

II. Thin Film Deposition

Physical Vapor Deposition (PVD)

- Film is formed by atoms 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)

Oxidation

Spin Coating

Plating



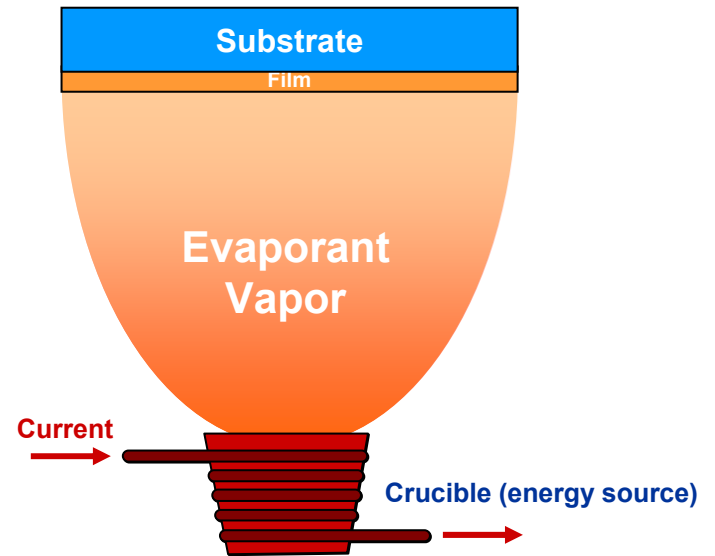
General Characteristics of Thin Film Deposition

- **Deposition Rate**
- **Film Uniformity**
 - Across wafer uniformity
 - Run-to-run uniformity
- **Materials that can be deposited**
 - Metal
 - Dielectric
 - Polymer
- **Quality of Film – Physical and Chemical Properties**
 - Stress
 - Adhesion
 - Stoichiometry
 - Film density, pinhole density
 - Grain size, boundary property, and orientation
 - Breakdown voltage
 - Impurity level
- **Deposition Directionality**
 - Directional: good for lift-off, trench filling
 - Non-directional: good for step coverage
- **Cost of ownership and operation**



Evaporation

- ➔ Load the source material-to-be-deposited (evaporant) into the container (crucible)
- ➔ Heat the source to high temperature
- ➔ Source material evaporates
- ➔ Evaporant vapor transports to and Impinges on the surface of the substrate
- ➔ Evaporant condenses on and is adsorbed by the surface



Langmuire-Knudsen Relation

Mass Deposition Rate per unit area of source surface:

$$R_m = C_m \left(\frac{M}{T} \right)^{\frac{1}{2}} \cos \theta \cos \varphi \frac{1}{r^2} (P_e(T) - P)$$

$$C_m = 1.85 \times 10^{-2}$$

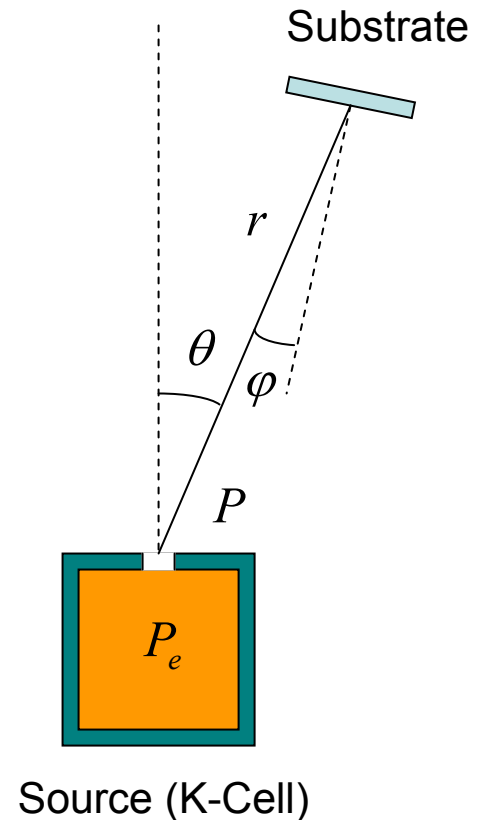
r : source-substrate distance (cm)

T : source temperature (K)

P_e : evaporant vapor pressure (torr), function of T

P : chamber pressure (torr)

M : evaporant gram-molecular mass (g)



➔ Maximum deposition rate reaches at high chamber vacuum ($P \sim 0$)



Uniform Coating

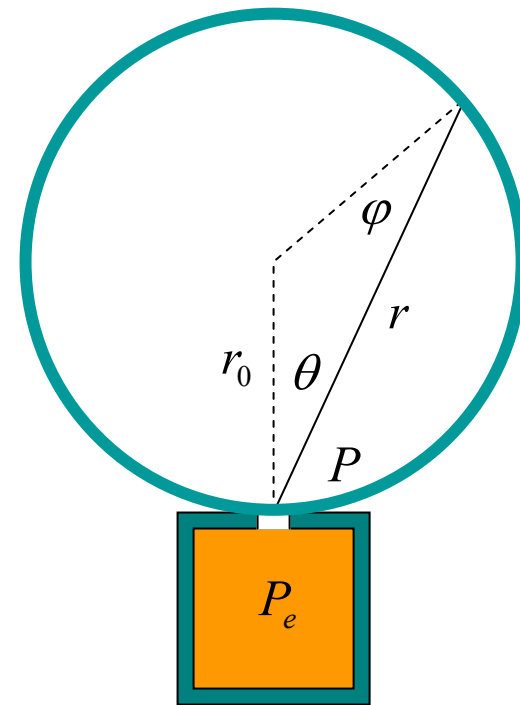
Spherical surface with source on its edge:

$$\cos \theta = \cos \varphi = \frac{r}{2r_0}$$
$$R_m = C_m \left(\frac{M}{T} \right)^{\frac{1}{2}} \frac{P_e}{4r_0^2}$$

➔ Angle Independent – uniform coating!

