

Modern Manufacturing Processes,

Physical Vapour Deposition
& Chemical vapour Deposition

[PVD & CVD]

Minimization of Tool wear: Coating of Tools

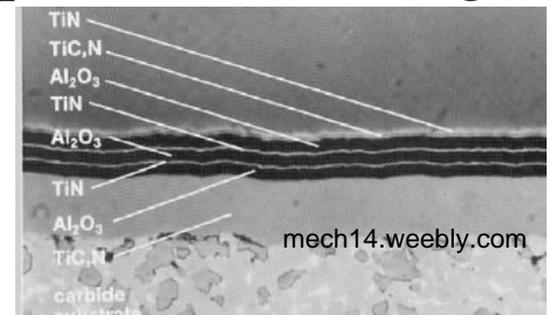
Stable & hard coatings that do not readily chemically react.

Coatings that resist oxidation up to 1000° C.

Low friction coatings that reduce heat generation and improve wear and corrosion resistance

Hard Ceramic Coatings:

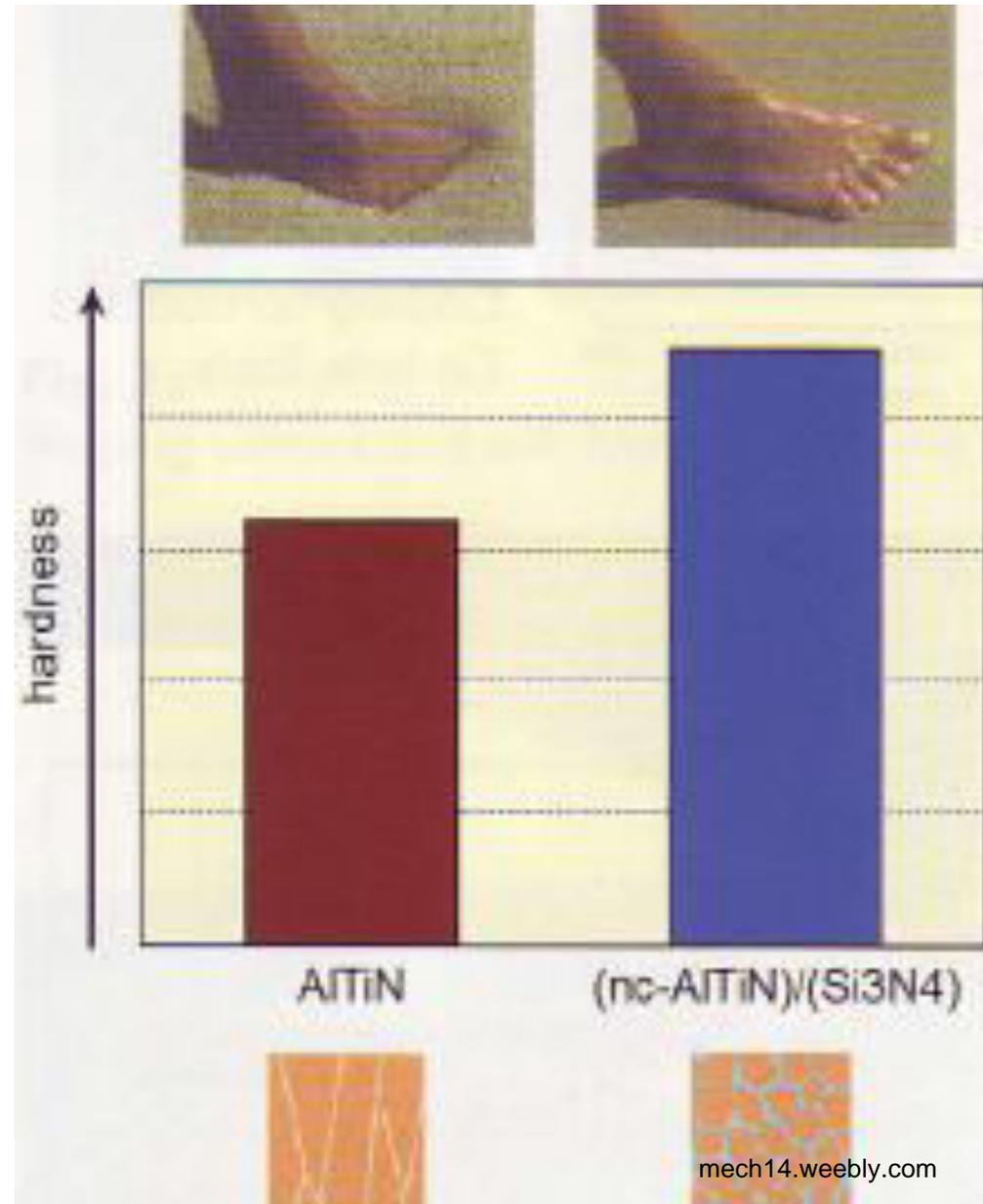
1. Single metal nitride e.g. TiN, CrN, ZrN (Stable up to 450°C)
2. Alloyed ceramic coating e.g. TiAlN; Improved oxidation resistance
3. Hard PVD ceramic multilayer (each ~10nm)super-lattices coatings
TiN/VN and TiN/NbN
4. Hard PVD nanocomposite coatings



4. Hard PVD nanocomposite coatings -

Consists of at least two phases- a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases.

Example: Nanocrystalline TiAlN or AlCrN-grains embedded in an amorphous Si_3N_4 -matrix.



Deposition Process

■ Physical Deposition Process

- Evaporation
- Sputtering

■ Chemical Deposition Process

- Chemical Vapor Deposition (CVD)

Thin Film Deposition

Physical Vapor Deposition (PVD)-Film is formed by atoms or molecules directly transported from source to the substrate through gas phase

- **Evaporation**
 - Thermal evaporation
 - E-beam evaporation
- **Sputtering**
 - DC sputtering
 - DC Magnetron sputtering
 - RF sputtering
- **Reactive PVD**

Chemical Vapor Deposition (CVD)-Film is formed by chemical reaction on the surface of substrate

- Low-Pressure CVD (LPCVD)
- Plasma-Enhanced CVD (PECVD)
- Atmosphere-Pressure CVD (APCVD)
- Metal-Organic CVD (MOCVD)

Physical Evaporation

Three Steps:

1. Vapour Generation : Removal of material from the target or cathode

i. Thermal Evaporation:

