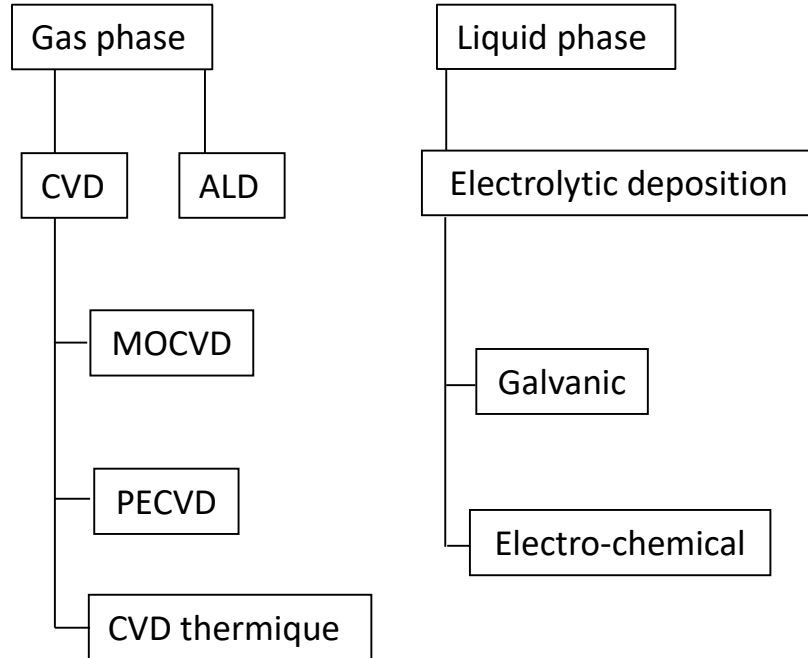


Physical Vapor Deposition

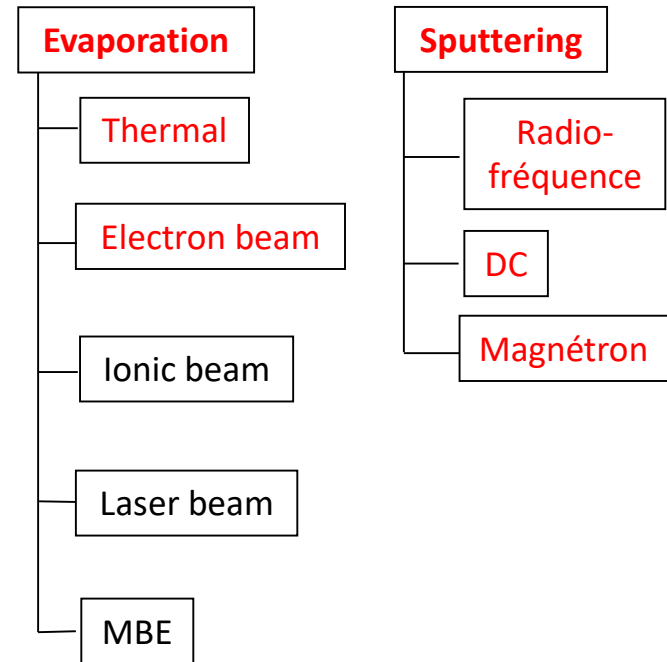
« El Nano » Thematic School, Aussois, 12-16 June 2023

Overview of thin films deposition processes

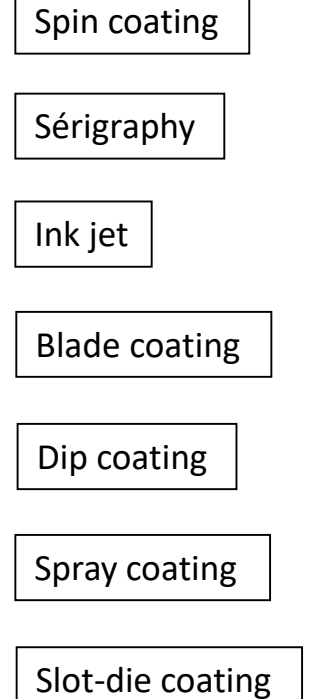
Chemical deposition



Physical deposition (PVD)



Impression (from an ink)



Acronyms :