➔ Used to coat instruments with spherical surfaces

Spherical Surface



Source (K-Cell)



Uniformity on a Flat Surface

Consider the deposition rate difference between wafer center and edge:

$$R_1 \propto \frac{1}{r_1^2}$$

$$R_2 \propto \frac{1}{r_2^2} \cos^2 \theta = \frac{r_1^2}{r_2^4}$$

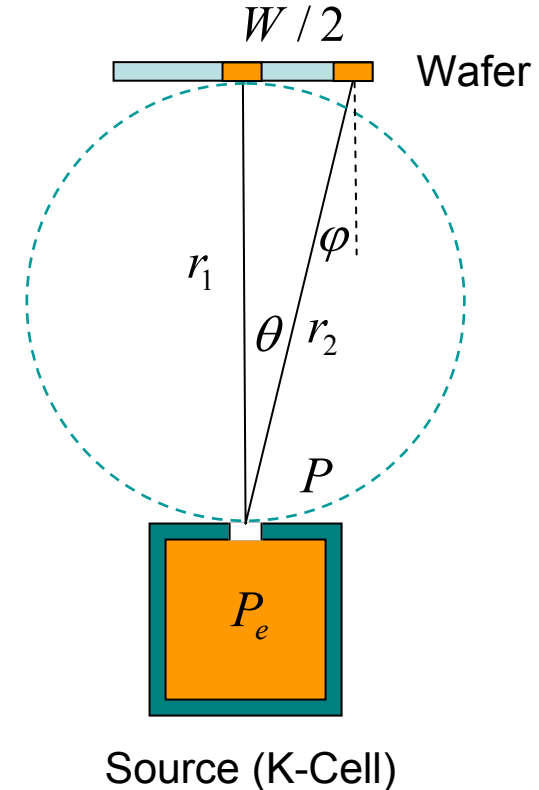
Define Uniformity:

$$\sigma(\%) = \frac{R_1 - R_2}{R_1} (\%)$$

$$\sigma = 1 - \left(1 + \left(\frac{W}{2r_1} \right)^2 \right)^{-2} \approx \frac{W^2}{2r_1^2}$$

or

$$\frac{W}{r_1} = \sqrt{2\sigma}$$



Uniformity Requirement on a Flat Surface

Source-substrate distance requirement:

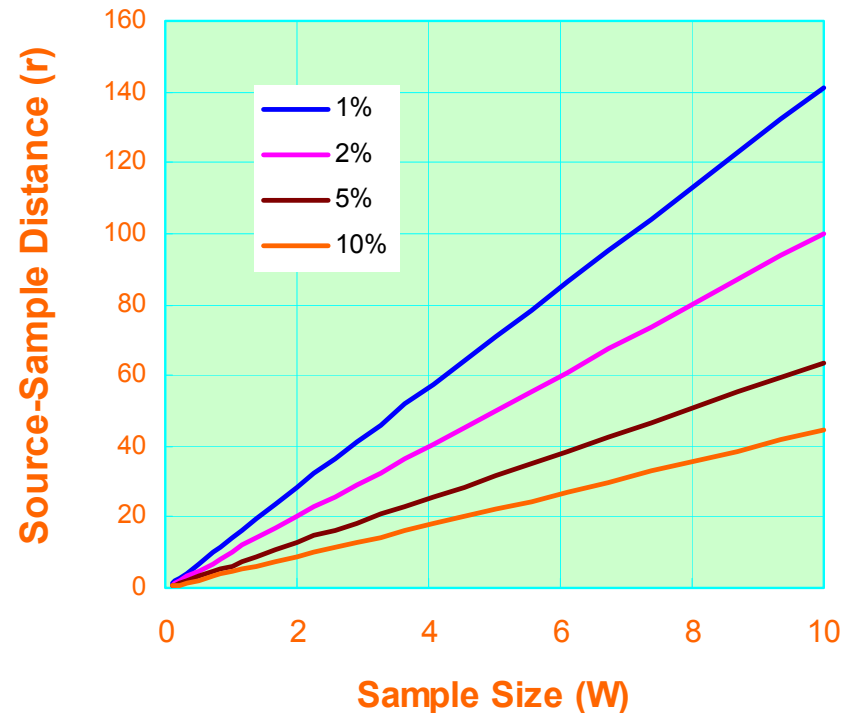
$$r > \frac{W}{\sqrt{2\sigma}}$$

In practice, it is typical to double this number to give some process margin:

$$r > W \sqrt{\frac{2}{\sigma}}$$

Larger r Means:

- ➔ bigger chamber
- ➔ higher capacity vacuum pump
- ➔ lower deposition rate
- ➔ higher evaporant waste



Another Common Solution:
off-axis rotation of the sample



Thickness Deposition Rate vs. Source Vapor Pressure

Thickness deposition rate $\frac{dh}{dt} = \frac{R_m}{\rho} A_e$

$$\frac{dh}{dt} = \frac{A_e}{\rho} C_m \left(\frac{M}{T} \right)^{\frac{1}{2}} \cos \theta \cos \varphi \frac{1}{r^2} P_e(T)$$

T : source temperature (K)
 A_e : source surface area (cm²)
 ρ : evaporant density (g/cm³)

P_e is function of source Temperature!

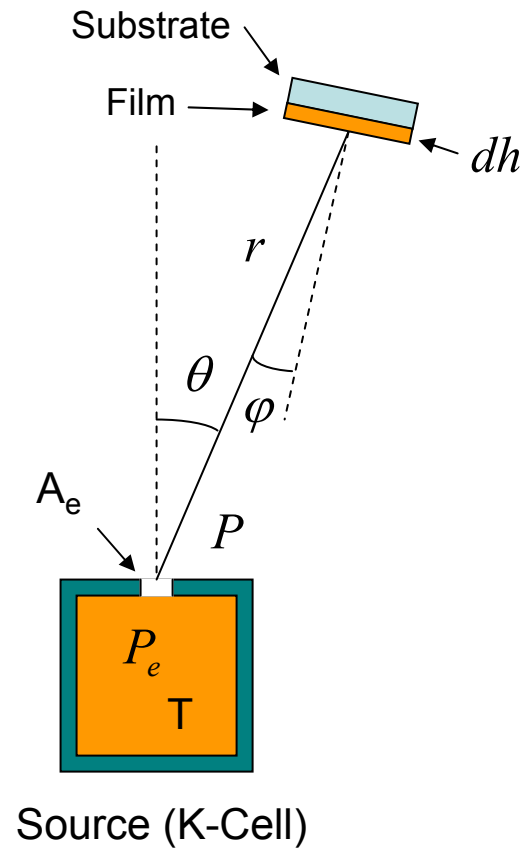
Example: Al

$M \sim 27$, $\rho \sim 2.7$, $A_e \sim 10^{-2}$ cm², $T \sim 900$ K

$R \sim 50$ cm (uniformity requirement)