Evaporate source material,
 $P_g \leq 10^{-6}$ Torr
Poor step coverage,

Resistive heating of a filament
Inductive heating
E-beam heating,
Laser heating

Noble or reactive gas
 $P \approx 10 - 100$ mTorr

ii. Sputtering by DC / RF Ion source

Magneto Sputtering

iii. Arc evaporation

2. Transportation: Travel of evaporated material from the target to the Substrate

3. Condensation: Nucleation and growth of the coating on the substrate

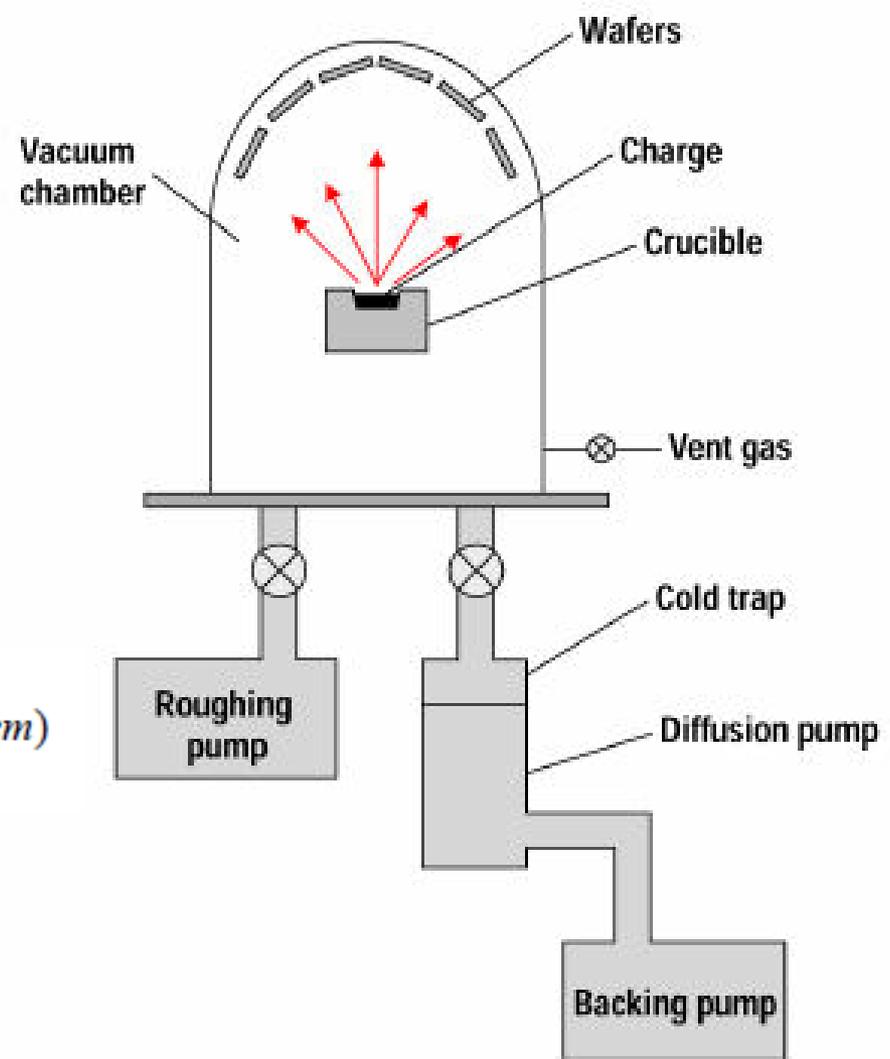
Thermal Evaporator

- Pump down to $< 10^{-6}$ Torr
(1 Torr = 1 mmHg)
- Place tools /wafers
- Heat sources until white hot
- Low pressure \Rightarrow

Mean-free path, $\lambda \sim \frac{5 \times 10^{-3}}{P(\text{torr})}$ (cm)

Typical λ at 10^{-6} Torr, ≈ 50 m
(i.e., Very long mean path,
directional deposition, poor
step coverage)

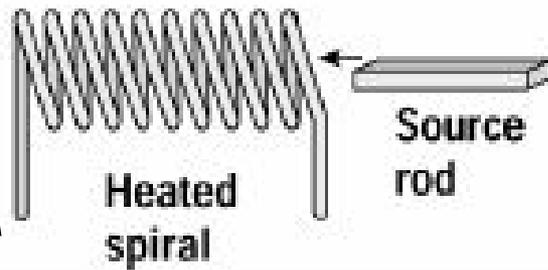
- Use shutter for better timing



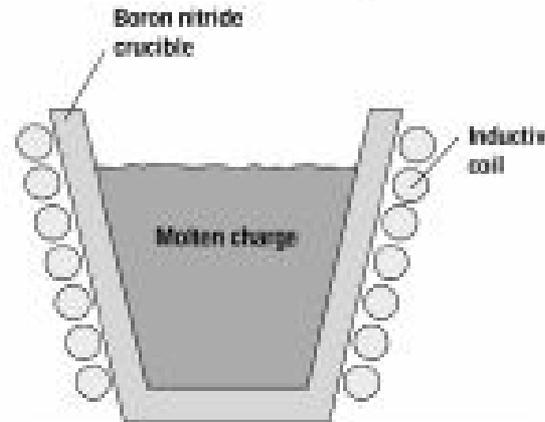
Diffusion pumped evaporator showing vacuum plumbing & location of charge-containing crucible and wafers

Crucible Heating Techniques

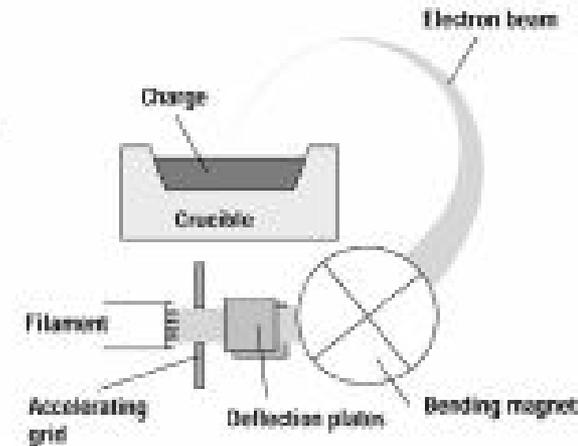
1. Filament coil heating



2. Inductive heating



3. E-beam heating

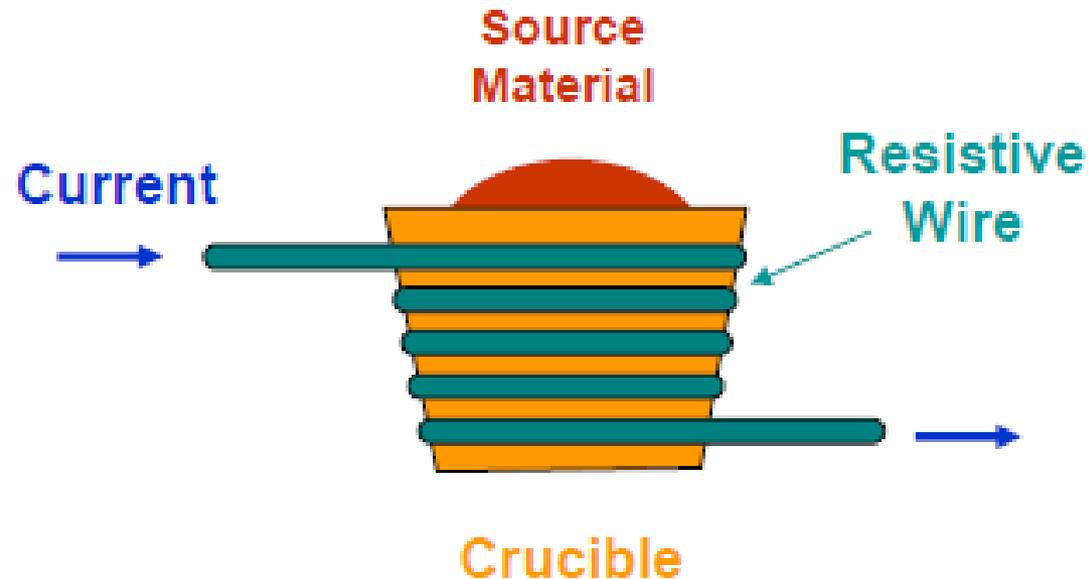


Current

- + Simple, inexpensive
- Contamination due to outgoing from the wire (occurring when depositing refractory metals)
- Limited to low melting temperature materials
- Small size- limited coating thickness

