

# Thin Film deposition techniques

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# Thin film deposition techniques

## Physical Vapour 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

Other coating processes  
Spin coating, PLD, MBE  
Plating, SILAR

## Chemical Vapour 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)

## Difference in PVD and CVD

- PVD reliance on solid or molten sources, as opposed to generally gaseous precursors in CVD
- The physical mechanisms by which source atoms enter into the gas phase
- The general absence of chemical reactions in the gas phase and at the substrate surface

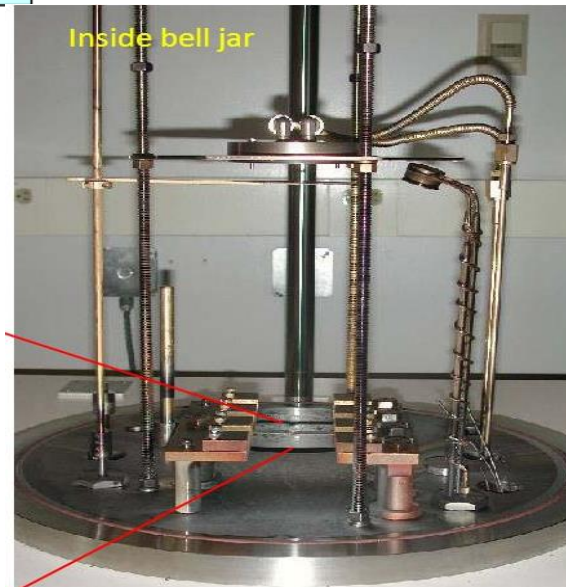
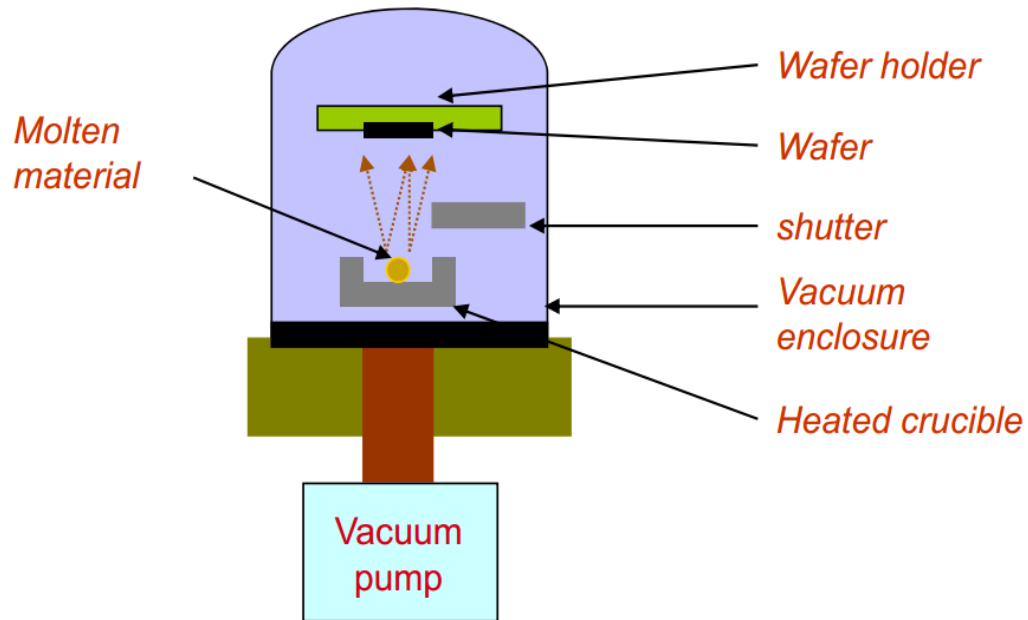
# Thin film deposition techniques

## ❑ Physical Vapour Deposition (PVD)

Physical Vapor Deposition (PVD) comprises a group of surface coating technologies used for decorative coating, tool coating, and other equipment coating applications. It is fundamentally a vaporization coating process in which the basic mechanism is an atom by atom transfer of material from the solid phase to the vapor phase and back to the solid phase, gradually building a film on the surface to be coated. In the case of reactive deposition, the depositing material reacts with a gaseous environment of co-deposited material to form a film of compound material, such as a nitride, oxide, carbide or carbonitride.

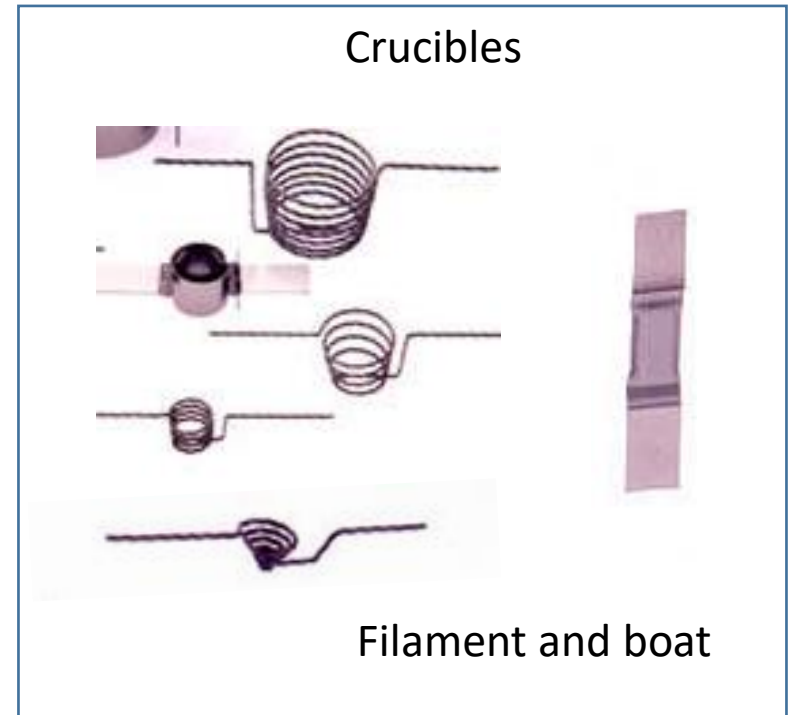
Physical evaporation is one of the oldest methods of depositing metal films. Aluminum, gold and other metals are heated to the point of vaporization, and then evaporate to form a thin film covering the surface of the substrate. All film deposition takes place under vacuum or very carefully controlled atmosphere.

# Thermal evaporation



# Procedure of thermal evaporation

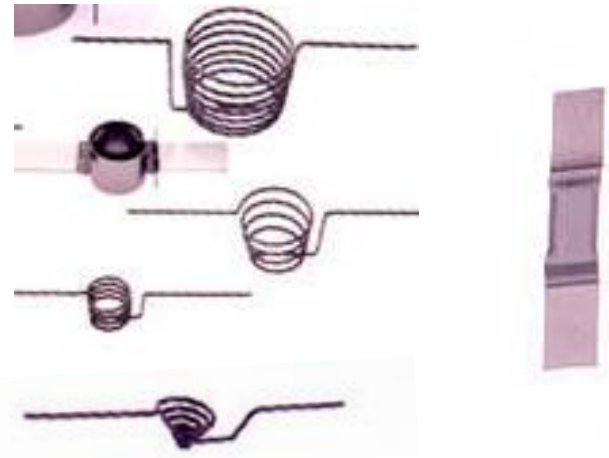
- metal to be deposited is placed in an inert crucible or filament
- chamber is evacuated to a pressure of  $10^{-6}$ – $10^{-7}$  Torr
- Crucible or filament is heated by resistive heating by passing high current through it and flash-evaporation of the metal from the crucible occur and condense onto the cold substrate to form a thin film



# Procedure of thermal evaporation

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

Crucibles



Filament and boat



# Advantages of having vacuum

- The material will be heated at a lower temperature in vacuum
- There will be reduction of the number of impurities in the deposit material
- There is reduction to the effect of oxides formed on the boiling on the surface.
- The main advantage of the vacuum is that the adhesion to the film increases due to increase in (mean free path) and better film can be formed. Due to less collisions between atoms, finally the atoms will deposit having high kinetic energy so that adhesion will be better

# Thermal evaporation

The evaporation rate is a function of the vapour pressure of the metal

Depending on experimentation on the evaporation of mercury, Hertz in 1882 observed that

1. Not limited by insufficient heat supplied to the surface of the molten molten evaporant.
2. Proportional to the difference between the equilibrium pressure ,  $P_e$  of Mercury at given temperature and the hydrostatic pressure  $P_h$  acting on the evaporant.

