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)

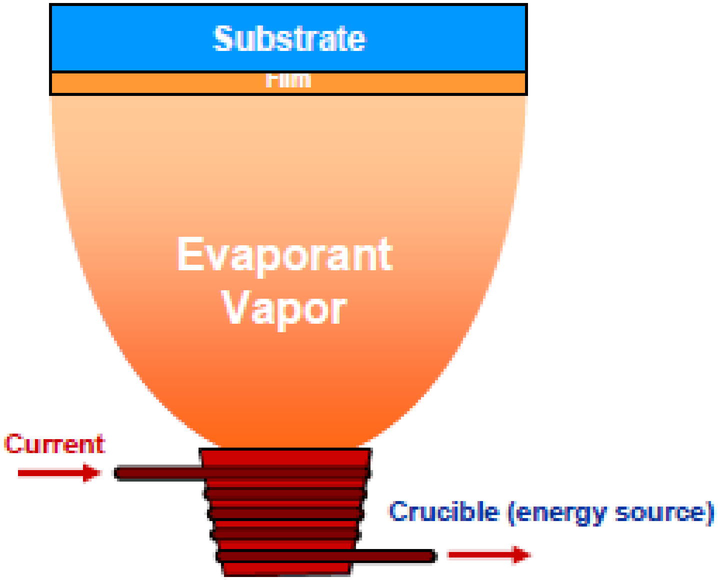
- Film is formed by chemical reaction on the surface of substrate

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

Oxidation
Spin Coating
Platting

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



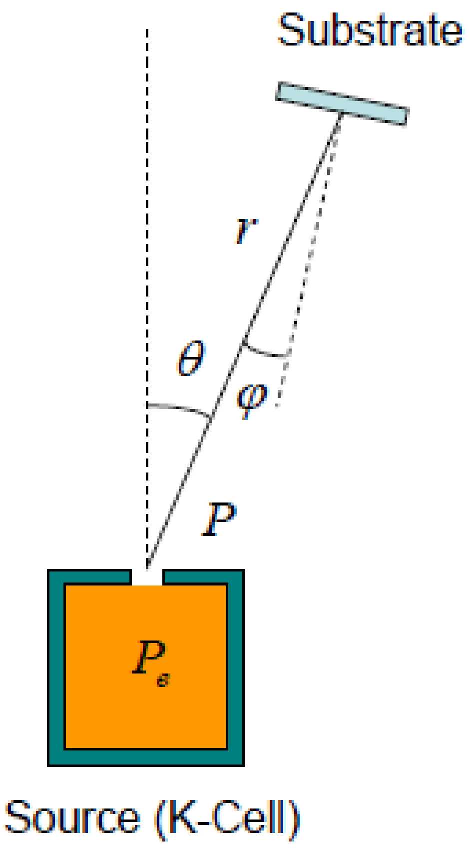
Langmuire-Knudsen Relation

Mass Deposition Rate per unit area of source surface:

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

C_m = 1.85x10^{-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 ~ 0)**



Uniform Coating

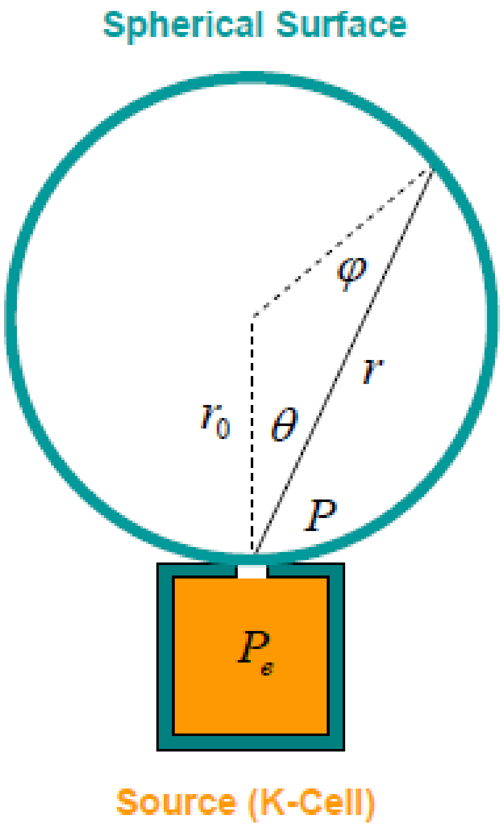
Spherical surface with source on its edge:

$$\cos\theta = \cos\varphi = \frac{r}{2r_0}$$

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

➡ Angle Independent – uniform coating!