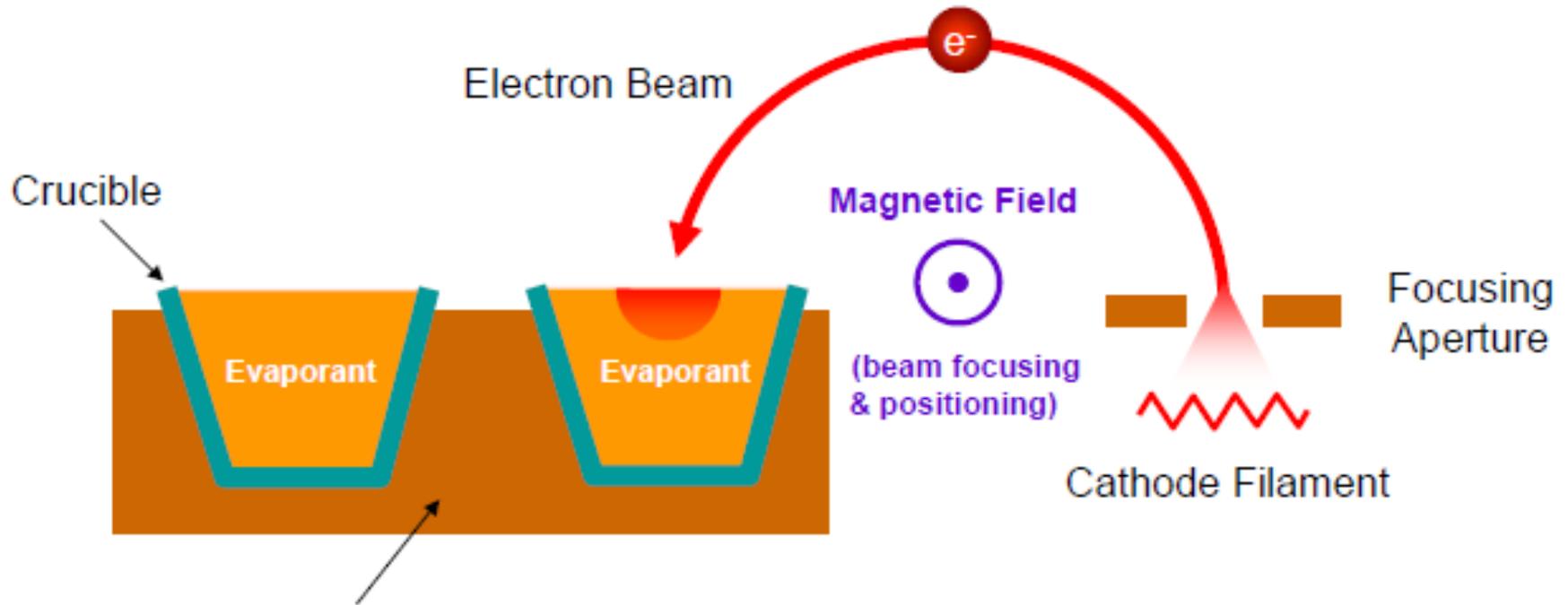
- RF through inductive coils generate eddy current to the charge
- The coil can be water cooled to keep its temperature below 100 °C.
- + Simple, inexpensive
- Contamination from the crucible can still occur)

- Focused beam of electrons are used to locally heat the source 5-30keV
- Can be used to heat/evaporate even high melting point materials
- + Little Contamination
- Expensive
- X-ray



Contamination Problem with Thermal Evaporation

Container material also evaporates, which
contaminates the deposited film



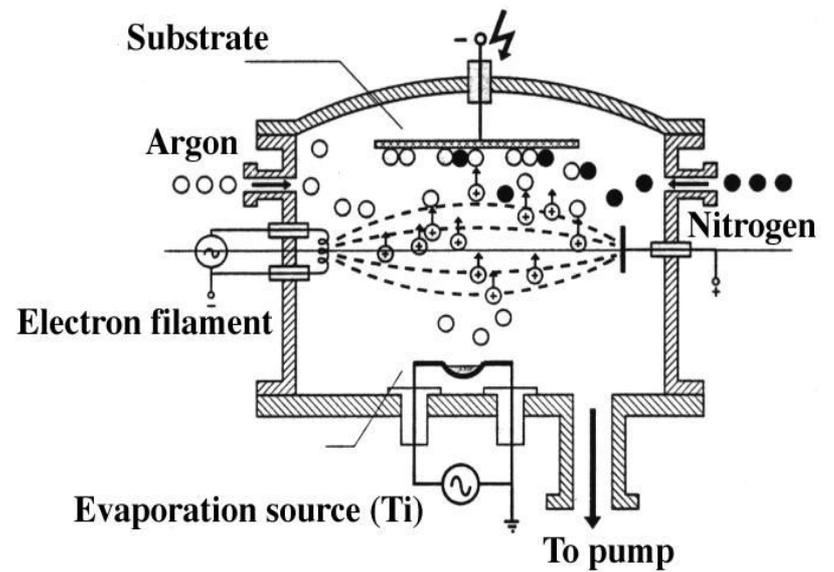
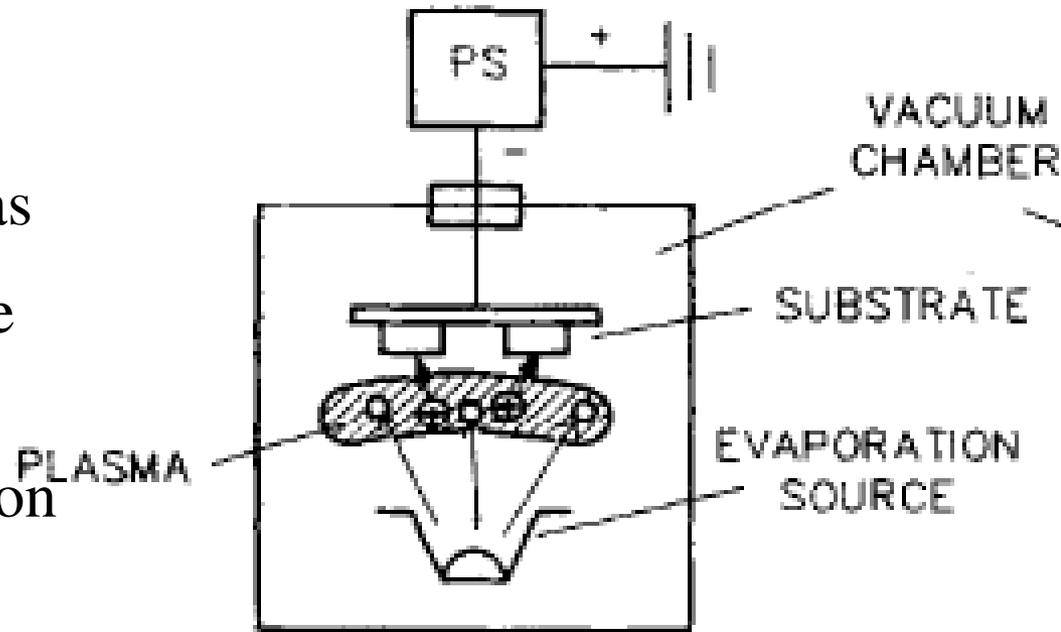
Water Cooled Rotary Copper Hearth
(Sequential Deposition)

Advantage of E-Beam Evaporation:
Very low container contamination

Plasma-assisted deposition processes:

Evaporative ion plating

- * Low pressure plasma in an inert gas or a reactive gas
- * Substrate held at (-)ve Voltage
- * Cleaning of substrate by ion bombardment before deposition
- * Control of film properties by ion bombardment during deposition process.
- * Plasma-assisted ion plating is commonly applied for metal films, oxides, nitrides, carbides, carbonitrides, alloy films and multi-component materials.