$$\frac{dh}{dt} = 50 P_e \quad (\text{Å/s})$$

→ The higher the vapor pressure, the higher the material's deposition rate

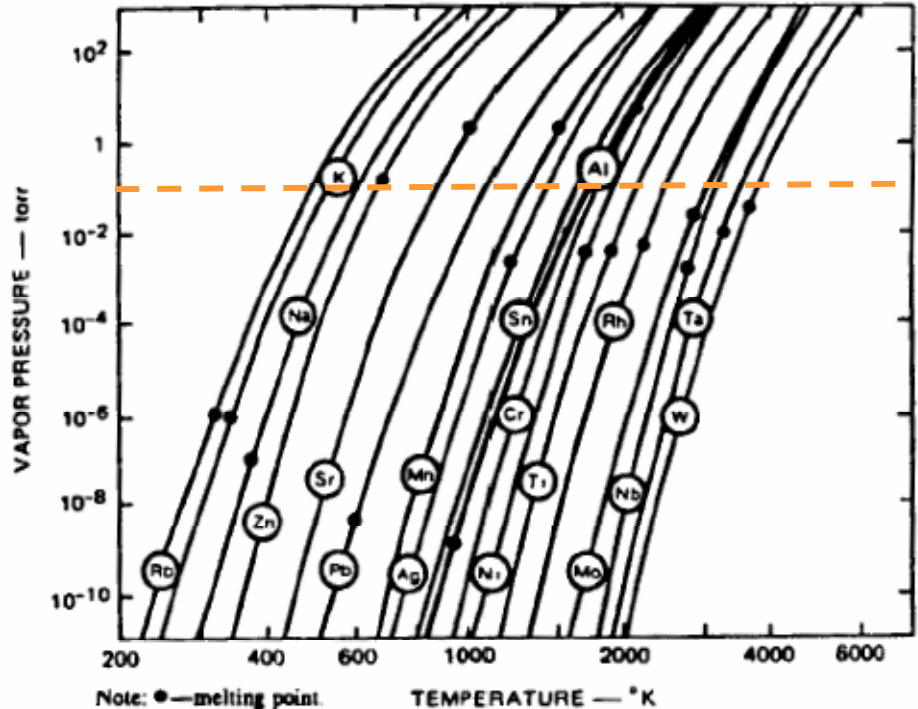


Deposition Rate vs. Source Temperature

Typically for different material:

$$\frac{dh}{dt} = (10 \sim 100)P_e(T) \quad (A/s)$$

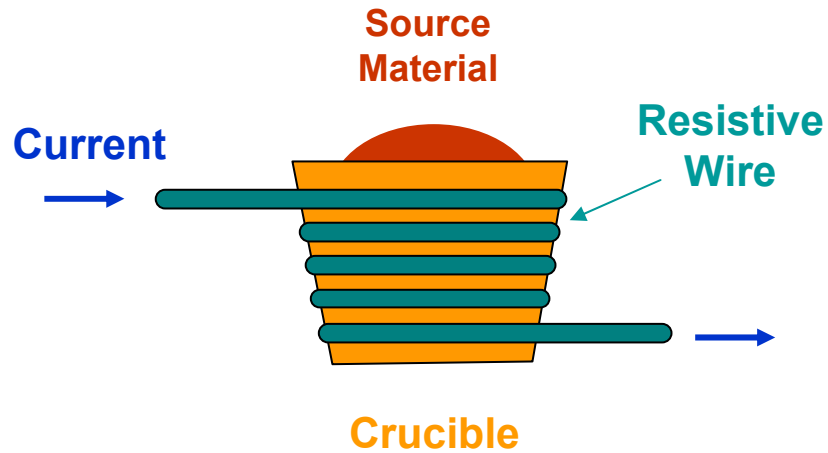
- For deposition rate > 1 A/s:
 $P_e > \sim 100$ mtorr
- P_e depends on: 1) material and 2) temperature
- Deposition rates are significantly different for different materials
- Hard to deposit multi-component (alloy) film without losing stoichiometry



Example: for $P_e > 100$ mtorr
 $T(\text{Al}) > 1400\text{K}$, $T(\text{Ta}) > 2500\text{K}$



Heating Method – Thermal (Resist Heater)