Maximum evaporation is possible when the number of vapour molecule s emitted corresponds to that required for equilibrium

$$\Phi_e = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MRT)^{1/2}} \quad \text{Molecules/cm}^2\text{-sec}$$

$\Phi_e$  Is the evaporated flux and  $\alpha_e$  is the coefficient of evaporation

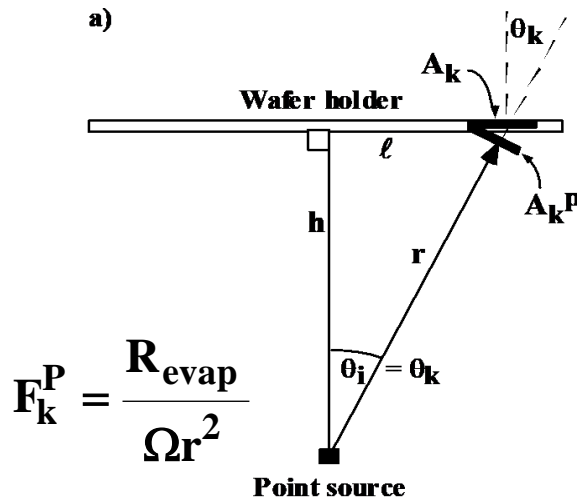


# Thermal evaporation

The evaporation rate is a function of the **vapour pressure of the metal**

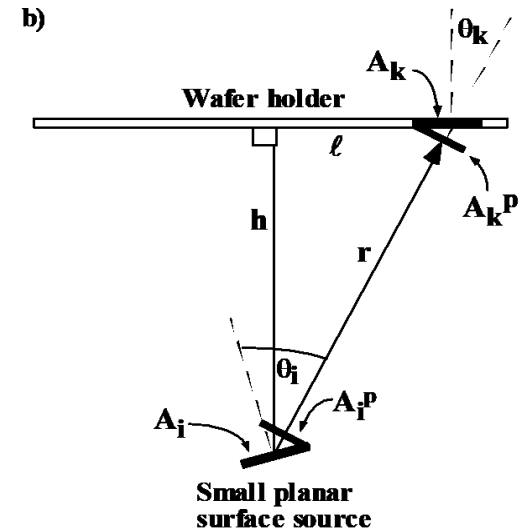
Mass evaporation rate

$$R_{evap} = 5.83 \times 10^{-2} \left( \frac{m}{T} \right)^{1/2} P_e$$



$$F_k^P = \frac{R_{evap}}{\Omega r^2}$$

$$v = \frac{R_{evap}}{\Omega N r^2} \cos \theta_k$$



$$F_k^P = \frac{R_{evap}}{\Omega r^2} \cos \theta_i$$

$$v = \frac{R_{evap}}{\Omega N r^2} \cos \theta_i \cdot \cos \theta_k$$

F: flux that strikes area A (atoms or grams per  $\text{cm}^{-2}\text{sec}$ ).

v: deposition rate (nm/sec).

N: density of the material (atoms or grams per  $\text{cm}^3$ ).

$R_{evap}$ : evaporation rate from the source, in atoms or grams per second.

$\Omega$ : solid angle,  $=4\pi$  if source emits in all directions;  $=2\pi$  if emits only upward.

# Thermal evaporation

## Vapour pressure of the elements

Clausius –Clapyeron equation

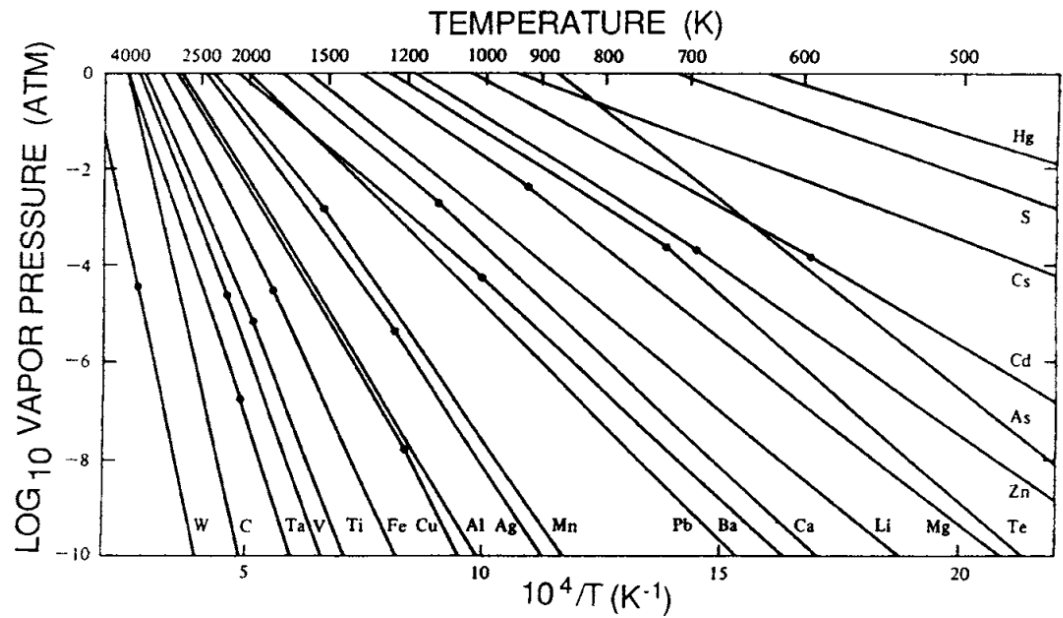
$$\frac{dP}{dT} = \frac{\Delta H(T)}{T\Delta V}$$