Comparison

Deposition	Material	Typical Evaporant	Impurity	Deposition Rate	Temperature Range	Cost
Thermal	Metal or low melt-point materials	Au, Ag, Al, Cr, Sn, Sb, Ge, In, Mg, Ga CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF ₂ , CaF ₂ , PbCl ₂	High	1 ~ 20 Å/s	~ 1800 °C	Low
E-Beam	Both metal and dielectrics	Everything above, plus: Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo Al ₂ O ₃ , SiO, SiO ₂ , SnO ₂ , TiO ₂ , ZrO ₂	Low	10 ~ 100 Å/s	~ 3000 °C	High

Stoichiometrical Problem of Evaporation

- Compound material breaks down at high temperature
- Each component has different vapor pressure, therefore different deposition rate, resulting in a film with different stoichiometry compared to the source

Laser Beam Deposition

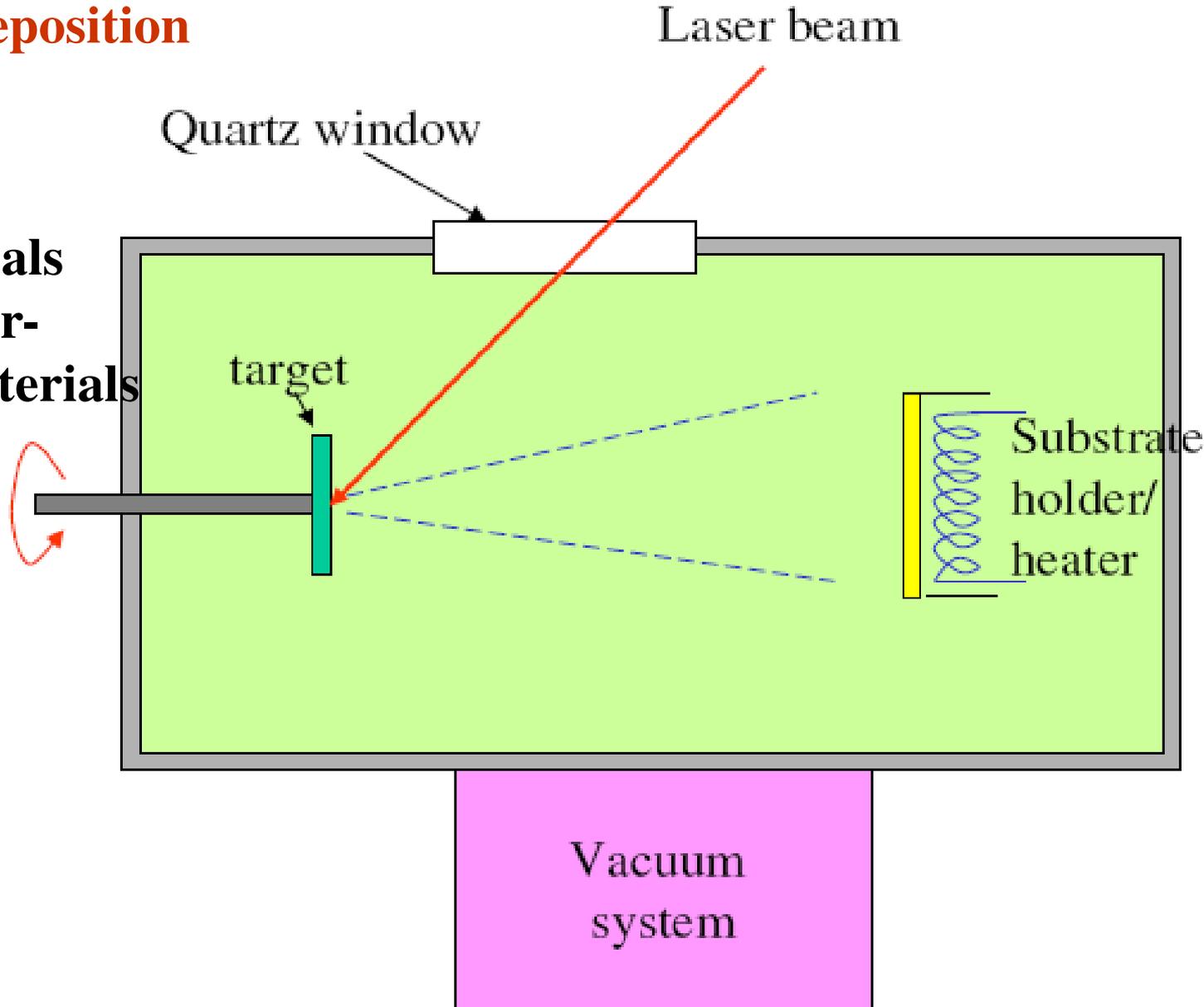
**Pulsed Laser
Deposition:**

**Various materials
including Super-
conducting materials**

$YBa_2Cu_3O_{7-x}$

**Stoichiometry
maintained**

Expensive



Sputtering

* Noble (Inert) or reactive gas

$P \approx 10 - 100$ mTorr

* Target (Cathode) made of coating material

* Target held at (-) 2-5kV Voltage

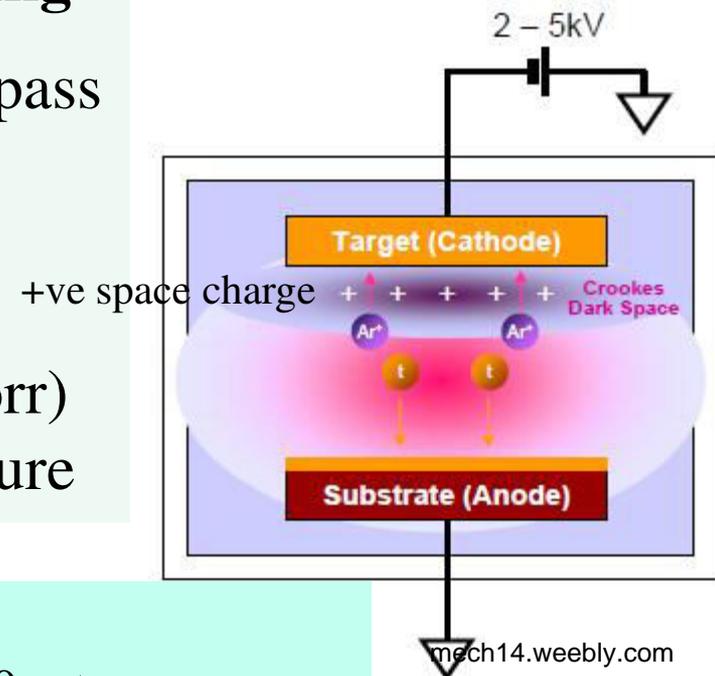
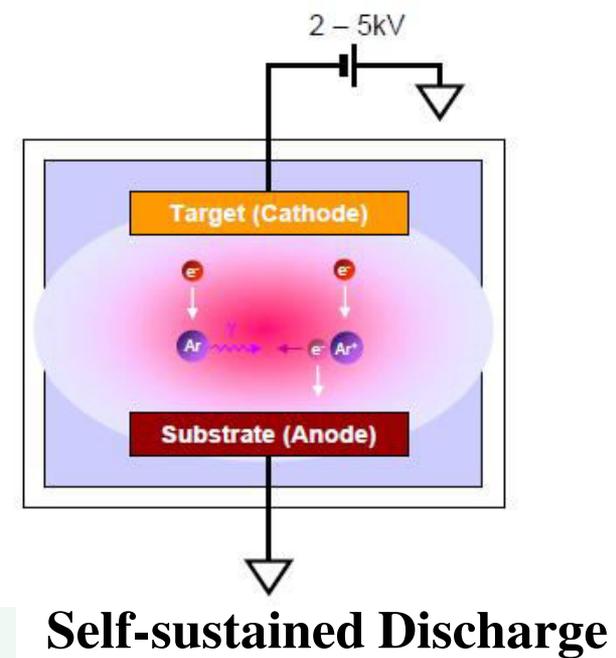
* + ve ions of working gas (Ar) bombard the target with sufficient energy to knock off target atoms (without melting) - **Sputtering**