Contamination Problem with Thermal Evaporation

Container material also evaporates, which contaminates the deposited film



Foil Dimple Boat

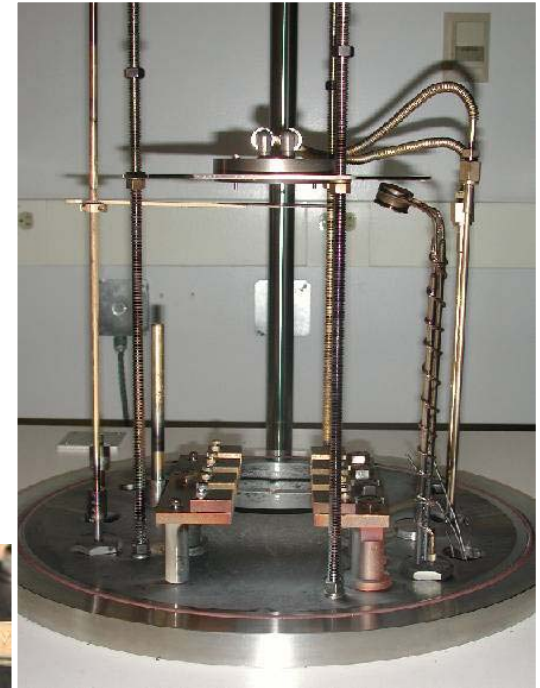


Alumina Coated Foil Dimple Boat

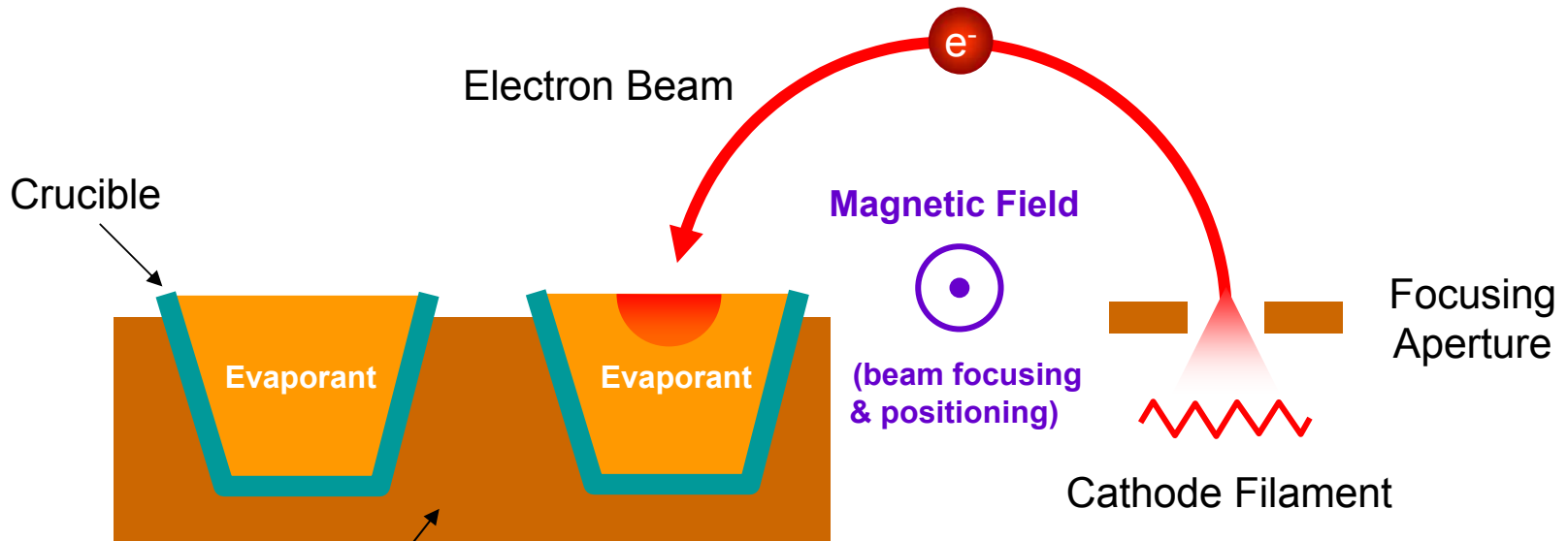


Cr Coated Tungsten Rod

CIMS' Sharon Thermal Evaporator



Heating Method – e-Beam Heater

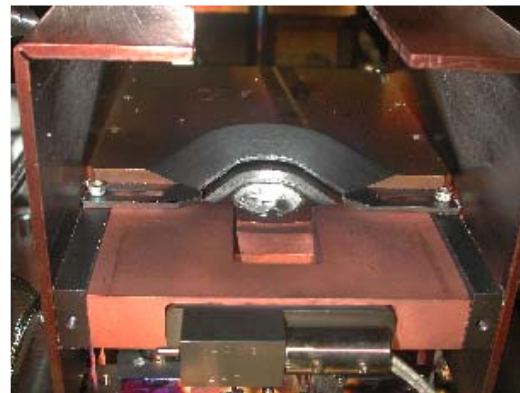
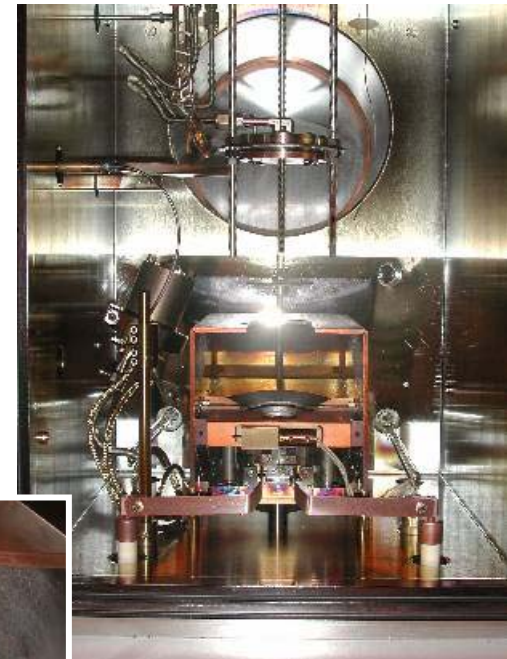
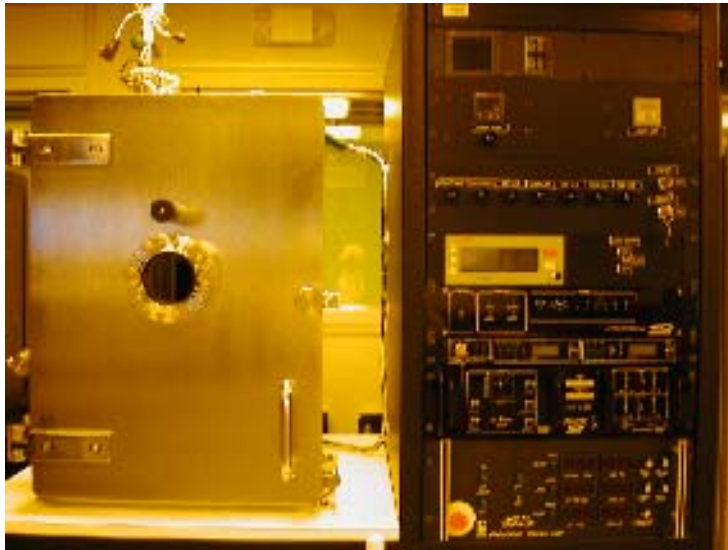


Advantage of E-Beam Evaporation:

Very low container contamination



CIMS' Sharon E-Beam Evaporator



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



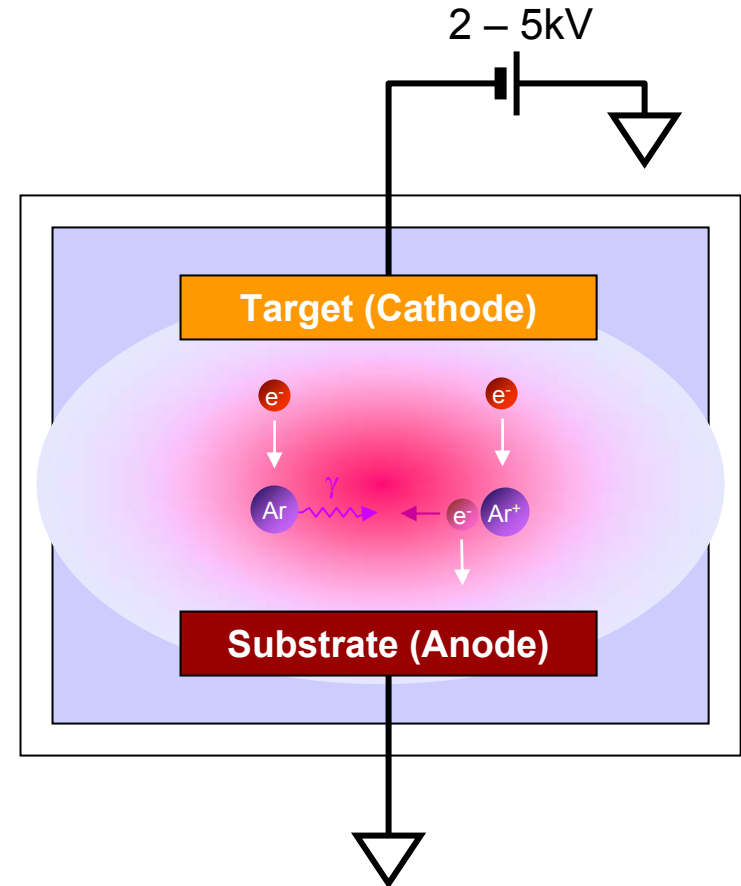
Typical Boat/Crucible Material

Refractory Metals		
Material	Melting Point (°C)	Temperature for 10-mtorr Vapor Pressure (P_e) (°C)
Tungsten (W)	3380	3230
Tantalum (Ta)	3000	3060
Molybdenum (Mo)	2620	2530
Refractory Ceramics		
Graphitic Carbon (C)	3799	2600
Alumina (Al_2O_3)	2030	1900
Boron Nitride (BN)	2500	1600