PVD = Physical Vapor Deposition

CVD = Chemical Vapor Deposition

MOCVD = Metal-Organic Chemical Vapor Deposition

PECVD = Plasma Enhanced CVD

ALD = Atomic Layer Deposition

MBE = Molecular Beam Epitaxy

1 - Introduction

- Examples of applications

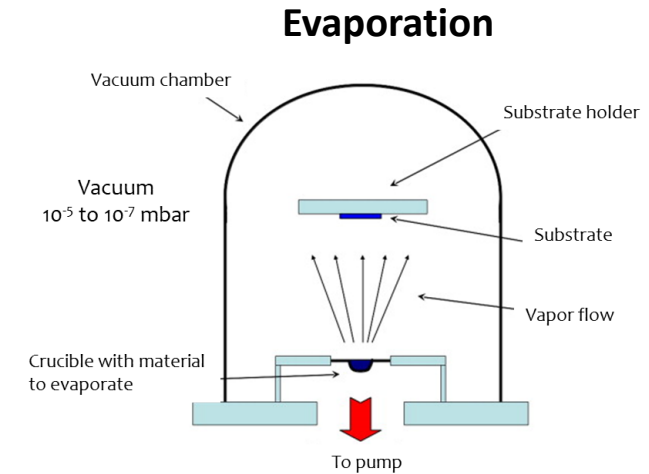
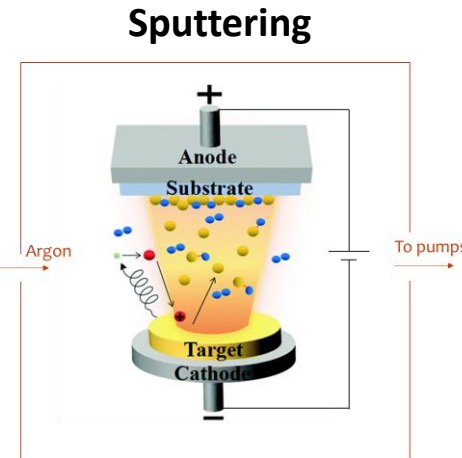
2 - Sputtering

- Principle
- Collisions regimes
- Sputtering yield
- Cathodic sputtering
- DC and RF systems
- Magnetron
- Hysteresis
- Sputtered films properties
- Systems

3- Thermal evaporation

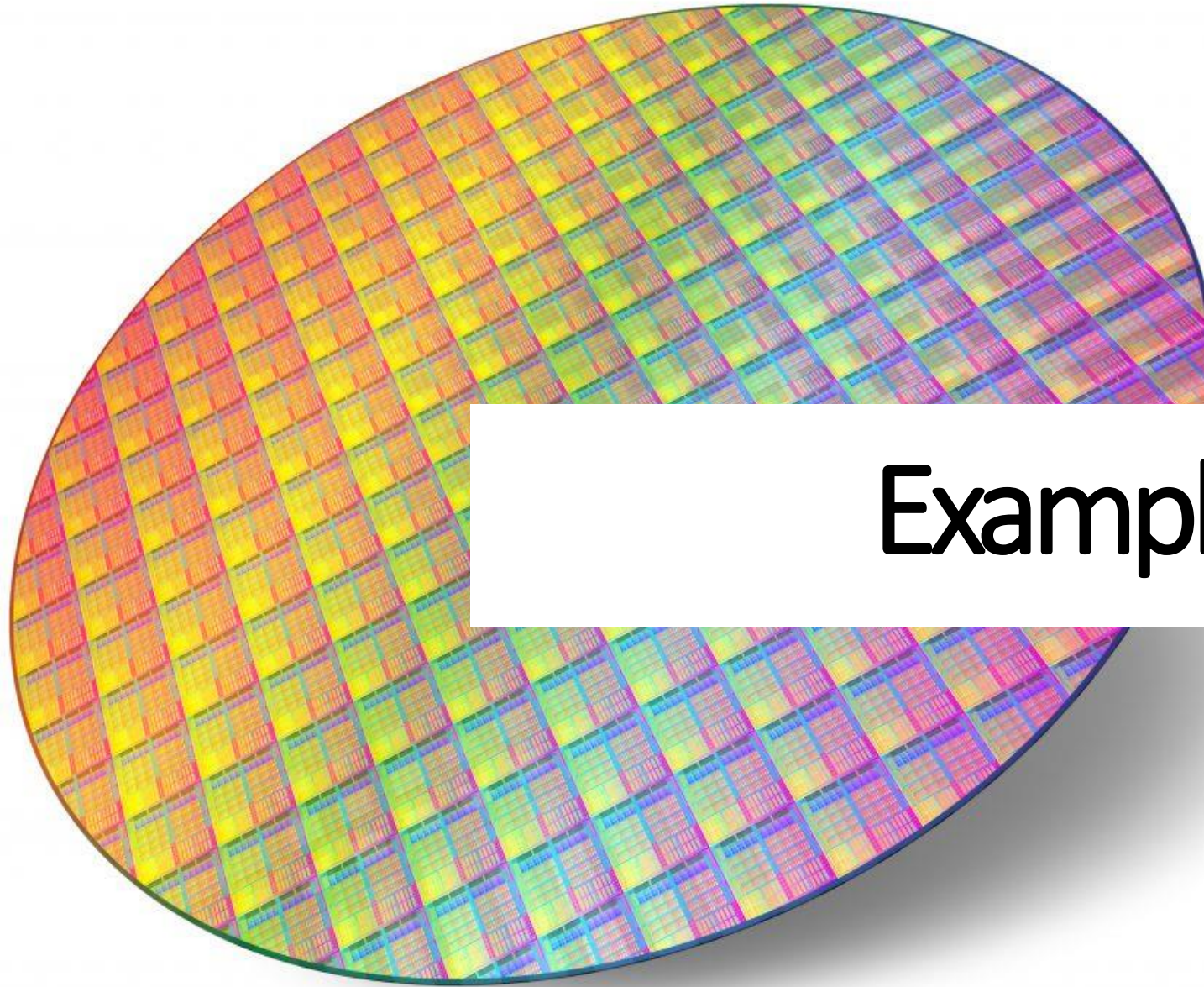
- Principle
- Evaporation sources
- Vapor pressure, atoms flux, mass flux
- Vacuum conditions
- Thickness uniformity
- Thin film growth and microstructure