➥ Used to coat instruments with spherical surfaces



Uniformity on a Flat Surface

Consider the deposition rate difference between wafer center and edge:

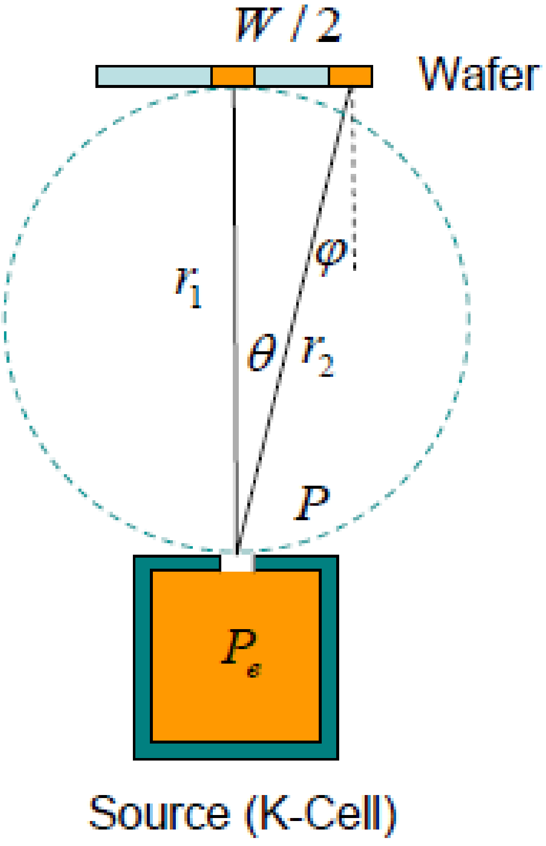
$$R_1 \propto \frac{1}{r_1^{\,2}}$$

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

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



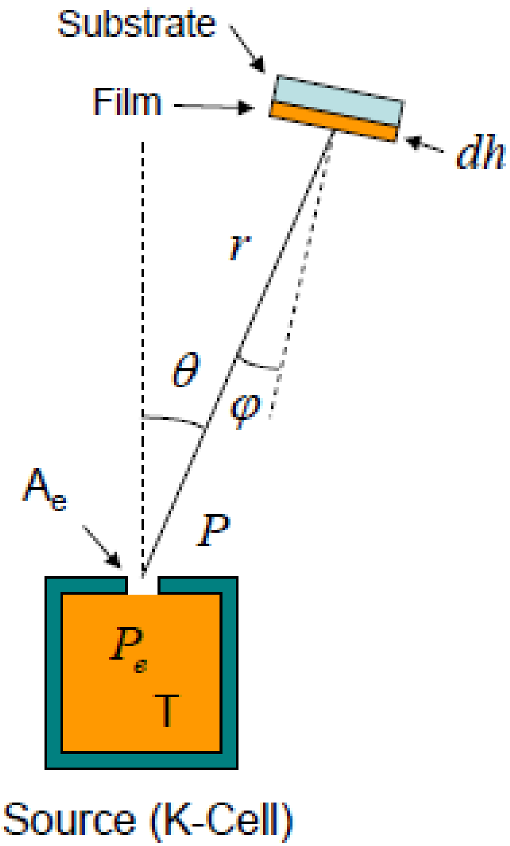
Thickness Deposition Rate vs. Source Vapor Pressure

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 (cm^2)
ρ: evaporant density (g/cm^3)

P_e is function of source Temperature!

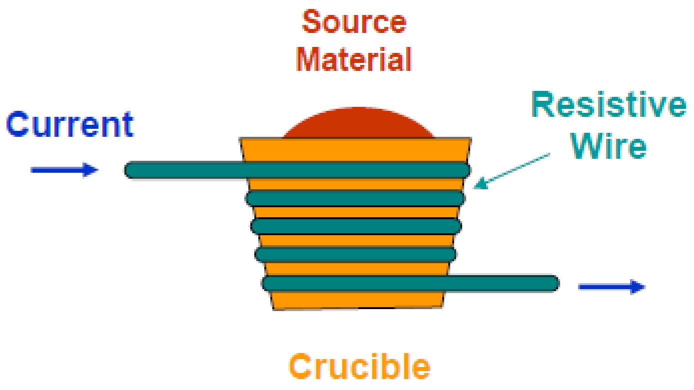


Source (K-Cell)