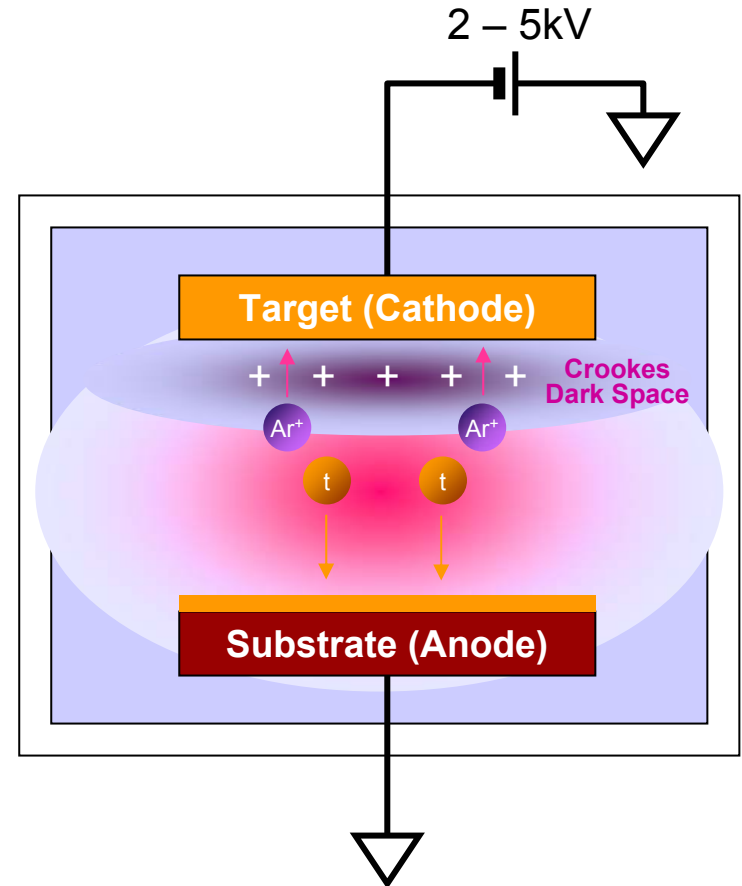
DC Diode Sputtering Deposition

- Target (source) and substrate are placed on two parallel electrodes (diode)
- They are placed inside a chamber filled with inert gas (Ar)
- DC voltage (\sim kV) is applied to the diode
- Free electron in the chamber are accelerated by the e-field
- These energetic free electrons inelastically collide with Ar atoms
 - ★ excitation of Ar \rightarrow gas glows
 - ★ ionization of Ar \rightarrow Ar^+ + 2nd electron
- 2nd electrons repeat above process
 - \rightarrow “gas breakdown”
 - \rightarrow discharge glow (plasma)



Self-Sustained Discharge

- Near the cathode, electrons move much faster than ions because of smaller mass
 - positive charge build up near the cathode, raising the potential of plasma
 - less electrons collide with Ar
 - few collision with these high energetic electrons results in mostly ionization, rather than excitation
 - dark zone (Crookes Dark Space)
- Discharge causes voltage between the electrodes reduced from $\sim 10^3$ V to $\sim 10^2$ V, mainly across the dark space
- Electrical field in other area is significantly reduced by screening effect of the positive charge in front of cathode
- Positive ions entering the dark space are accelerated toward the cathode (target), bombarding (sputtering) the target
 - atoms locked out from the target transport to the substrate (momentum transfer, not evaporation!)
 - generate 2nd electrons that sustains the discharge (plasma)



Requirement for Self-Sustained Discharge

- If the cathode-anode space (L) is less than the dark space length
 - ➔ ionization, few excitation
 - ➔ cannot sustain discharge
- On the other hand, if the Ar pressure in the chamber is too low
 - ➔ Large electron mean-free path
 - ➔ 2nd electrons reach anode before colliding with Ar atoms
 - ➔ cannot sustain discharge either

Condition for Sustain Plasma:

$$L \cdot P > 0.5 \text{ (cm} \cdot \text{torr)}$$

L: electrode spacing, P: chamber pressure

For example:

Typical target-substrate spacing: $L \sim 10\text{cm}$

➔ $P > 50 \text{ mtorr}$



Deposition Rate vs. Chamber Pressure

High chamber pressure results in low deposition rate

Mean-free path of an atom in a gas ambient:

$$\lambda \sim \frac{5 \times 10^{-3}}{P(\text{torr})} \quad (\text{cm})$$

Use previous example:

$$L = 10 \text{ cm}, P = 50 \text{ mtorr}$$

- ➔ $\lambda \sim 0.1 \text{ cm}$
- ➔ sputtered atoms have to go through hundreds of collisions before reaching the substrate
- ➔ significantly reduces deposition rate
- ➔ also causes source to deposit on chamber wall and redeposit back to the target

In fact, sputtering deposition rate R:

$$R \propto \frac{1}{L \cdot P}$$

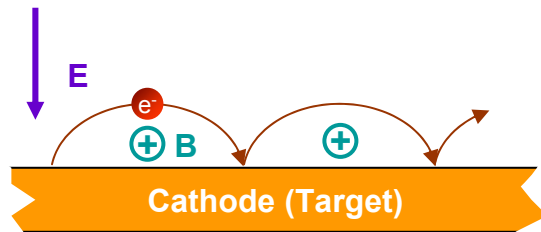
- ★ Large LP to sustain plasma
- ★ small LP to maintain good deposition rate and reduce random scattering

?



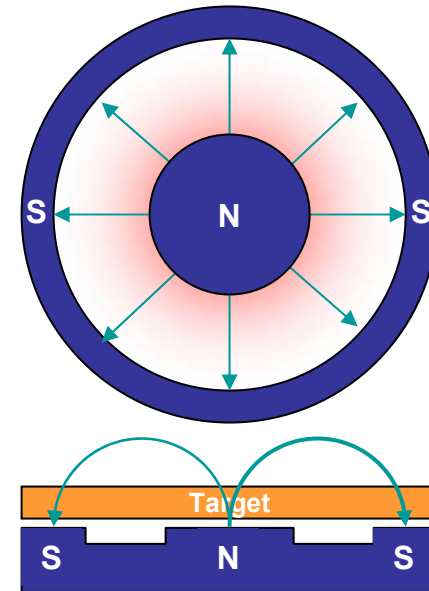
DC Magnetron Sputtering

- Using low chamber pressure to maintain high deposition rate
- Using magnetic field to confine electrons near the target to sustain plasma



Apply magnetic field parallel to the cathode surface

➔ electrons will hop (cycloid) near the surface (trapped)



Impact of Magnetic Field on Ions

Hopping radius r :