* Target atoms, being electrically neutral, pass through the plasma and condense on the substrate

* Condition for sustaining Self-sustained Electrical Discharge $\Rightarrow L.p > 0.5$ (cm. torr)
 L = Electrode spacing, p = Chamber pressure

For example:

Typical target-substrate spacing: $L \sim 10$ cm, $P > 50$ mtorr



Deposition Rate vs. Chamber Pressure

Mean-free path of an atom in a gas ambient: $\lambda \sim \frac{5 \times 10^{-3}}{P(\text{torr})} \text{ (cm)}$

Use previous example:

$$L = 10 \text{ cm, } P = 50 \text{ mtorr} \Rightarrow \lambda \sim 1 \text{ mm}$$

- Sputtered atoms have to go through hundreds of collisions (random motion) before reaching the substrate
- Significantly reduces deposition rate
- Causes source to deposit on chamber wall and redeposit back to the target

$$\text{Sputtering Rate : } R \propto \frac{1}{L \cdot P}$$

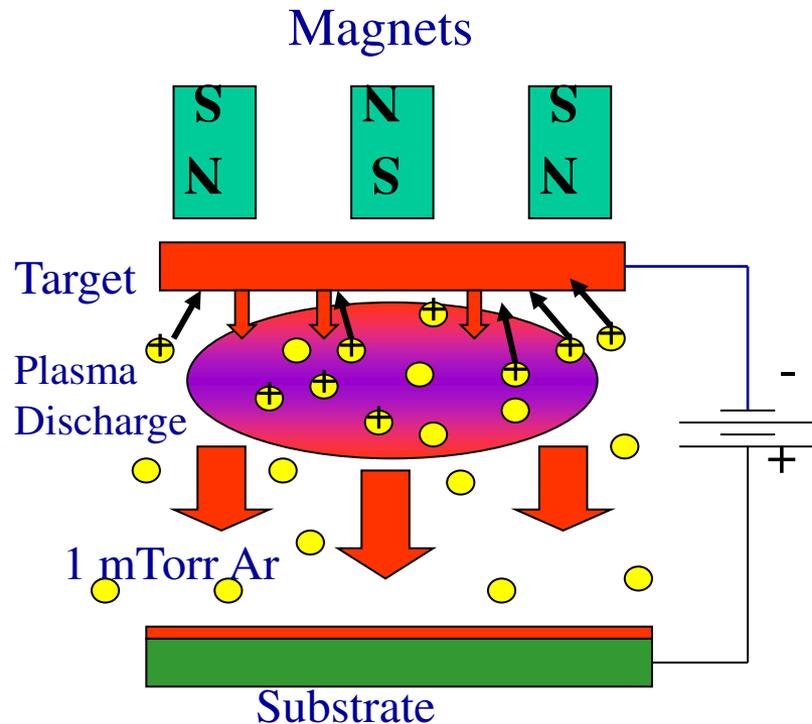
High chamber pressure results in low deposition rate, but better step coverage

- * Large LP to sustain plasma
- * Small LP to maintain good deposition rate and reduce random scattering
- ? Contradictory requirement

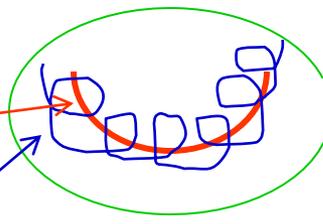
DC Magnetron Sputtering Process

In a magnetron magnets are arranged behind the target with alternating polarity.

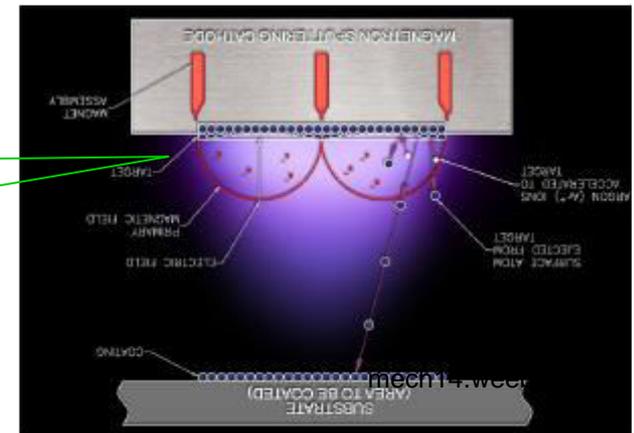
- * Electrons (e^-) are trapped in the plasma by the magnetic field.
- * e^- collide with argon gas atoms to produce further argon ions near target
- * Ar^+ are accelerated in an electric field such that they strike the target with sufficient energy to eject target atoms.
- * Target atoms condense on the substrate.
- * Due to more frequent collision of electrons in presence of magnetic field, discharge can be sustained at a relatively lower L.P values



Line of Magnetic field

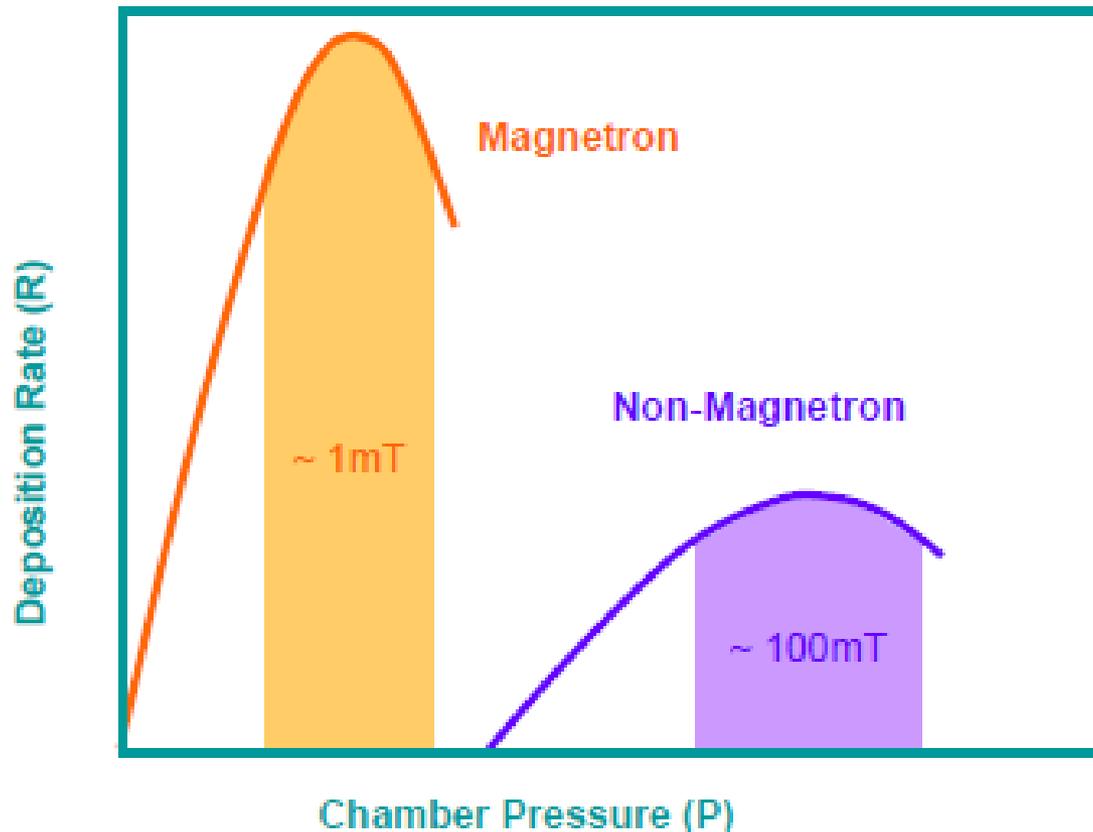


Helical path of e^- , Longer path, more collisions with Ar atoms



As A Result of Magnetic field at low pressure discharge ...