Example: Al
M ~ 27, ρ ~ 2.7, A_e ~ 10^{-2} cm^2, T ~ 900 K
R ~ 50 cm (uniformity requirement)

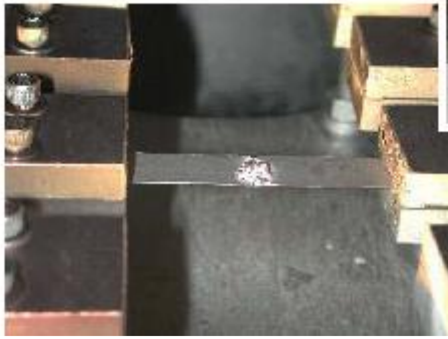
$$\frac{dh}{dt}=50P_e \quad (\text{A/s})$$

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

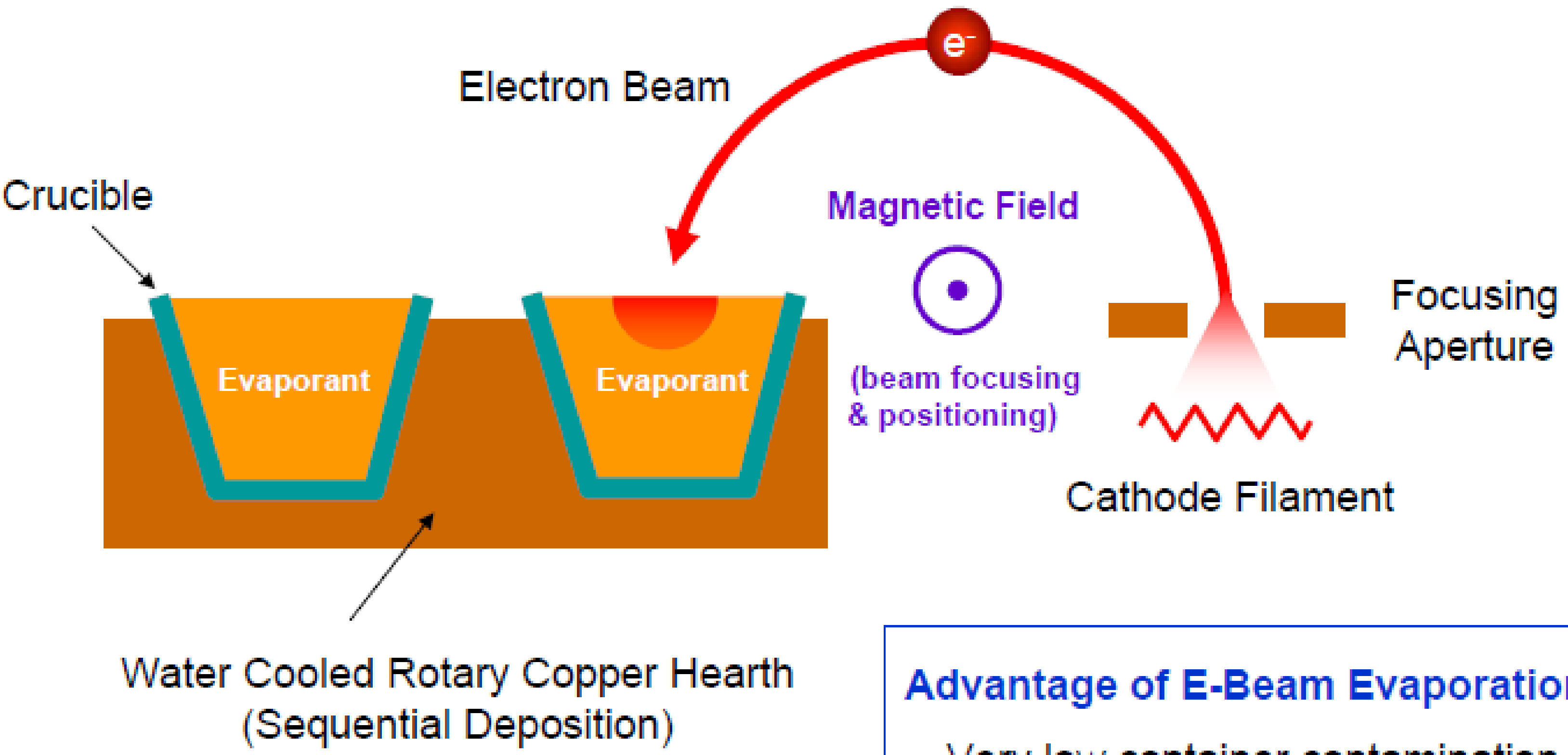


**Contamination Problem
with Thermal Evaporation**

Container material also evaporates, which contaminates the deposited film



Heating Method – e-Beam Heater



Advantage of E-Beam Evaporation:

Very low container contamination

CIMS' Sharon E-Beam Evaporator

Comparison

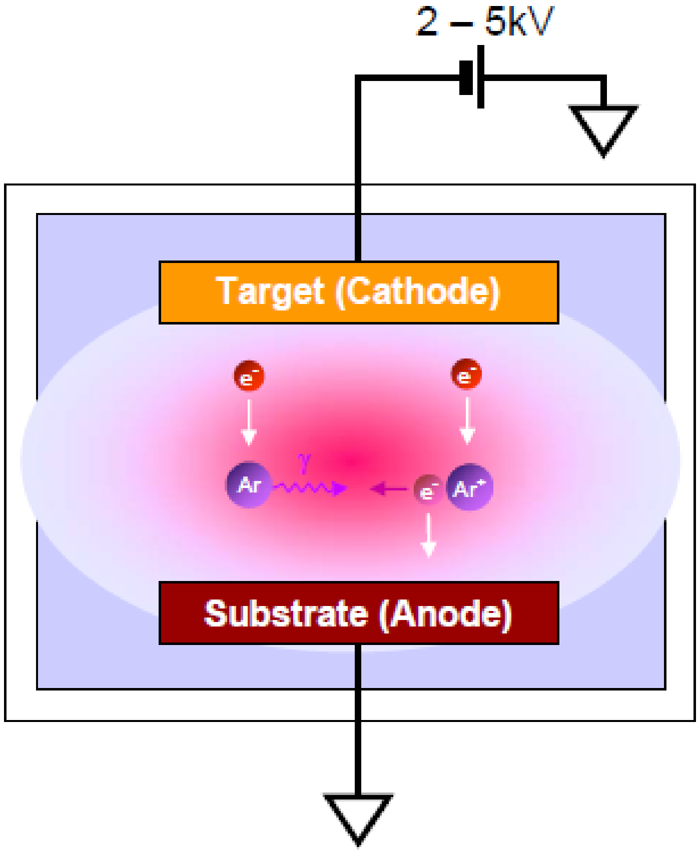
Deposition	Material	Typical Evaporant	Impurity	Deposition Rate	Temperature Range	Cost
Thermal	Metal or low melt-point materials	Au, Ag, Al, Cr, Sn, Sb, Ge, In, Mg, Ga CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$	High	1 ~ 20 A/s	~ 1800 ºC	Low
E-Beam	Both metal and dielectrics	Everything above, plus: Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo Al2O3, SiO, SiO2, SnO2, TiO2, ZrO2	Low	10 ~ 100 A/s	~ 3000 ºC	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

