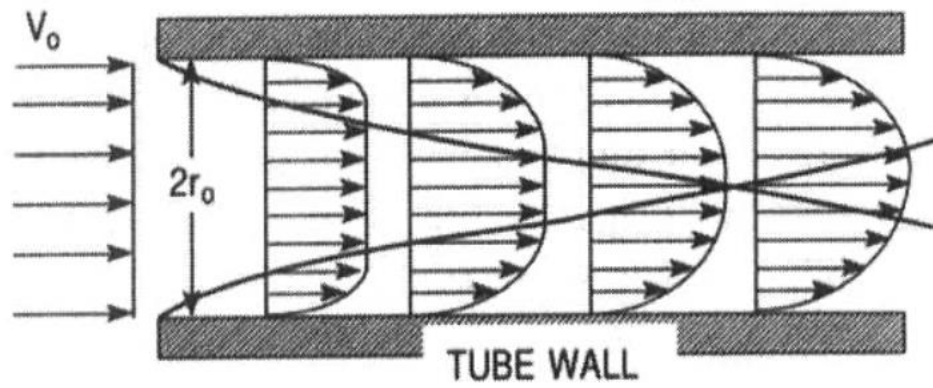
ΔG^0 - standard free energy change

$$K = \frac{P_{HCl}^4}{P_{SiCl_4} P_{H_2}^2}$$

Therefore, the possibility of any chemical reaction is decided by the temperature and pressures of the reacting species!

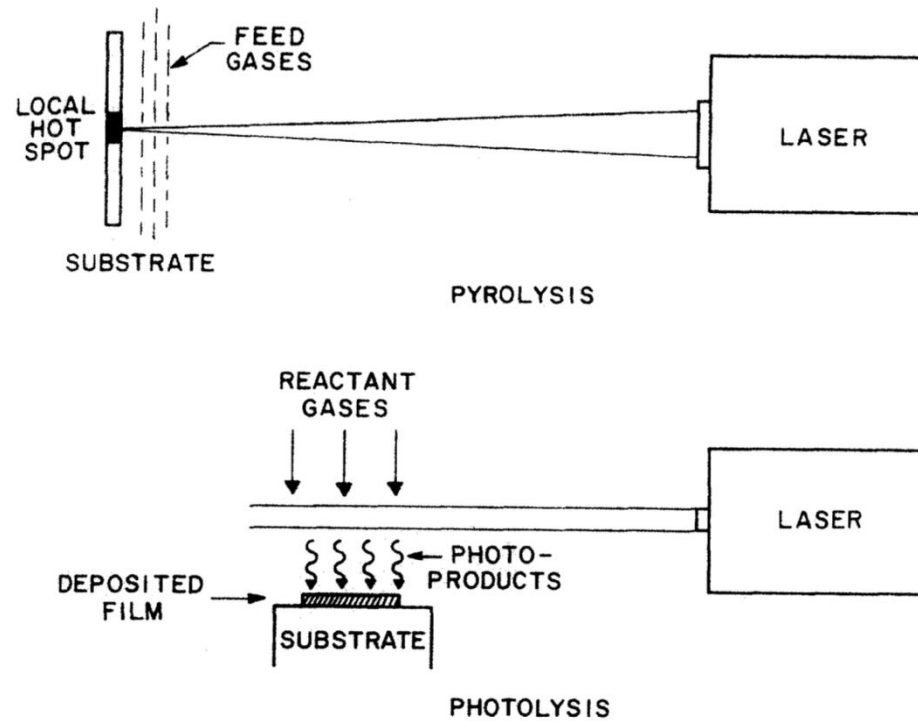
Gas Transport in CVD

- Uniformity of the deposited film depends on the reactant flow rates
- Rapid deposition depends on the thermodynamic variables and the flow type
- Computer modelling is usually required for better results.

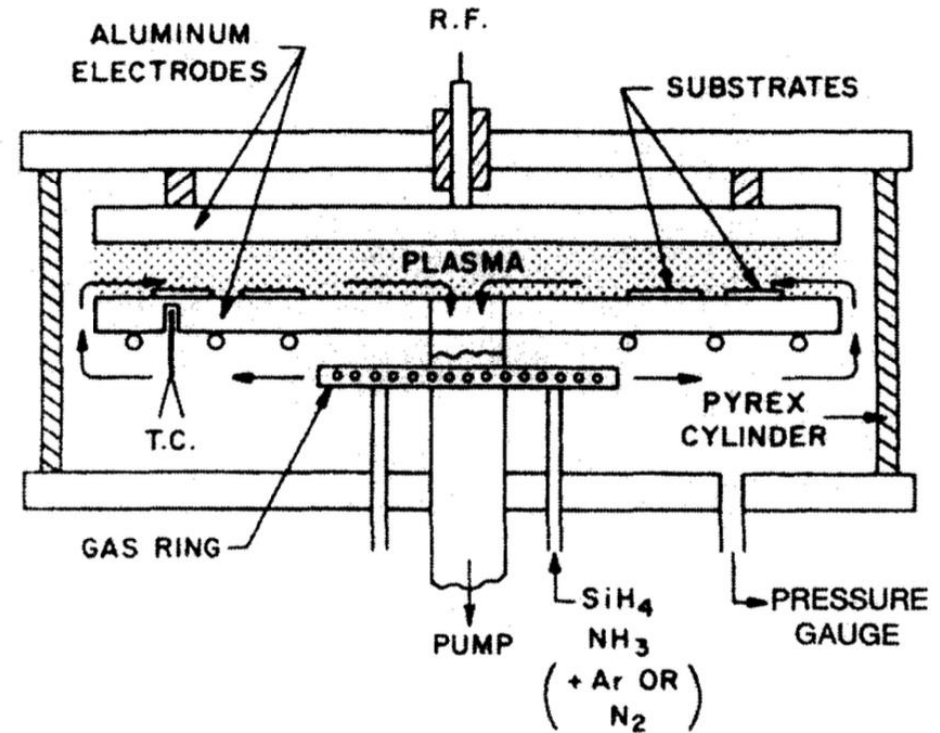


Lower Boundary layer thickness are typically
red for uniform growth layer

Various other CVD techniques



Laser Assisted CVD



Plasma assisted CVD