- * Current density (proportional to ionization rate) increases by 100 times
- * Required discharge pressure drops ~ 100 times
- * Deposition rate increases ~ 100 times



RF (Radio Frequency) Sputtering

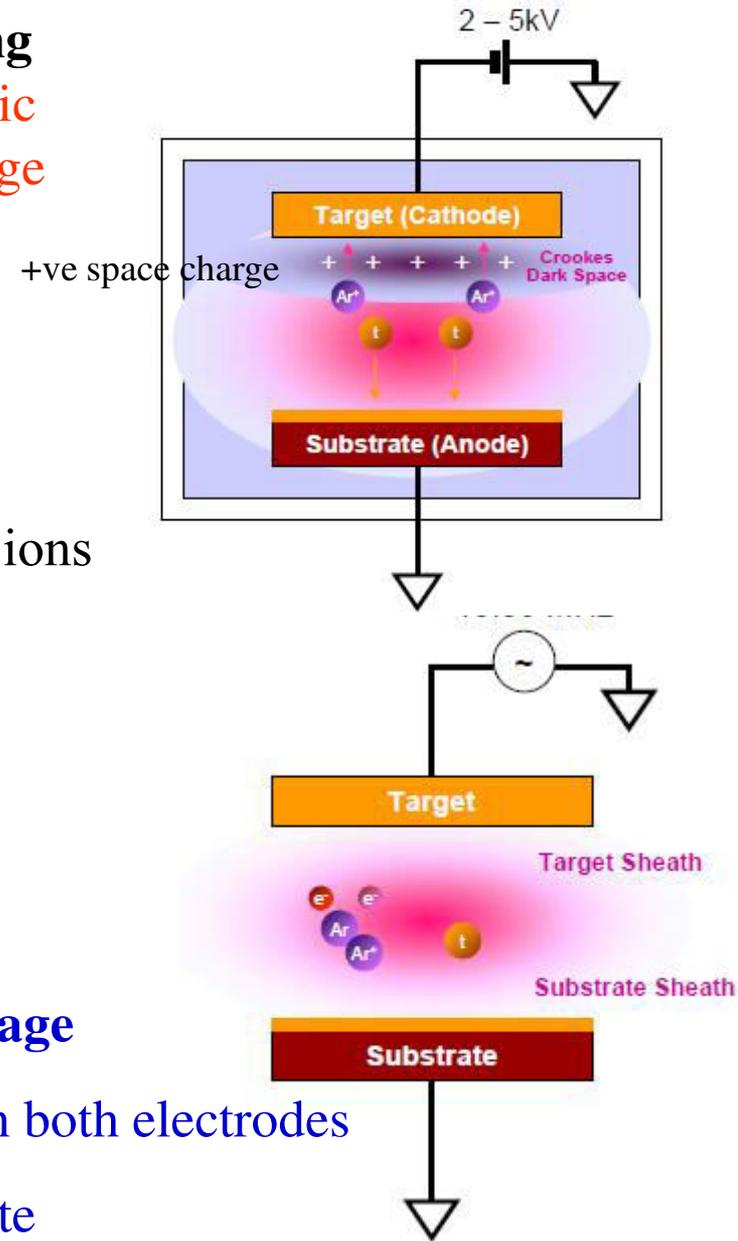
DC sputtering cannot be used for depositing dielectric materials because insulating cathode will cause charge build up during Ar^+ bombarding

- ❖ Reduce the voltage between electrodes
- ❖ Discharge extinguishes

Solution: use AC power

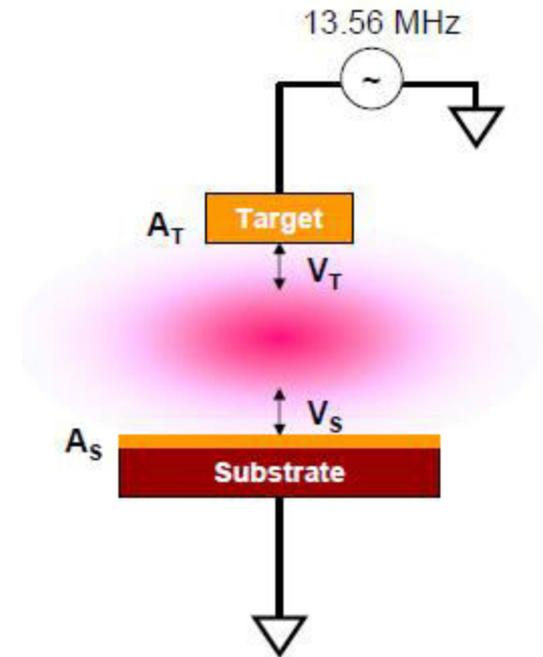
- At low frequency (< 100 KHz), both electrons and ions can follow the alternating switching of the voltage
 \Rightarrow Similar to DC sputtering

- At high frequency (> 1 MHz), heavy ions can no longer follow the fast alternating switching
- Ions are accelerated by space (sheath) charge **Voltage**
- Electron neutralizes the positive charge build up on both electrodes
- However, space charge near both Target & Substrate
- **Sputter both target and substrate at different cycle**



$$\frac{V_T}{V_S} \propto \left(\frac{A_S}{A_T} \right)^n \quad (n \sim 2)$$

- V_T —voltage across target sheath
 - V_S —voltage across substrate sheath
 - A_T —area of target electrode
 - A_S —area of substrate electrode
- Larger dark-space voltage develops at the electrode with smaller area
 \Rightarrow **Make target electrode small**



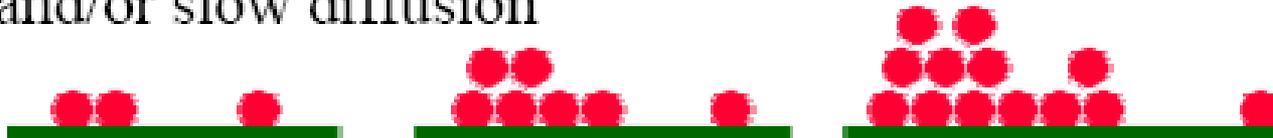
Comparison between Evaporation and Sputtering

Evaporation	Sputtering
Low energy atoms (~ 0.1 eV)	High energy atoms / ions (1 – 10 eV) <ul style="list-style-type: none"> • denser film • smaller grain size • better adhesion
High Vacuum <ul style="list-style-type: none"> • directional, good for lift-off • lower impurity 	Low Vacuum <ul style="list-style-type: none"> • poor directionality, better step coverage • gas atom implanted in the film
Point Source <ul style="list-style-type: none"> • poor uniformity 	Parallel Plate Source <ul style="list-style-type: none"> • better uniformity
Component Evaporate at Different Rate <ul style="list-style-type: none"> • poor stoichiometry 	All Component Sputtered with Similar Rate <ul style="list-style-type: none"> • maintain stoichiometry

1. Island growth (Volmer - Weber)

$R = \text{Arrival Rate} /$
 Diffusion rate

- form three dimensional islands $R > 1$
- film atoms more strongly bound to each other than to substrate
- and/or slow diffusion



2. Layer by layer growth (Frank - van der Merwe)

- generally highest crystalline quality $R < 1$
- film atoms more strongly bound to substrate than to each other
- and/or fast diffusion