Considering  $\Delta V = V_v - V_c \approx \Delta V_v$ ;  
 $PV_v = RT$

$$\frac{dP}{dT} = \frac{P\Delta H(T)}{RT^2}$$

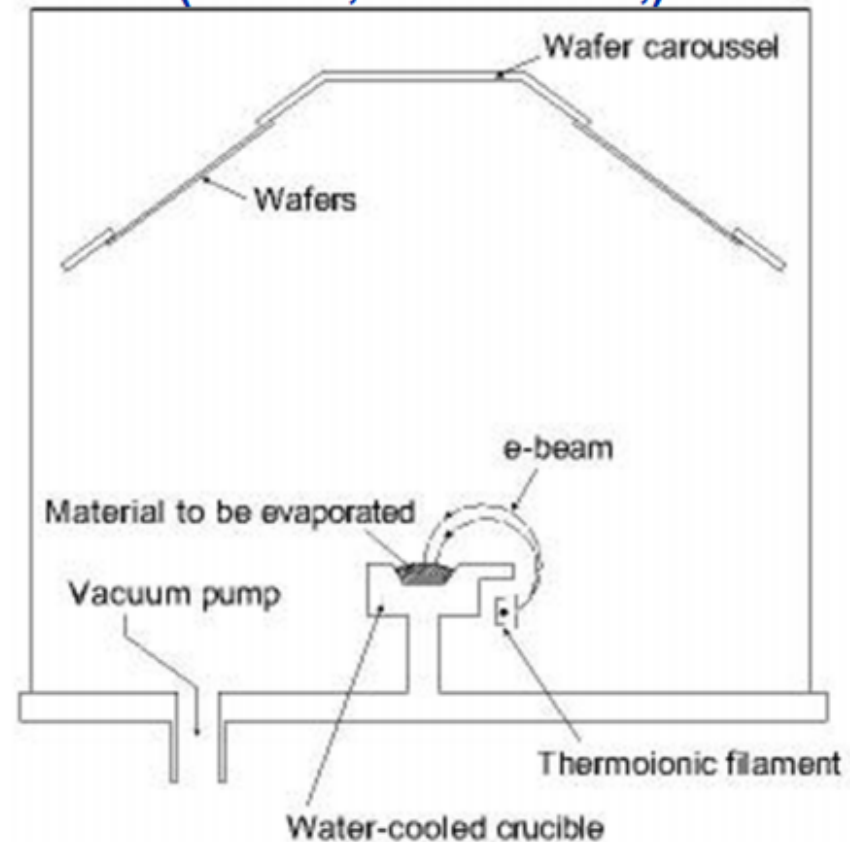
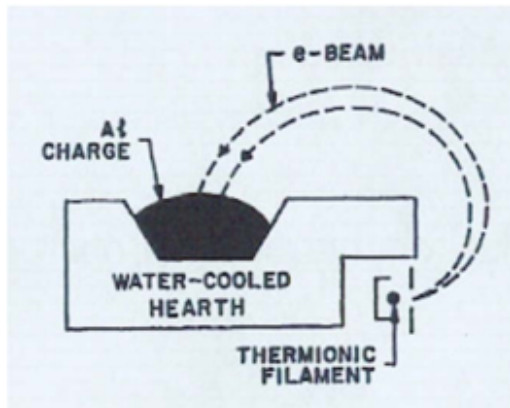
$$\ln P \simeq -\frac{\Delta H_e}{RT} + I \quad \text{or} \quad P = P_0 \exp -\frac{\Delta H_e}{RT}$$

$\Delta H_e$  is latent heat of vaporization



# Electron beam evaporation

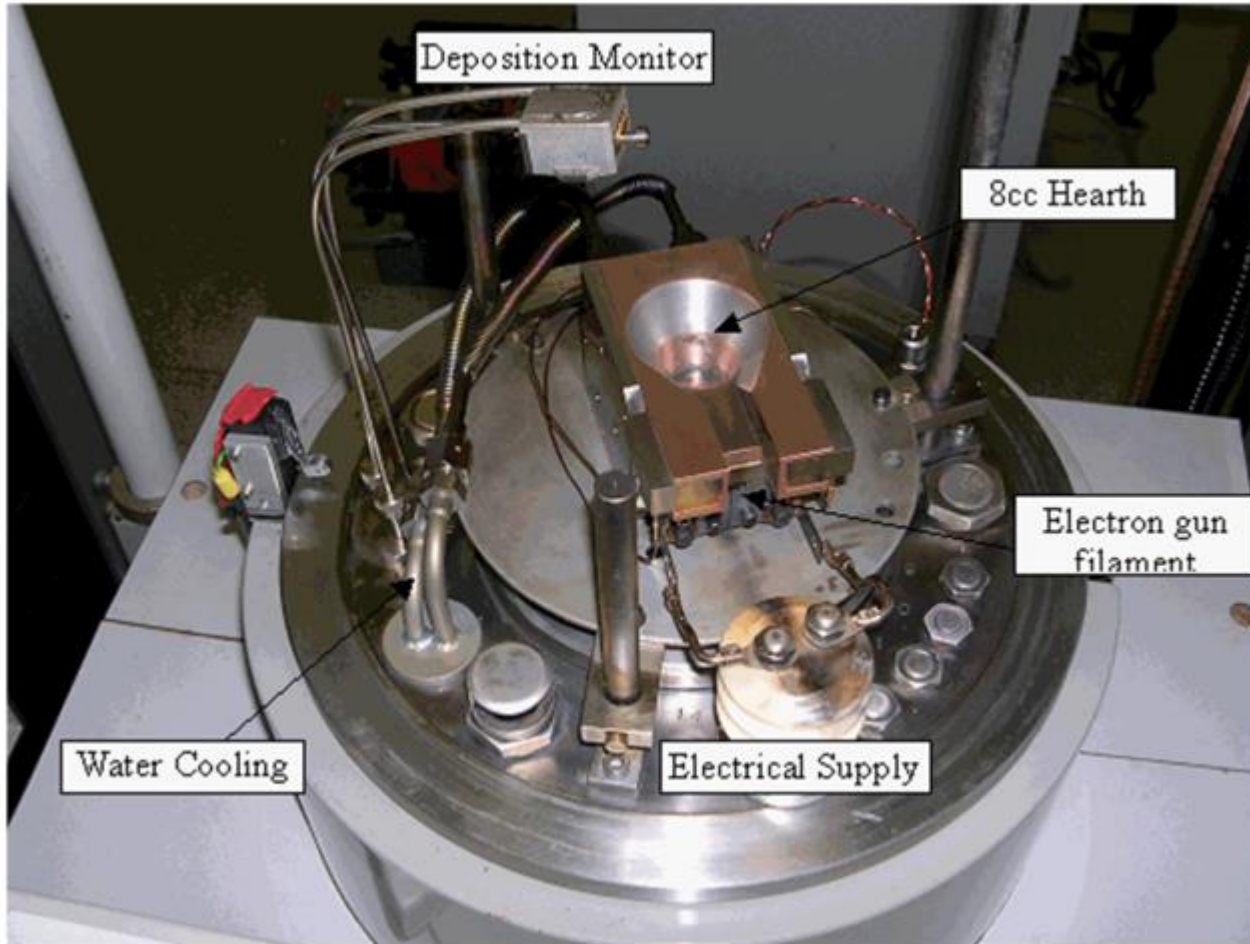
- Focused beam of electrons are used to locally heat the Source
- Can be used to heat / evaporate even high melting point materials
- Alloys could be deposited without dissociation of constituent elements
- Ideally suited for reactive evaporation (Oxides, Nitrides etc.,)



# Electron beam evaporation

- **High intensity electron beam gun (3 to 20 keV) is focused on the target material that is placed in a copper hearth ( water cooled)**
- **The electron beam is magnetically directed onto the evaporant, which melts locally.**
- **No contamination from crucible.**
- **High quality films.**
- **High deposition rate 50 to 500nm/min.**
- **Disadvantages:**
  - Process might induce x-ray damage and ion damage at the substrate.
  - At high energy(> 10keV), the incident electron beam causes x-ray emission.
  - Deposition equipment is more costly.

# Electron beam evaporation



# Thermal evaporation

## **Advantages:**

Versatile – deposits almost any material

Very few chemical reactions

Little wafer damage

## **Limitations:**

Line-of-sight

Shadowing

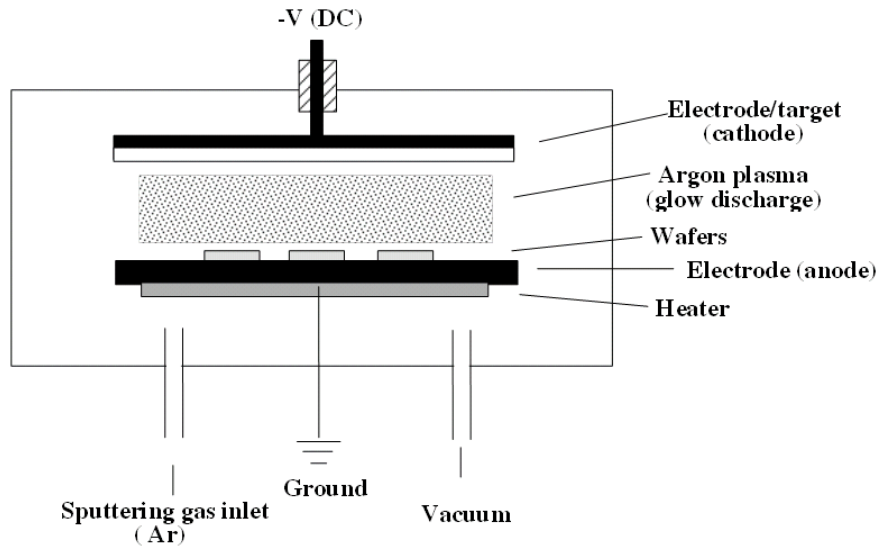
Thickness uniformity

Difficult to evaporate materials with low vapor pressures

# Other PVD Techniques

- Other deposition techniques include
  - Sputter deposition (DC, RF, and reactive)
  - Bias sputtering
  - Magnetron sputtering
  - Collimated and ionized sputter deposition
  - Hot sputter deposition

# DC Sputtering technique



Schematic diagram of DC-powered sputter deposition equipment.