- Create a vapor or flux of metallic atoms
- ... which condensates at the surface of a substrate
- ... to grow a thin film



⇒ Change the properties of the surface, while the properties of the bulk remain (**coatings**)
(anti-corrosion layers, anti-reflective coatings...)

⇒ Use specific properties of the material as a **thin films**
(thin film solar cells, microelectronics...)



Examples of applications

Applications

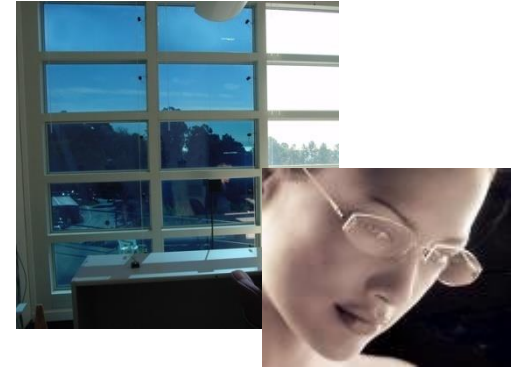


Aerospace

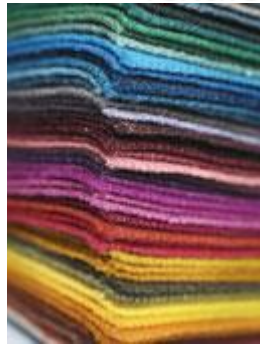


Automotive industry

Optics



Textile



Thin films deposition Surface coating



Microelectronics



Tools



Decoration



Paper
Industry



Waste treatments



Télécommunications



Solar energy

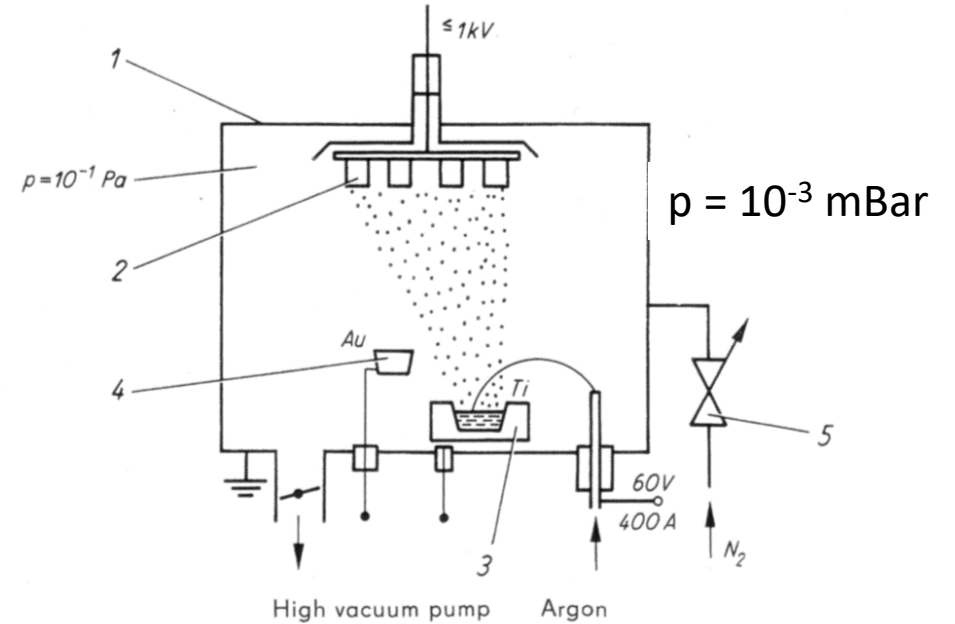
Example 1: evaporation of titanium nitride/gold thin films (TiN/Au)