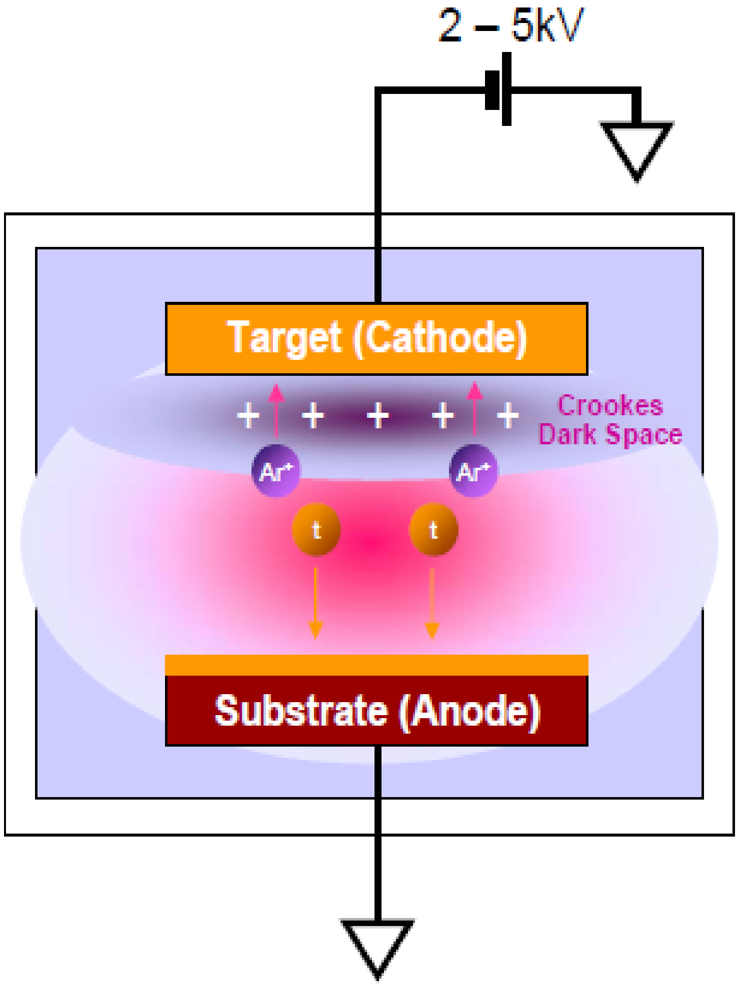
DC Diode Sputtering Deposition

- Target (source) and substrate are placed on two parallel electrodes (diode)
- They are placed inside a chamber filled with inert gas (Ar)
- DC voltage (~ 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 ➡ gas glows
    - ionization of Ar ➡ Ar^+ + 2nd electron
- 2nd electrons repeat above process
    - ➡ "gas breakdown"
    - ➡ 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 ~10^3 V to ~10^2V, mainly across the dark space
- Electrical field in other area is significantly reduced by screening effect of the position 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: $\boxed{L \cdot P > 0.5 \ \ (cm \cdot torr)}$

L: electrode spacing, P: chamber pressure

For example:

Typical target-substrate spacing: L ~ 10cm

➡ P > 50 mtorr

RF (Radio Frequency) Sputtering

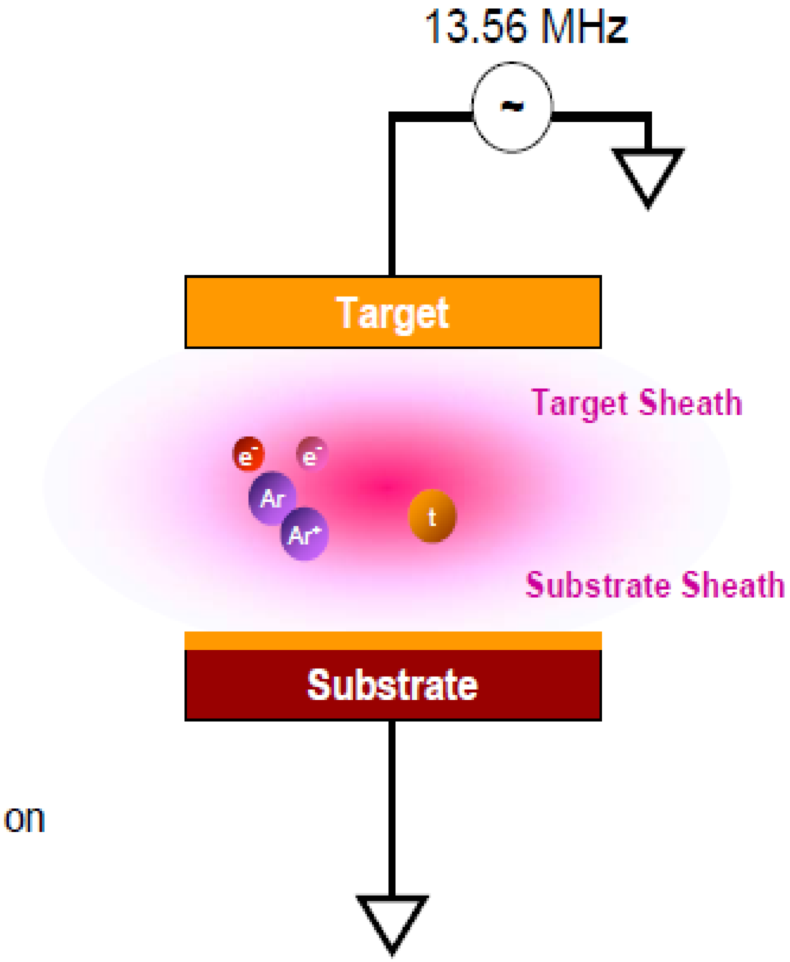
DC sputtering cannot be used for depositing dielectrics because insulating cathode will cause charge build up during Ar^+ bombarding

➡ 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), heave 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