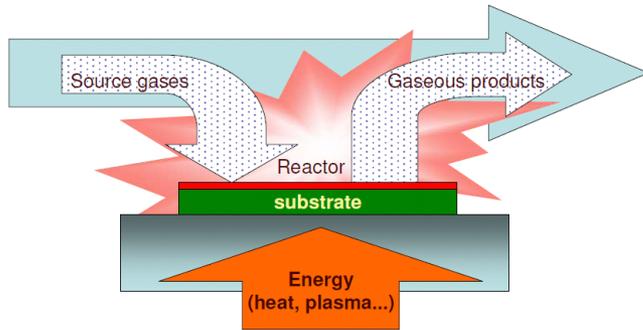
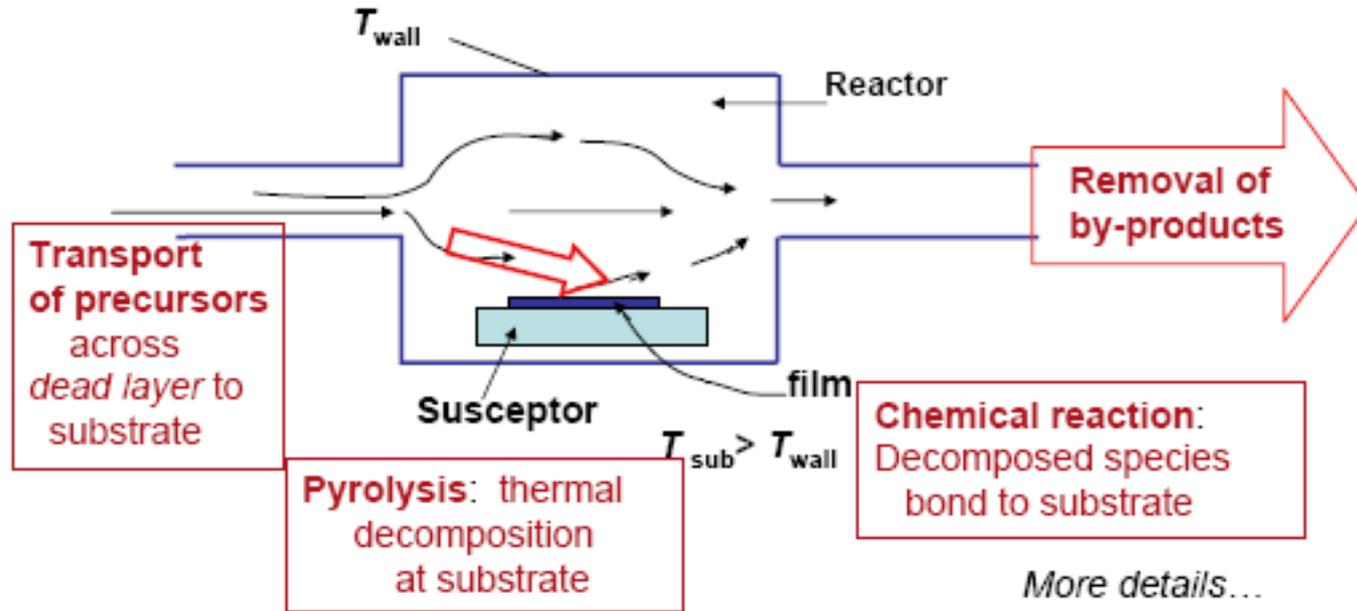
3. Mixed growth (Stranski - Krastanov)

- initially layer by layer, then forms three dimensional islands



Chemical Vapor Deposition (CVD)

CVD forms a thin film on the surface by thermal decomposition and/or chemical reaction of precursor molecules (gaseous compounds)



1. Vaporization and transport of precursor molecules into a reactor
2. Diffusion of precursor molecules to the surface of the substrate
3. Adsorption of precursor molecules to the surface
4. Decomposition of precursor molecules and incorporation into solid films
5. Desorption of volatile byproducts into the gas phase

Semiconductor Industry:

Silicon : $\text{SiH}_4(\text{g}) \Rightarrow \text{Si}(\text{s}) + 2\text{H}_2(\text{g})$ [Pyrolysis – Thermal Decomposition]

Silicon dioxide: $\text{SiH}_4(\text{g}) + \text{O}_2 \Rightarrow \text{SiO}_2(\text{s}) + 2\text{H}_2(\text{g})$ [Oxidation]

Silicon Nitride: $3\text{SiH}_4 + 4\text{NH}_3 \Rightarrow \text{Si}_3\text{N}_4 + 12 \text{H}_2$ [Compound formation]

Mechanical Industry:

Tungsten: $\text{WF}_6 \Rightarrow \text{W} + 3\text{F}_2$

TiC: $\text{TiCl}_4 (\text{l}) + \text{CH}_4 (\text{g}) \Rightarrow \text{TiC} (\text{s}) + 4 \text{HCl} (\text{g})$

TiN: $2\text{TiCl}_4 (\text{l}) + \text{N}_2 + 4\text{H}_2 (\text{g}) \Rightarrow 2\text{TiN} (\text{s}) + 8 \text{HCl} (\text{g})$

TiCN: $\text{TiCl}_4 (\text{l}) + \text{CH}_3\text{CN} (\text{g}) + \text{H} \Rightarrow \text{TiCN} (\text{s}) + 4\text{HCl} (\text{g})$

Al_2O_3 : $2 \text{AlCl}_3 (\text{g}) + 3 \text{CO}_2 + 3 \text{H}_2 \Rightarrow \text{Al}_2\text{O}_3 (\text{s}) + 3\text{CO}(\text{g}) + 6\text{HCl}(\text{g})$

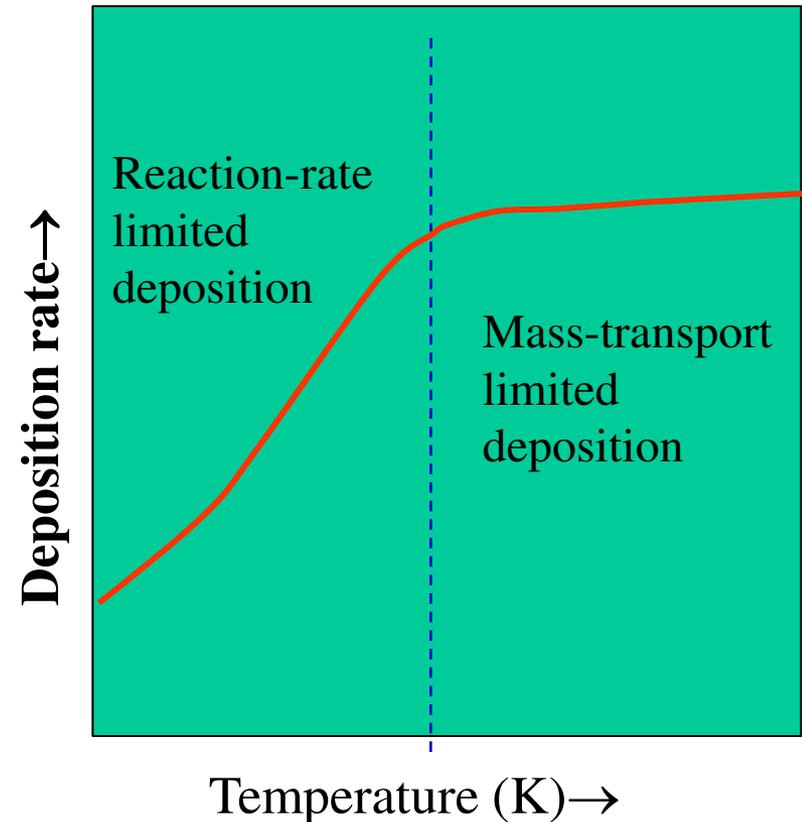
CVD Deposition Condition

Reaction –rate Limited Deposition

- Substrate at relatively low temperature
- Reaction Rate slower than gas arrival rate
- Substrate Temperature, i.e. Reaction at the substrate Controls film deposition rate