- Plasma is needed to make the gas conductive, and generated ions can then be accelerated to strike the target.
- Higher pressures than evaporation: 1-100 mTorr.



- Major process parameters:
  - Operation pressure (~1-100mTorr)
  - Power (few 100W)
  - For DC sputtering, voltage -2 to -5kV.
  - Additional substrate bias voltage.
  - Substrate temperature (20-700°C)



# DC Sputtering technique

## ➤ Advantages over thermal evaporation

A wide range of industrial products use sputtering: LCD, computer hard drives, hard coatings for tools, metals on plastics.

It is more widely used for industry than evaporator, partly because that, for evaporation:

- There are very few things (rate and substrate temperature) one can do to tailor film property.
- The step coverage is poor.
- It is not suitable for compound or alloy deposition.
- Considerable materials are deposited on chamber walls and wasted.



# DC Sputtering technique

## ➤ Advantages

- Able to deposit a wide variety of metals, insulators, alloys and composites.
- Replication of target composition in the deposited films.
- Capable of in-situ cleaning prior to film deposition by reversing the potential on the electrodes .
- Better film quality and step coverage than evaporation.
- More reproducible deposition control – same deposition rate for same process parameters (not true for evaporation), so easy film thickness control via time.
- Can use large area targets for uniform thickness over large substrates.
- Sufficient target material for many depositions.

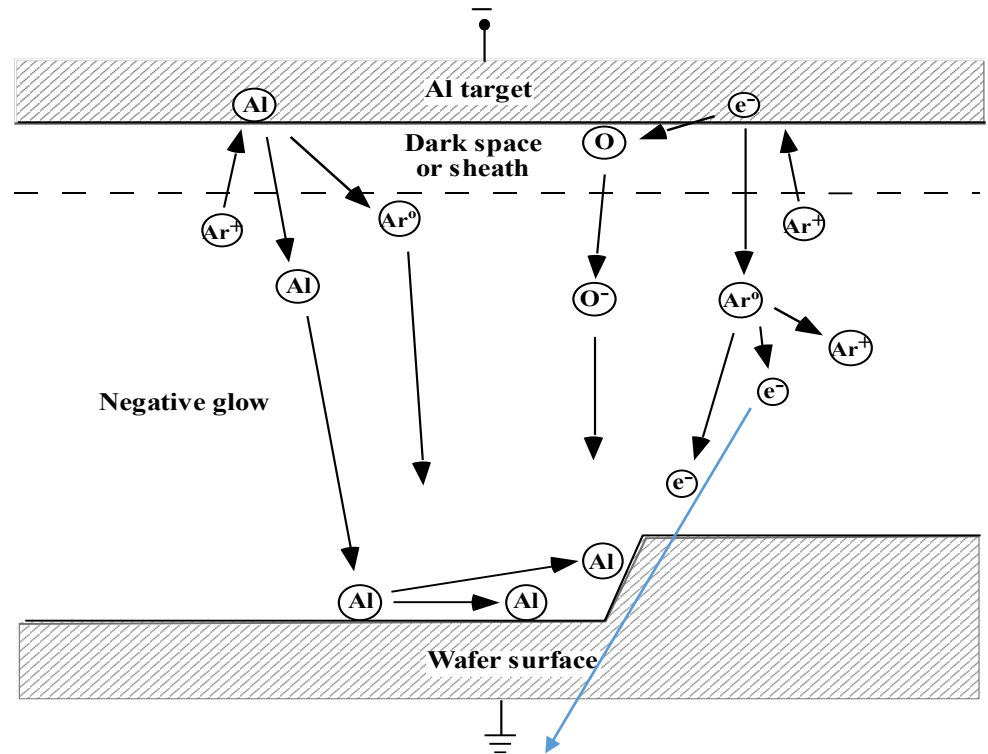
## Disadvantages:

- Substrate damage due to ion bombardment or UV generated by plasma.
- Higher pressures 1 –100 mtorr (  $< 10^{-5}$  torr in evaporation), more contaminations unless using ultra clean gasses and ultra clean targets.
- Deposition rate of some materials quite low.
- Some materials (e.g., organics) degrade due to ionic bombardment.
- Most of the energy incident on the target becomes heat, which must be removed.



# DC Sputtering technique

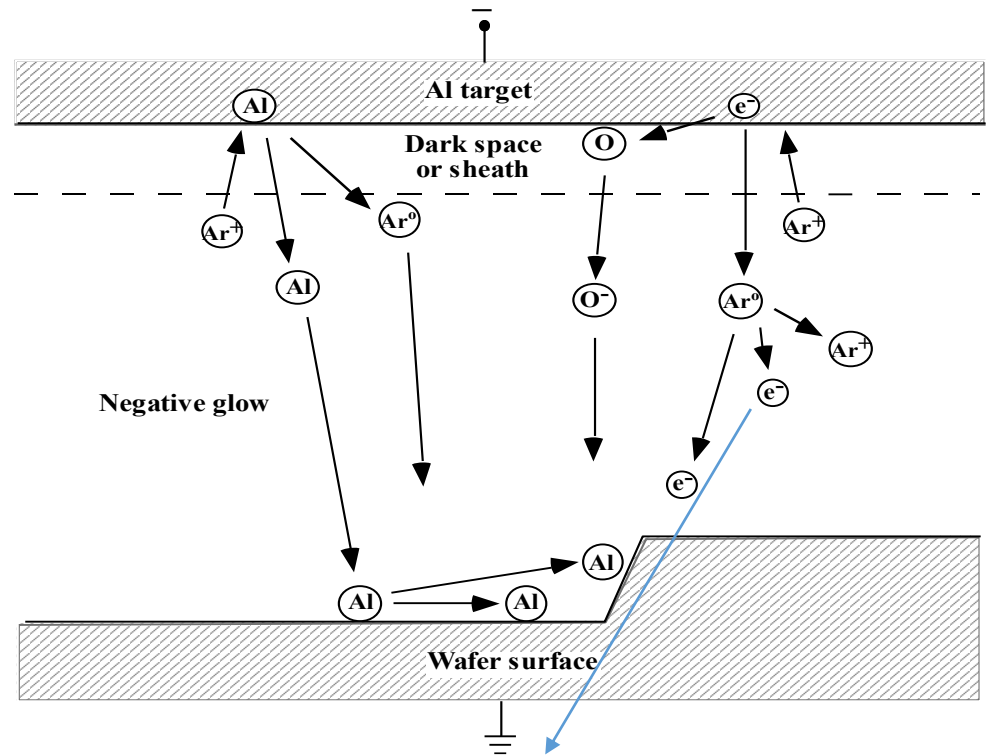
- When energetic ions strike a surface, material is ejected by the transfer of momentum from the ion to the target atoms (akin to billiard ball collisions at the atomic scale). This can be conveniently achieved in a low pressure glow discharge of an inert gas such as argon.
- In such a process the target material is made the cathode and is raised to a potential of several hundred volts. Electrons leaving the cathode stream out into the gas phase where they can impact with argon atoms, ionising them. The positively charged argon is then accelerated to the cathode where it impacts and sputters away material.
- The sputtering yields of different elements for given impact conditions do not vary very much so target alloy compositions can be maintained in the coating except in cases where there are large differences in the atomic weights of alloy constituents.