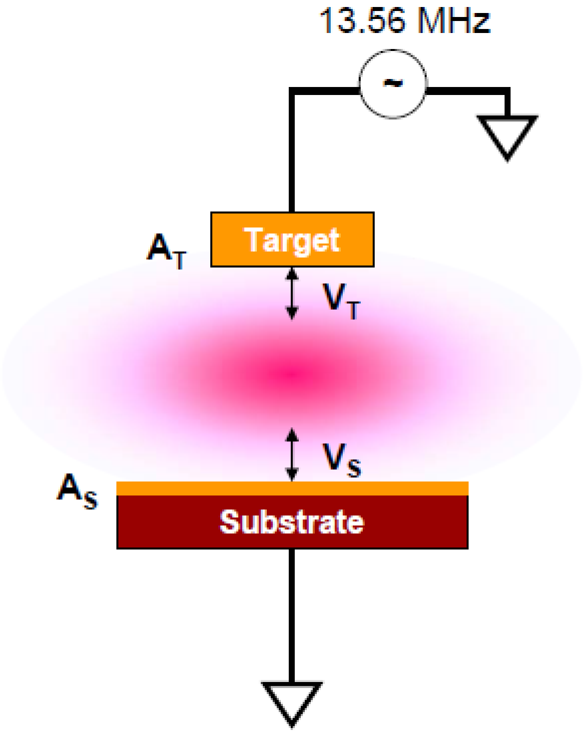
RF (Radio Frequency) Sputtering

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

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



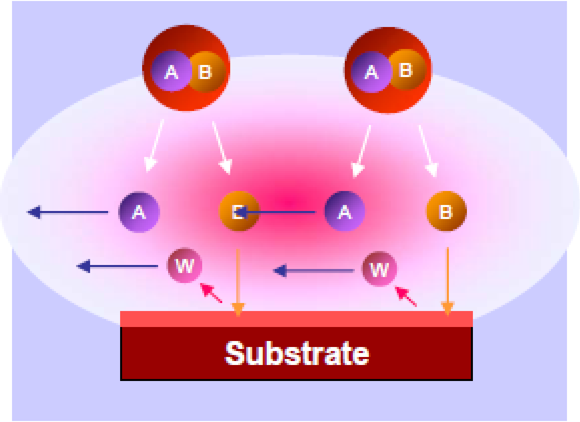
Comparison between Evaporation and Sputtering

Evaporation	Sputtering
Low energy atoms (~ 0.1 eV)	High energy atoms / ions (1 – 10 eV) • denser film • smaller grain size • better adhesion
High Vacuum • directional, good for lift-off • lower impurity	Low Vacuum • poor directionality, better step coverage • gas atom implanted in the film
Point Source • poor uniformity	Parallel Plate Source • better uniformity
Component Evaporate at Different Rate • poor stoichiometry	All Component Sputtered with Similar Rate • 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 firmed
- Transport of volatile byproducts away form substrate
- Exhaust waste



Types of CVD Reactions

Pyrolysis (Thermal Decomposition)

$$AB\,(gas) \rightarrow A\,(solid) + B\,(gas)$$

Example

α-Si deposited at 580 - 650 ºC:

$$SiH_4\,(gas) = Si\,(solid) + 2H_2\,(gas)$$

Reduction (lower temperature than Pyrolysis)

$$AB\,(gas) + H_2(gas, commonly\,used) \leftrightarrow A\,(solid) + HB\,(gas)$$

Example

W deposited at 300 ºC:

$$WF_6\,(gas) + 3H_2(gas) = W\,(solid) + 6HF\,(gas)$$

Reversible process, can be used for chamber cleaning

Types of CVD Reactions (Cont.)

Compound Formation

$$AB\,(gas\ or\ solid) + XY\,(gas\ or\ solid) \leftrightarrow AX\,(solid) + BY\,(gas)$$

Example
SiO2 formed through wet oxidation at 900 - 1100 ºC:

$$Si\,(Solid) + 2H_2O(vapor) = SiO_2\,(solid) + 2H_2$$

Example
SiO2 formed through PECVD at 200 - 400 ºC:

$$Si\,H_4(gas) + 2N_2O(gas) = SiO_2\,(solid) + 2N_2 + 2H_2$$

Example
Si_3N_4 formed through LPCVD at 700 - 800 ºC:

$$3Si\,H_2Cl_2(gas) + 4NH_3(gas) = Si_3N_4\,(solid) + 6H_2 + 6HCl$$

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