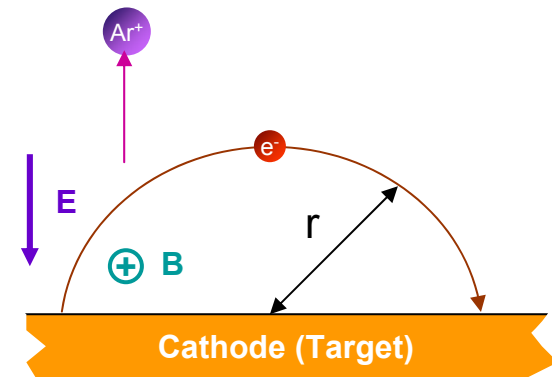
$$r \sim \frac{1}{B} \sqrt{\frac{2m}{e}} V_d$$

V_d – voltage drop across dark space
(~ 100 V)

B – Magnetic field (~ 100 G)

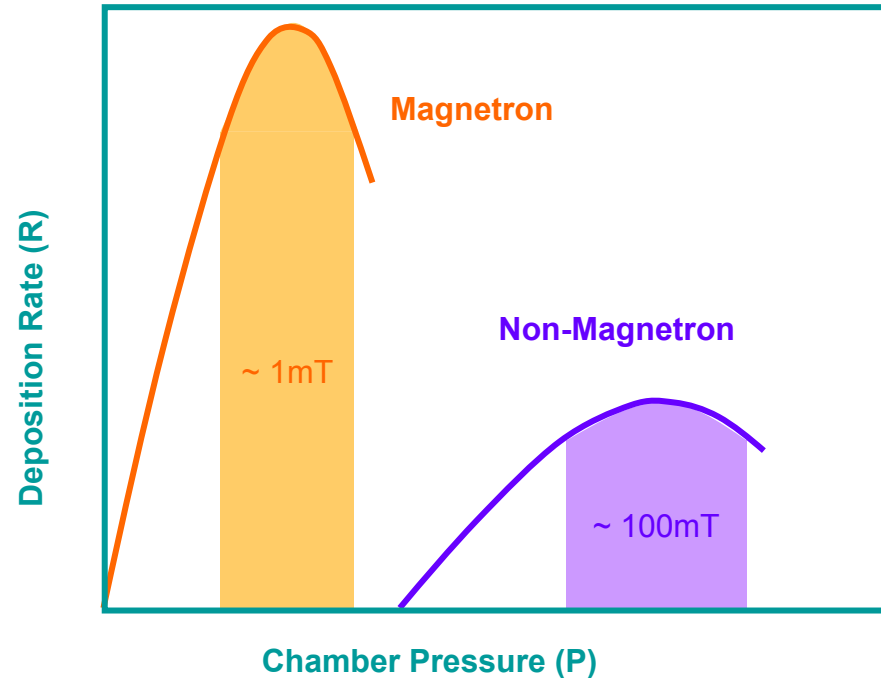
For electron $r \sim 0.3$ cm

For Ar^+ ion: $r \sim 81$ cm



As A Result ...

- current density (proportional to ionization rate) increases by 100 times
- required discharge pressure drops 100 times
- deposition rate increases 100 times



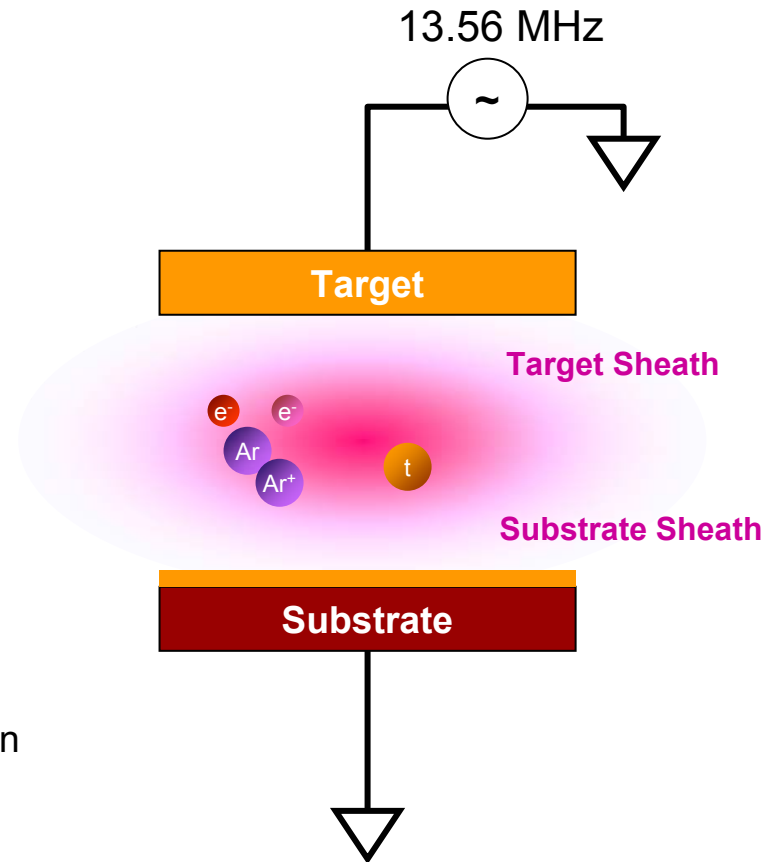
RF (Radio Frequency) Sputtering

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

- ➔ reduce the voltage between electrodes
- ➔ discharge distinguishes

Solution: use AC power

- at low frequency (< 100 KHz), both electrons and ions can follow the switching of the voltage –
 - ➔ DC sputtering
- at high frequency (> 1 MHz), heavy ions cannot no long follow the switching
 - ➔ ions are accelerated by dark-space (sheath) voltage
 - ➔ electron neutralizes the positive charge buildup on both electrodes
- However, there are two dark spaces
 - ➔ sputter both target and substrate at different cycle