After collision ionization, there are now TWO free electrons. This doubles the available electrons for ionization. This ongoing doubling process is called "impact ionization", which sustains a plasma.

# DC Sputtering technique

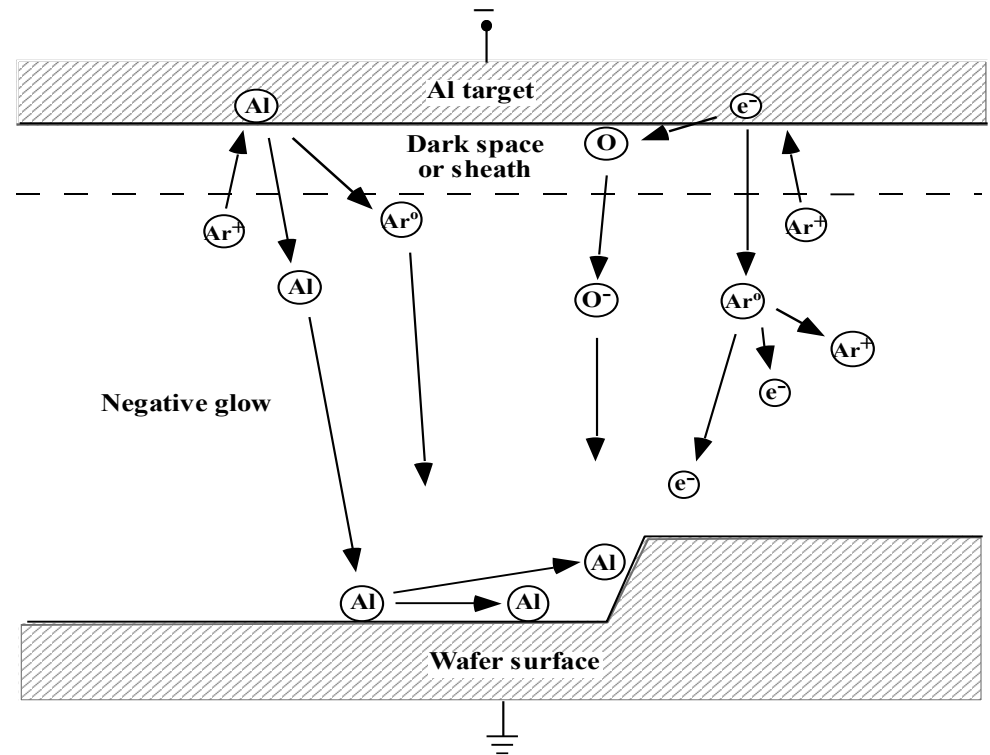
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Sputter off an Al atom, generate secondary electrons, which are accelerated across the sheath region and 1) ionize/excite an Ar; or 2) ionize an impurity atom, here O<sup>-</sup> (for Ar, always positive ion Ar<sup>+</sup>). This O<sup>-</sup> is accelerated toward substrate and may go into the film (bad).

# Sputtering technique

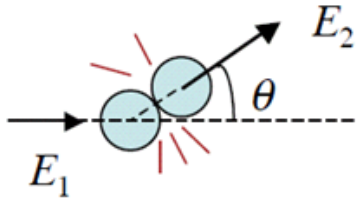
- Energy of each incoming ion is 500-1000eV. Energy of sputtered atoms is 3-10eV.
- Thus, the sputtering process is very inefficient from the energy point of view, 95% of incoming energy goes to target heating & secondary electron.
- High rate sputter processes need efficient cooling techniques to avoid target damage from overheating (serious problem).



- The energies of the atoms or molecules sputtered at a given rate are about one order of magnitude higher than those thermally evaporated at the same rate, which often lead to better film quality. But deposition rate is always lower than the thermal evaporation in normal condition

# Sputtering Yield

Elastic energy transfer



$$\frac{E_2}{E_1} \propto \frac{4M_1M_2}{(M_1 + M_2)^2} \cos^2 \theta$$

$E_2$  is greatest for  $M_1=M_2$ .

There is also inelastic energy transfer, which leads to secondary electrons emission...

$$Y = \frac{\text{sputtered atoms}}{\text{bombing ions}} = \alpha \frac{Mm}{(M+m)^2} \frac{E_m}{U_M}$$

$M$  : mass of target atom

$m$  : mass of bombing ion

$E_m$  : kinetic energy of bombing ion

$U_M$  : Bonding energy of target metal

$\alpha$  : depends on striking /incident angle

- Sputter yield  $Y$ : the number of sputtered atoms per impinging ion.
- Obviously, the higher yield, the higher sputter deposition rate.
- Sputter yield is 1-3: not too much difference for different materials.
- The sputter yield depends on: (a) the energy of the incident ions; (b) the masses of the ions and target atoms; (c) the binding energy of atoms in the solid; and (d) the incident angle of ions.
- The yield is rather insensitive to the target temperature except at very high temperatures where it show an apparent rapid increase due to the accompanying thermal evaporation.

# Dependence of sputter yield on ion energy

## Higher chamber pressure:

Mean-free path of an atom  $\lambda=4.8\times 10^{-3}/P(\text{torr})$  (cm). E.g.  $\lambda\sim 0.1\text{cm}$  for  $P=50\text{mTorr}$ .

Therefore, as typically target-substrate separation is many cm, sputtered atoms have to go through tens of collisions before reaching the substrate.

This reduces deposition rate – considerable materials are deposited onto chamber walls.

Too many collisions also prevent ionization (reduce ion density and deposition rate).

## Lower chamber pressure:

(For same power) higher ion energy that increases sputter yield/deposition rate.

But fewer Ar ions to bombard the target for deposition, which reduces deposition rate.

**Therefore**, there exist an optimum pressure (provided that such a pressure can sustain the plasma) for maximum deposition rate.

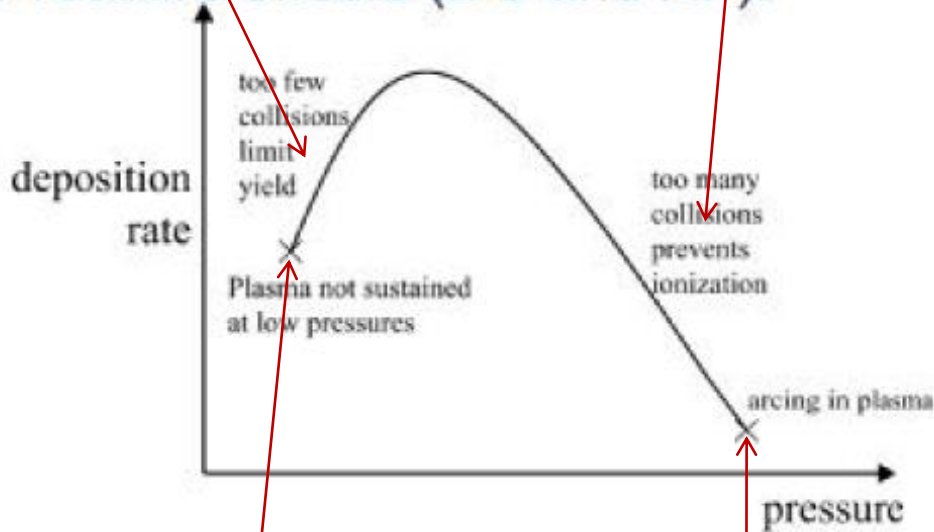
This optimum pressure depends on target-substrate configurations (their separation, target/substrate size...).