1. **Ti evaporation** by e-beam in N_2 atmosphere ($2\text{ }\mu\text{m}$)
2. **Au evaporation** by Joule effect (25 nm)

⇒ Gilding effect

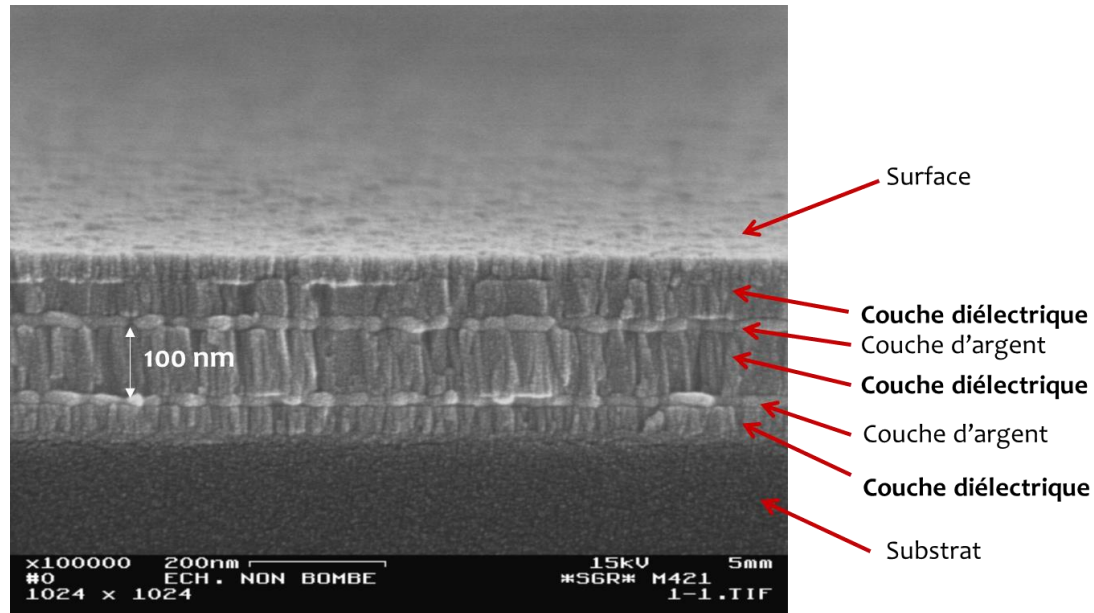
⇒ Mechanical properties (coating is harder than gold alone)

⇒ Low cost



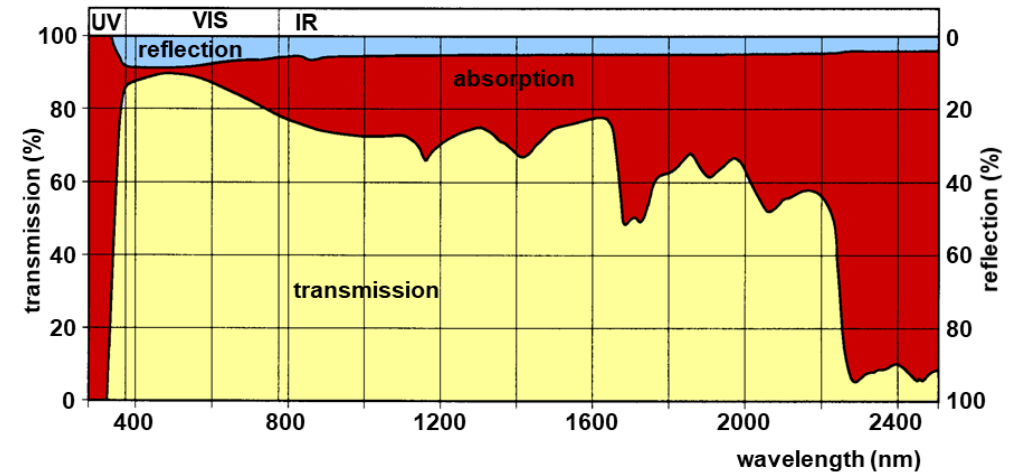
Example 2: Sputtering multilayers of silver and dielectric thin films