RF (Radio Frequency) Sputtering

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

V_T – voltage across target sheath

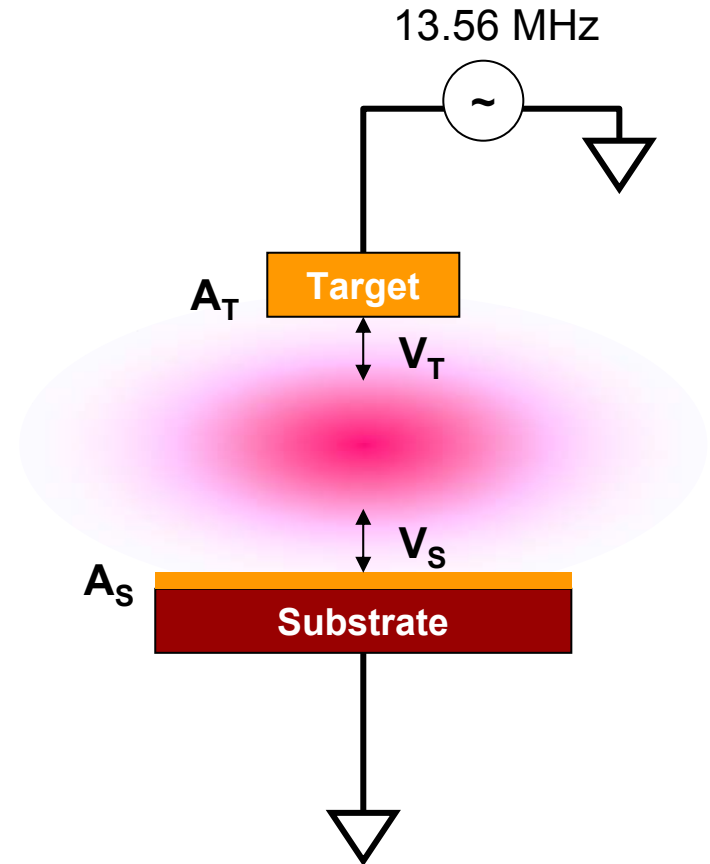
V_S – voltage across substrate sheath

A_T – area of target electrode

A_S – area of substrate electrode

Larger dark-space voltage develops at the electrode with smaller area

➔ make target electrode small



Comparison between Evaporation and Sputtering

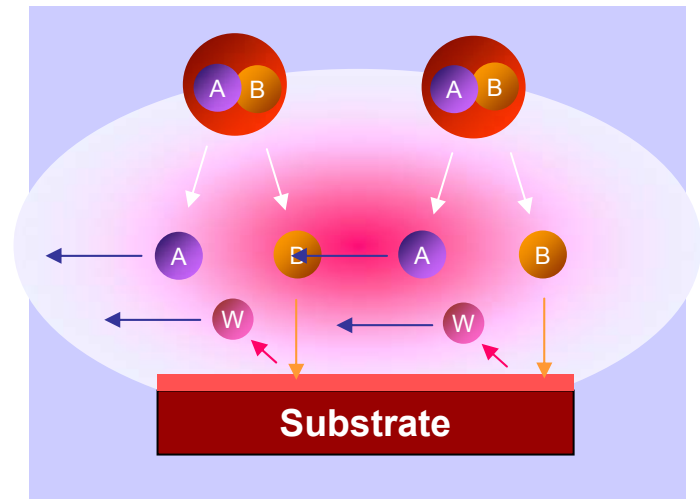
Evaporation	Sputtering
Low energy atoms (~ 0.1 eV)	High energy atoms / ions (1 – 10 eV) <ul style="list-style-type: none"> • denser film • smaller grain size • better adhesion
High Vacuum <ul style="list-style-type: none"> • directional, good for lift-off • lower impurity 	Low Vacuum <ul style="list-style-type: 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



Chemical Vapor Deposition (CVD)

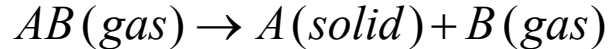
Deposit film through chemical reaction and surface absorption

- Introduce reactive gases to the chamber
- Activate gases (decomposition)
 - ↳ heat
 - ↳ plasma
- Gas absorption by substrate surface
- Reaction take place on substrate surface; film formed
- Transport of volatile byproducts away from substrate
- Exhaust waste



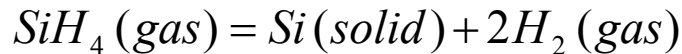
Types of CVD Reactions

Pyrolysis (Thermal Decomposition)

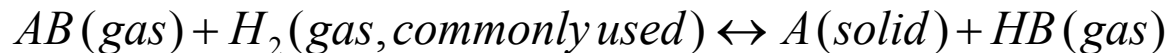


Example

α -Si deposited at 580 - 650 °C:

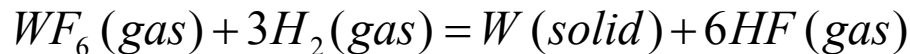


Reduction (lower temperature than Pyrolysis)



Example

W deposited at 300 °C:

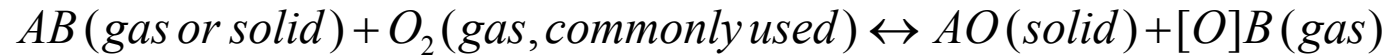


Reversible process, can be used for chamber cleaning



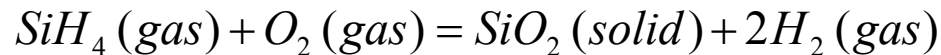
Types of CVD Reactions (Cont.)

Oxidation



Example

Low-temperature SiO_2 deposited at 450 °C:



Example

SiO_2 formed through dry oxidation at 900 - 1100 °C:



Types of CVD Reactions (Cont.)

Compound Formation



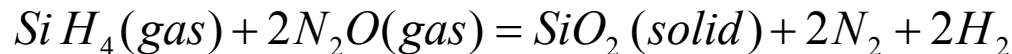
Example

SiO₂ formed through wet oxidation at 900 - 1100 °C:



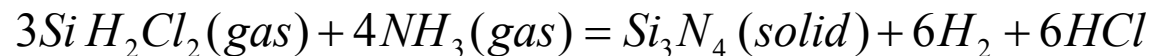
Example

SiO₂ formed through PECVD at 200 - 400 °C:



Example

Si₃N₄ formed through LPCVD at 700 - 800 °C:



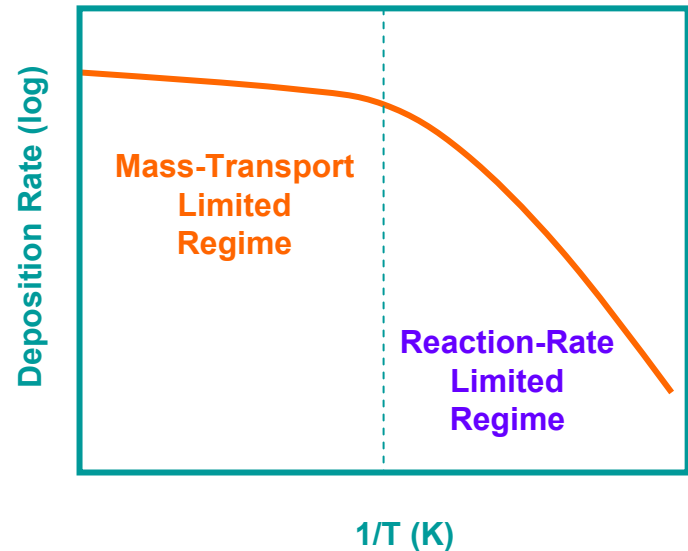
CVD Deposition Condition

Mass-Transport Limited Deposition

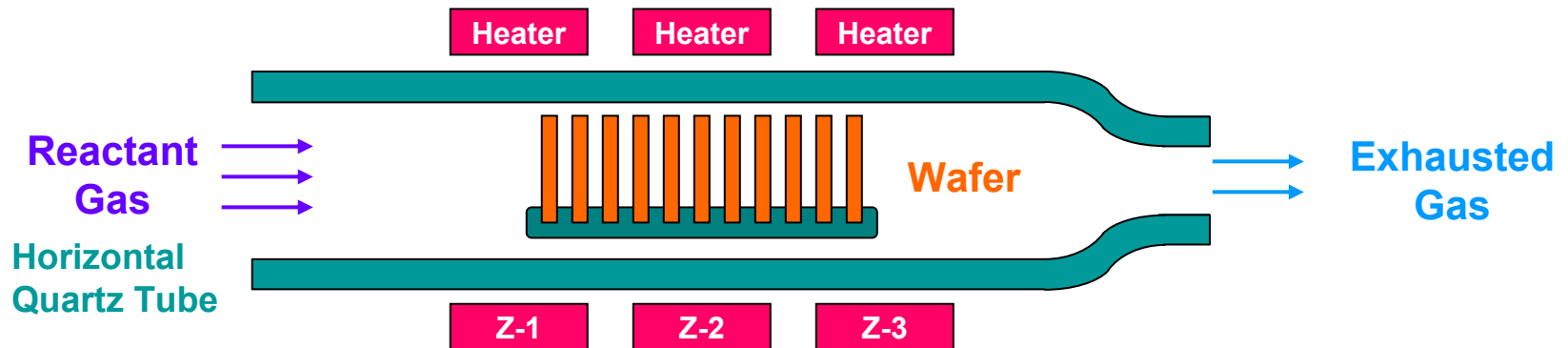
- At high temperature such that the reaction rate exceeds the gas delivering rate
- Gas delivering controls film deposition rate
- Film growth rate insensitive to temperature
- Film uniformity depends on whether reactant can be uniformly delivered across a wafer and wafer-to-wafer

Reaction-Rate Limited Deposition

- At low temperature or high vacuum such that the reaction rate is below gas arriving rate
- Temperature controls film deposition rate
- Film uniformity depends on temperature uniformity across a wafer and wafer-to-wafer



Low-Pressure CVD (LPCVD)

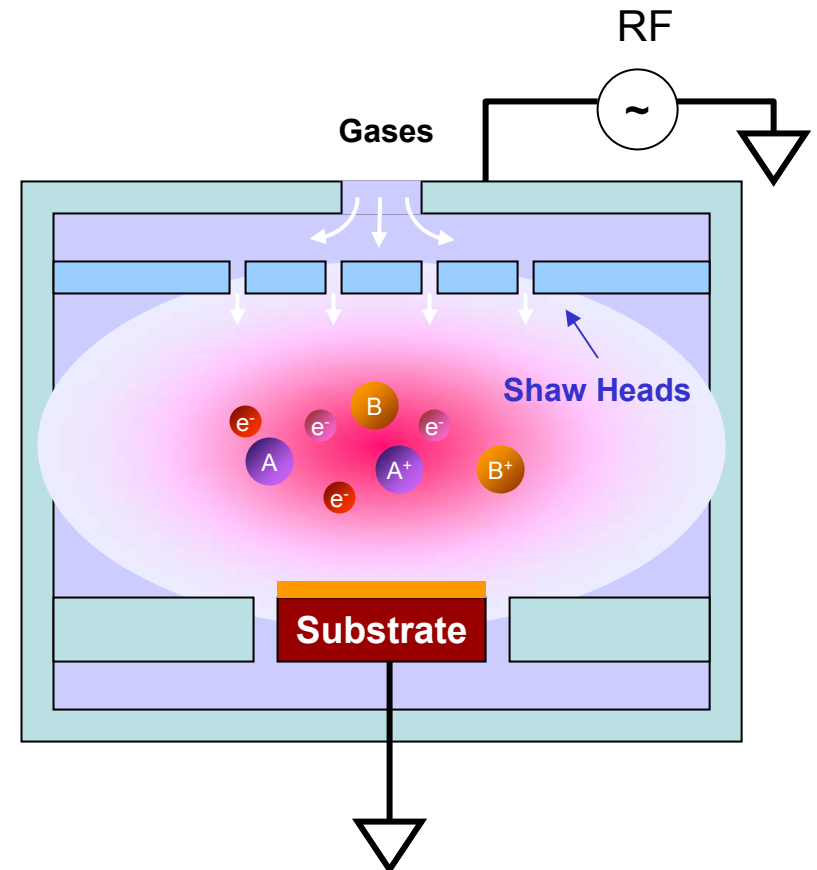


- Thermal energy for reaction activation
- System works at vacuum ($\sim 0.1 - 1.0$ torr), resulting in high diffusivity of reactants
 - ➔ reaction-rate limited
- Wafer can stacked closely without lose uniformity as long as they have the same temperature
- Temperature is controlled around $600 - 900^{\circ}\text{C}$ by “flat” temperature zone through using multiple heaters
- Low gas pressure reduce gas-phase reaction which causes particle cluster that contaminants the wafer and system



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 ($< 300\text{ }^{\circ}\text{C}$)
- For depositing film on metals and other materials that cannot sustain high temperature
- Surface reaction limited deposition; substrate temperature control (typically cooling) is important to ensure uniformity



Common CVD Reactants

Material	LPCVD	PECVD
α -Si	SiH_4	SiH_4 SiH_2Cl_2
SiO_2	$\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) $\text{SiH}_2\text{Cl}_2 + \text{N}_2\text{O}$	$\text{SiH}_4 + \text{N}_2\text{O}$ $\text{SiH}_4 + \text{O}_2$
Si_3N_4	$\text{SiH}_4 + \text{NH}_3$ $\text{SiH}_2\text{Cl}_2 + \text{NH}_3$	$\text{SiH}_4 + \text{NH}_3$ $\text{SiH}_4 + \text{N}_2$



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 A/s	50 ~ 100 °C	Yes	Very low
E-beam Evaporation	Both metal and dielectrics	Poor	Low	10 ~ 100 nm	Poor	10 ~ 100 A/s	50 ~ 100 °C	Yes	High
Sputtering	Both metal and dielectrics	Very good	Low	~ 10 nm	Good	Metal: ~ 100 A/s Dielectric: ~ 1-10 A/s	~ 200 °C	Some degree	High
PECVD	Mainly Dielectrics	Good	Very low	10 ~ 100 nm	Good	10 - 100 A/s	200 ~ 300 °C	Some degree	Very High
LPCVD	Mainly Dielectrics	Very Good	Very low	1 ~ 10 nm	Excellent	10 - 100 A/s	600 ~ 1200 °C	Isotropic	Very High