# Dependence of deposition rate on chamber pressure

Too few collisions limit yield

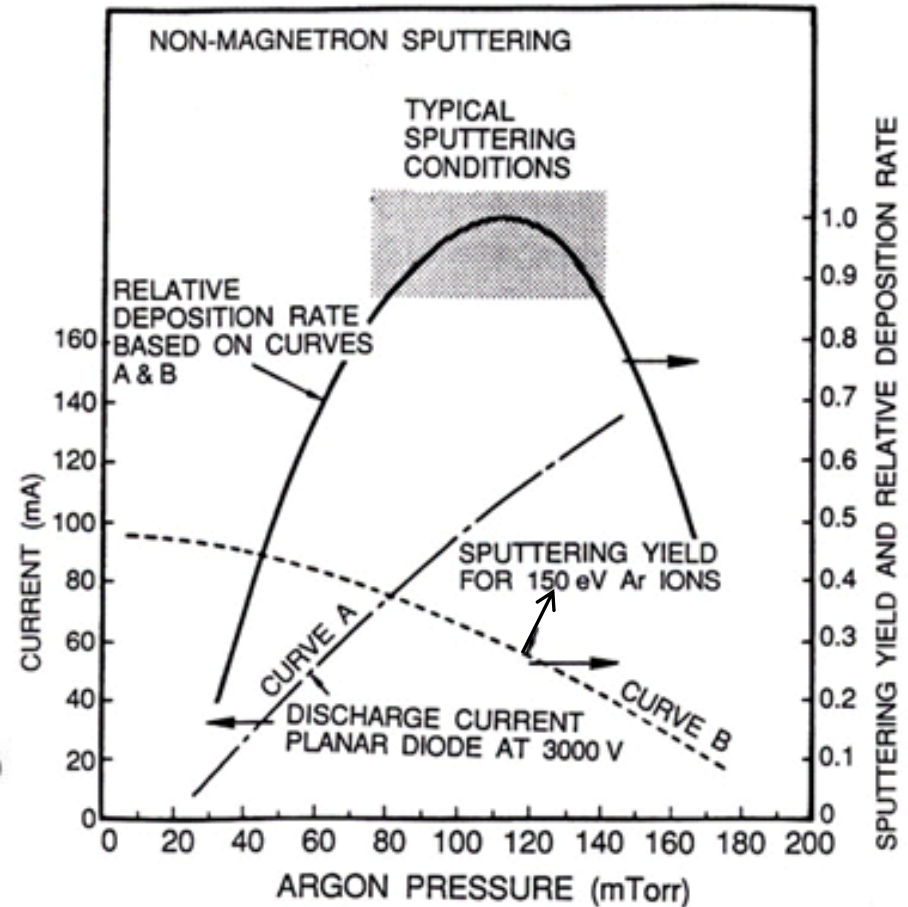
Too many collisions prevent ionization

Pressure effects (DC and RF):



Plasma not sustained at low pressure

Arcing in plasma (?)



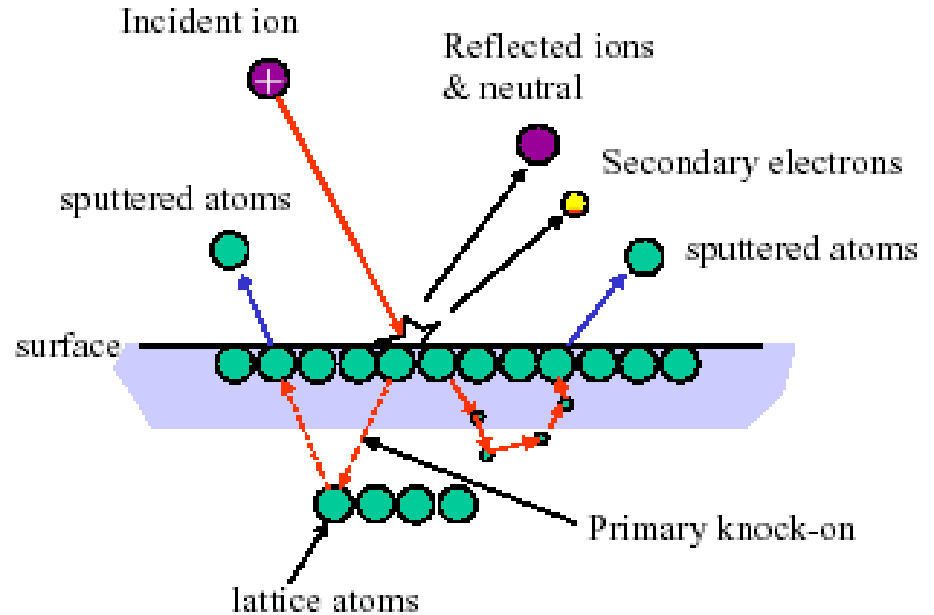
Influence of working pressure and current on deposition rate for non-magnetron sputtering.



# Mechanisms of sputtering and alloy sputtering

The ion impact may set up a series of collisions between atoms of the target, possibly leading to the ejection of some of these atoms. This ejection process is known as sputtering.

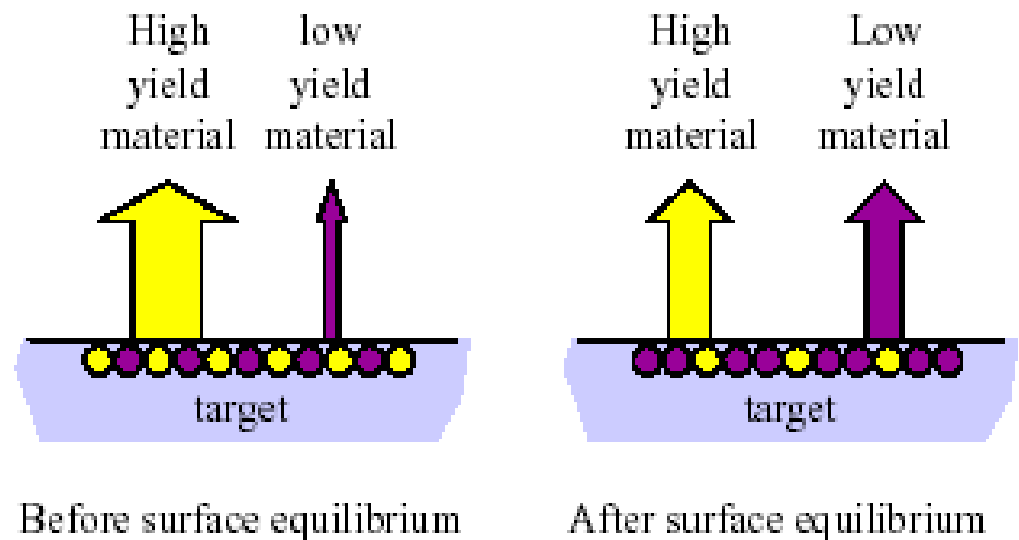
Here we are interested in sputter deposition. Of course sputter can also be used as an etching method (the substrate to be etched will be the 'target'), which is called sputter etching.



## Alloys

Unlike evaporation, composition of alloy film is approximately the same as target.

When target reaches steady state, surface composition balances sputter yield.



# DC plasma

Plasma is ionized gas, with nearly equal number of ions and electrons, plus neutrals (un-ionized molecules including those at ground state and excited state; free radicals such as atomic O, H, F – but no free radicals for Ar plasma).