thermally insulated windshield

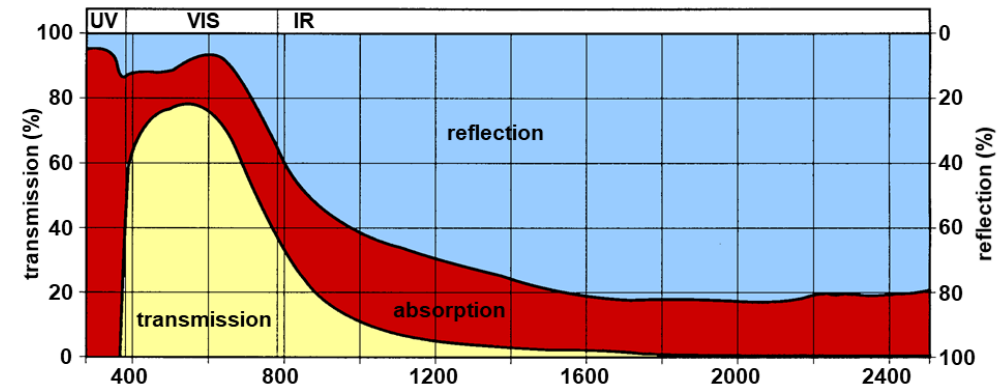


Cross-section SEM image of the stack.