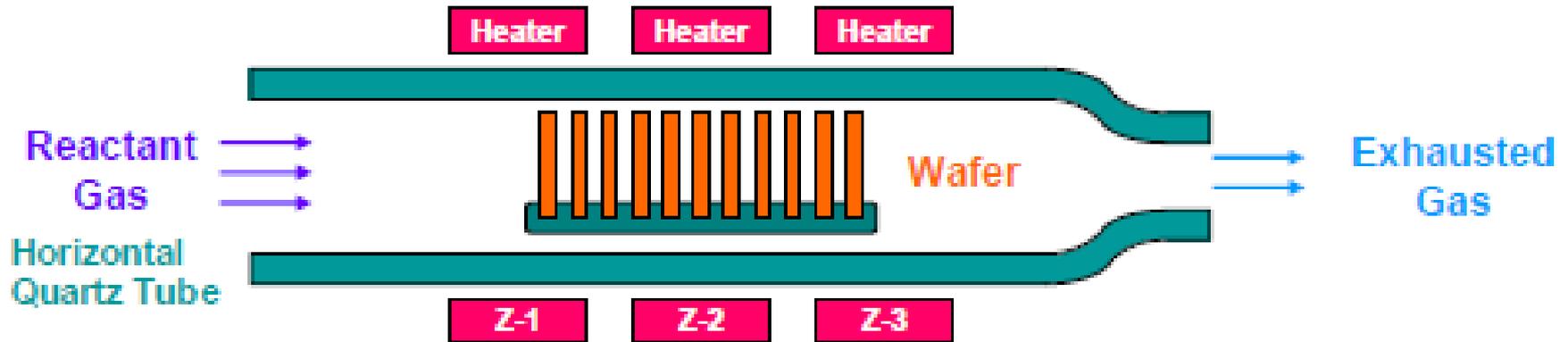
Mass-Transport Limited Deposition

- At high substrate temperature, reaction rate exceeds gas delivery rate
- Gas delivery controls film deposition rate



Types of CVD Process

Low-Pressure CVD (LPCVD)

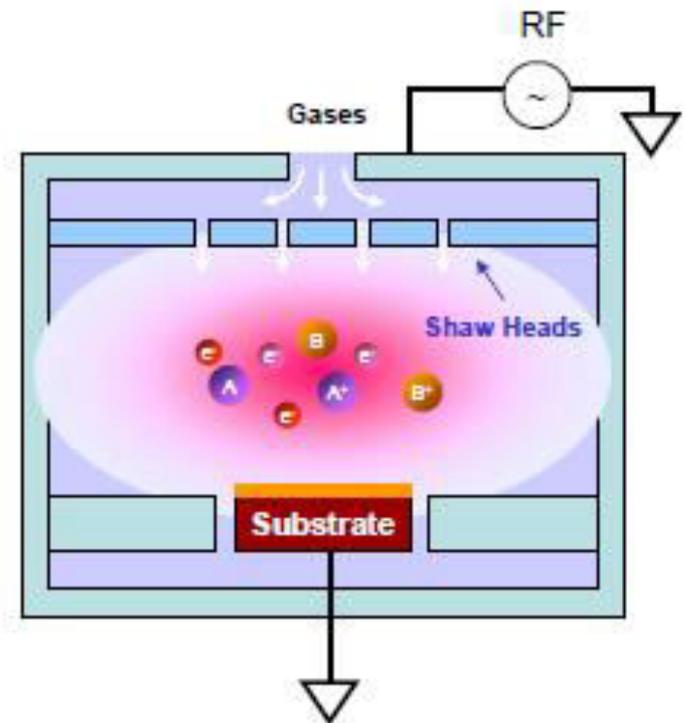


- Thermal energy for reaction activation
- System works at vacuum ($\sim 0.1 - 1.0$ torr), resulting in high diffusivity of reactants
 \Rightarrow reaction-rate limited
- Temperature is controlled around $600 - 900^{\circ}\text{C}$

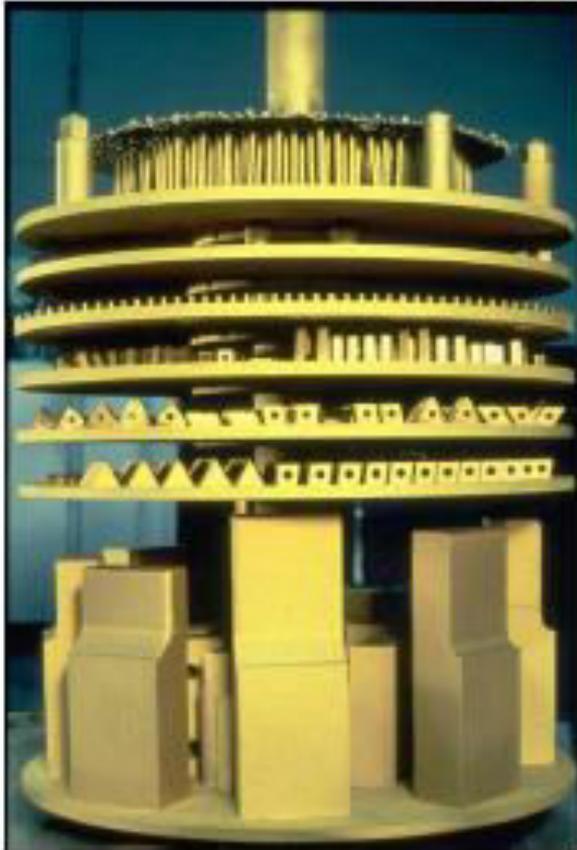
Plasma-Enhanced CVD (PECVD)

Use rf-induced plasma (as in sputtering case) to transfer energy into the reactant gases, forming radicals (decomposition)

- Low temperature process ($< 300\text{ }^{\circ}\text{C}$)
- Suited for depositing film on metals and other materials that cannot sustain high temperatures
- Surface reaction limited deposition; Substrate temperature control is important to ensure uniformity



CVD Fixturing



Everything Gets Coated

Masking is almost Impossible

Tree is placed inside retort

Graphite shelves required for high temperature

Gas distributed from centre to outside

A potentially explosive mixture

Excellent Step coverage

Substrates for CVD:

■ Steel

■ Inconels

■ Cemented Carbides

■ Ceramics

■ Graphite

Comparison of Typical Thin Film Deposition Technology

Process	Material	Uniformity	Impurity	Grain Size	Film Density	Deposition Rate	Substrate Temperature	Directional	Cost
Thermal Evaporation	Metal or low melting-point materials	Poor	High	10 ~ 100 nm	Poor	1 ~ 20 Å/s	50 ~ 100 °C	Yes	Very low
E-beam Evaporation	Both metal and dielectrics	Poor	Low	10 ~ 100 nm	Poor	10 ~ 100 Å/s	50 ~ 100 °C	Yes	High
Sputtering	Both metal and dielectrics	Very good	Low	~ 10 nm	Good	Metal: ~ 100 Å/s Dielectric: ~ 1-10 Å/s	~ 200 °C	Some degree	High
PECVD	Mainly Dielectrics	Good	Very low	10 ~ 100 nm	Good	10 - 100 Å/s	200 ~ 300 °C	Some degree	Very High
LPCVD	Mainly Dielectrics	Very Good	Very low	1 ~ 10 nm	Excellent	10 - 100 Å/s	600 ~ 1200 °C	Isotropic	Very High