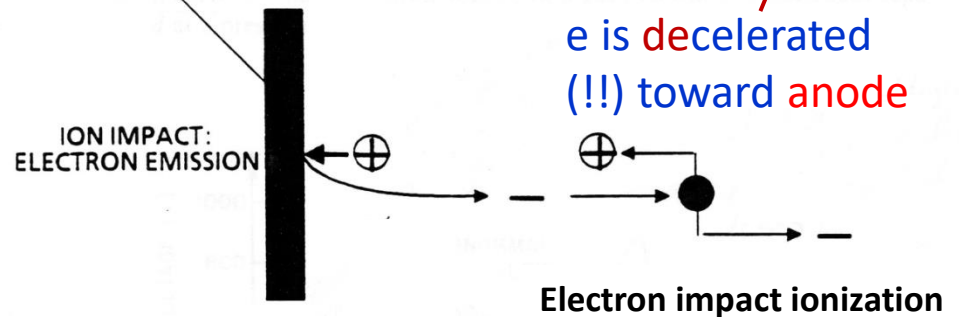
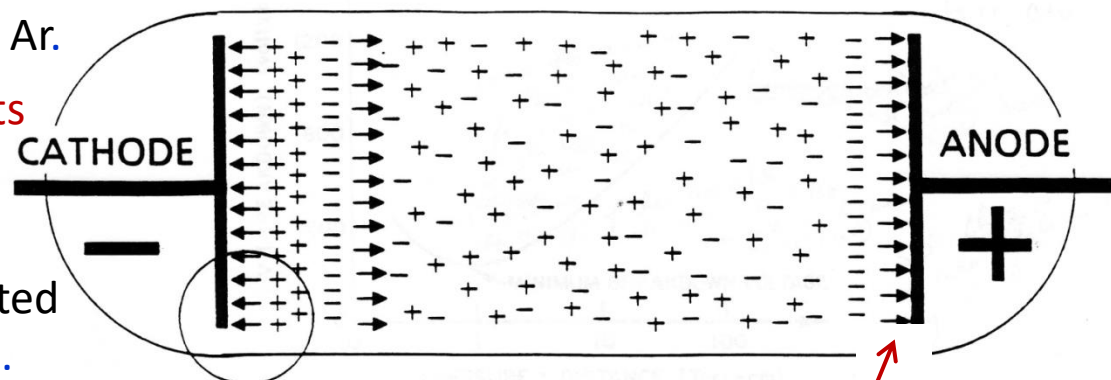
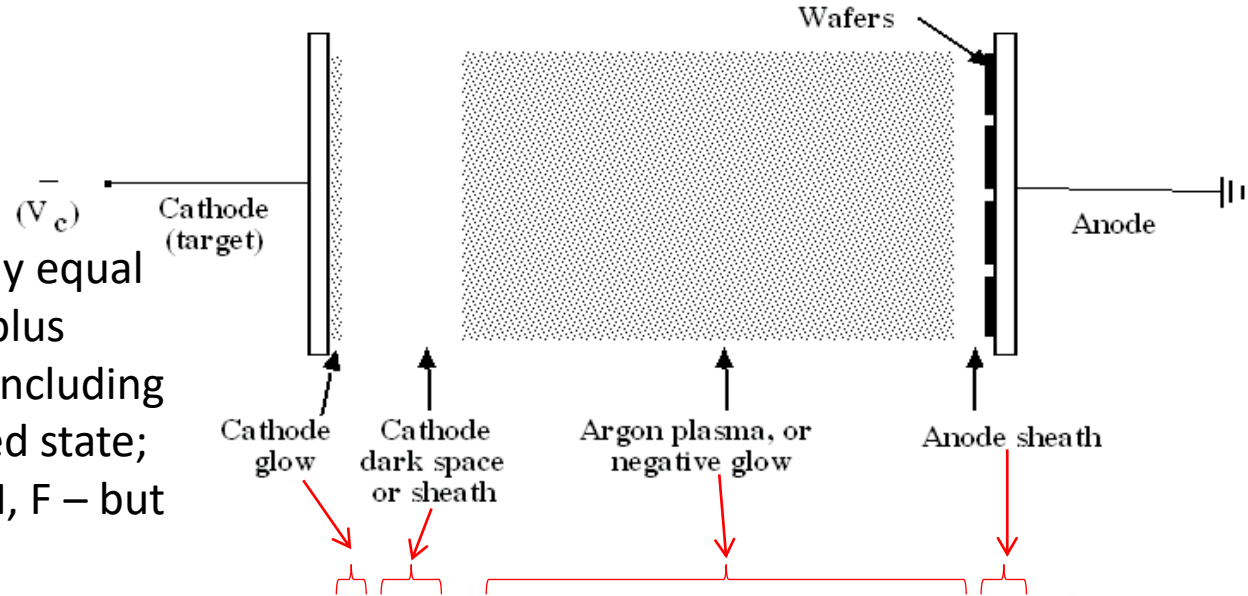
Glow is due to de-excitation of excited Ar.

So glow only exists where there are lots of electrons to excite Ar.

**Cathode glow region:** very close to cathode, secondary electrons are created by Ar bombardment of target material.

**Cathode dark space/sheath:** electrons pass too fast with little excitation.

**Anode sheath:** electrons lost to anode due to its faster *random* movement.



# Explanation of DC plasma structure

## Different velocities in a plasma:

Thermal energy random movement of Ar – 400 m/sec, order  $(k_B T/m_{Ar})^{1/2}$ .

Thermal energy random movement of electron – 10000 m/sec.

Velocity of Ar with energy 100eV – 20000 m/sec.

## Velocity of electrons with energy 100eV – 6000000 m/sec.

Thus plasma is highly conducting due to fast electrons – very little voltage drop in the plasma area where electrons are rich.

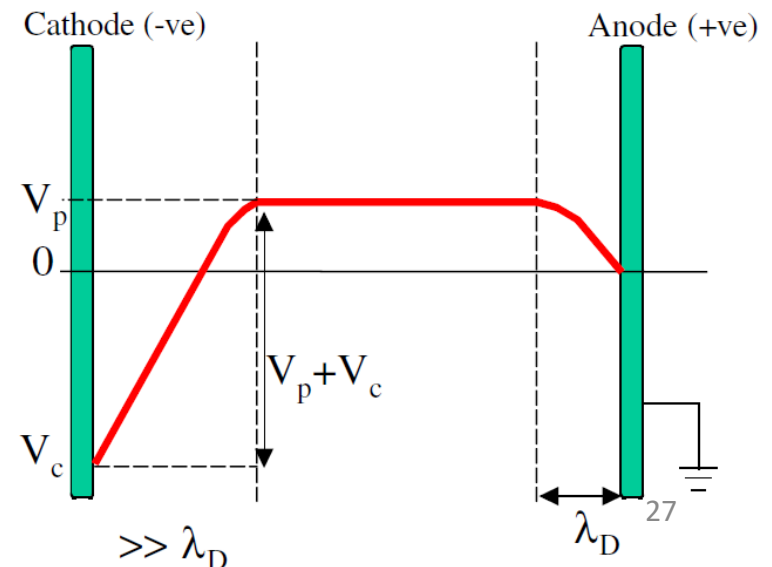
Voltage drop is only possible near the electrodes where electrons may be lost to the electrode. Even without applied voltage (assume plasma still exist), voltage drop may still exist due to faster *random* electrons movement that leads to their loss to electrode.

Therefore, the plasma is always positively biased relative to any electrode or anything (floating or not) inside the plasma.

This positive bias will accelerate positive Ar ion to strike the electrode.

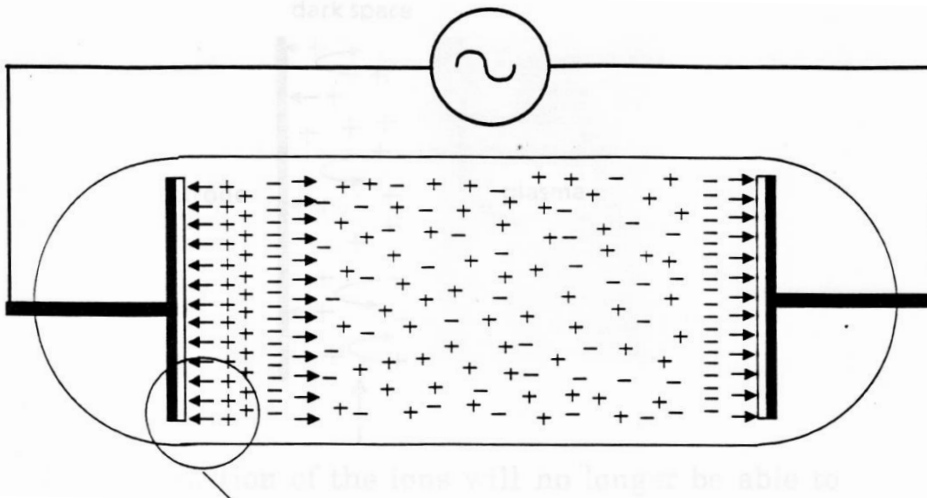
But the bias  $V_p$  near the anode is very small ( $\sim 10V$ ), so no significant sputtering of the substrate.

The total bias ( $V_p$  plus applied voltage) is very high, leading to sputtering of cathode (target).

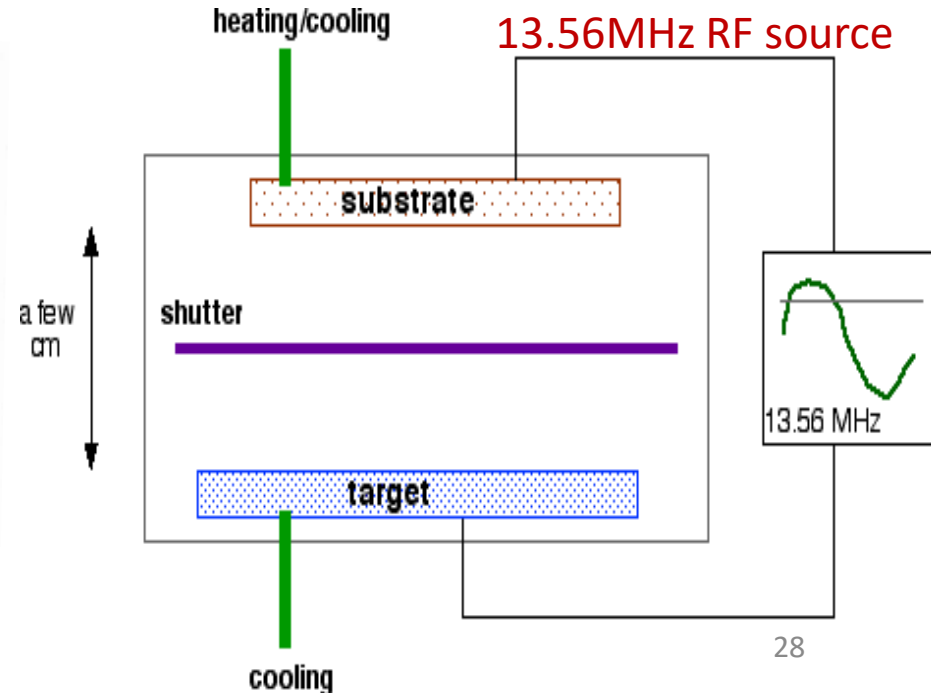


# RF (radio frequency) sputter deposition

- Good for insulating materials because, positive charge ( $\text{Ar}^+$ ) build up on the cathode (target) in DC sputtering systems. Alternating potential can avoid charge buildup
- When frequencies less than  $\sim 50\text{kHz}$ , both electrons and ions can follow the switching of the anode and cathode, basically DC sputtering of both surfaces.
- When frequencies well above  $\sim 50\text{kHz}$ , ions (heavy) can no longer follow the switching, and electrons can neutralize positive charge buildup on each electrode during each half cycle.
- As now electrons gain energy directly from RF powder (no need of secondary electrons to maintain plasma), and oscillating electrons are more efficient to ionize the gas, RF sputter is capable of running in lower pressure (1-15 mTorr), so fewer gas collisions and more line of sight deposition.



Switch polarities before the target surface saturates with ions.



# RF plasma

- For symmetric target-substrate configuration, sputtering of both surfaces will occur, though in the opposite half cycles.
- When the electrode areas are not equal, the field must be higher at the smaller electrode (higher current density), to maintain overall current continuity.
- It was found that voltage drop across the dark sheath of the two electrodes satisfy the relation: (A is the area of the electrode)

$$\frac{V_1}{V_2} = \left( \frac{A_2}{A_1} \right)^m \quad (m = 1-2 \text{ experimentally})$$

- Thus by making the target electrode much smaller, sputtering occurs "only" on the target.
- Wafer electrode can also be connected to chamber walls, further increasing  $V_2/V_1$ .

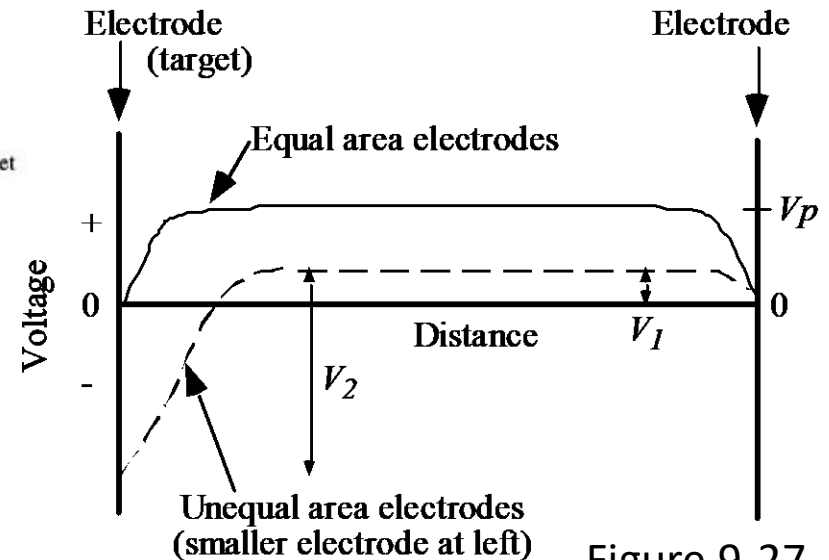
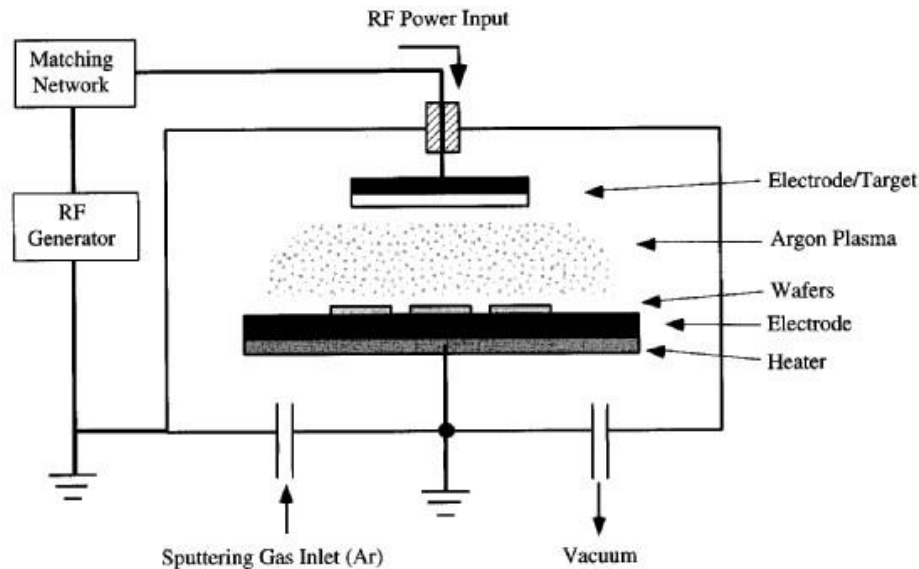


Figure 9-27

Figure 9-28 Schematic diagram of RF-powered sputter deposition system.