Standard glass

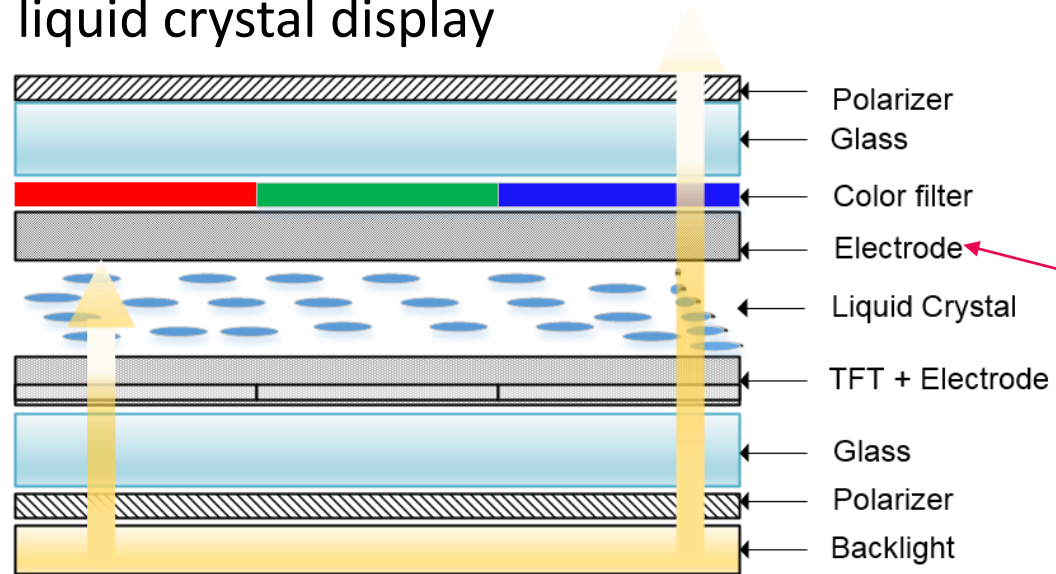


Thermally insulated windshield



Example 3: sputtering of transparent conductive oxides

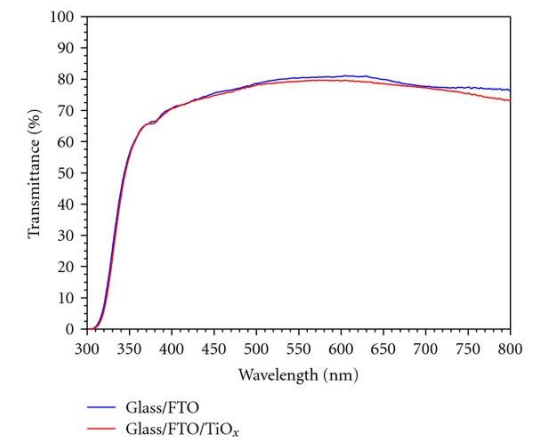
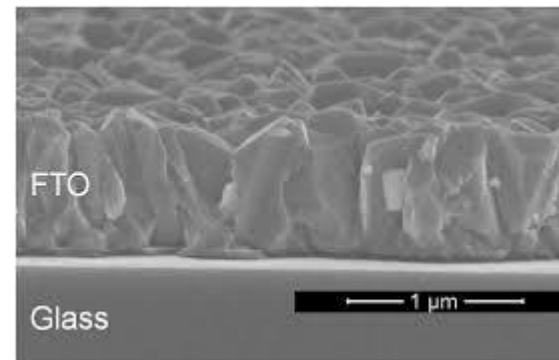
liquid crystal display



Thin films of transparent conductive oxides (TCO) that serve as contact electrodes (e.g. 100 nm indium tin oxide, ITO)

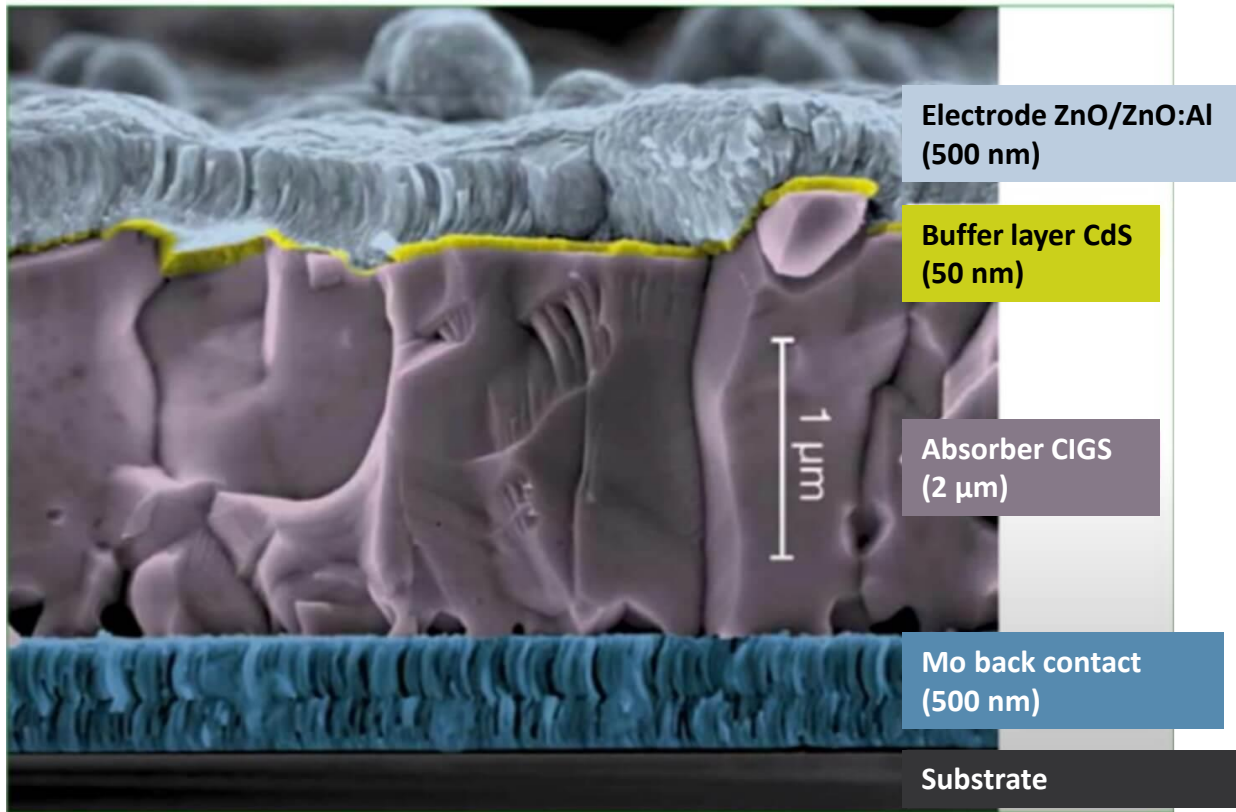
TCO = Transparent Conducting Oxyde

- ITO (oxyde d'indium étain)
- FTO (oxyde de fluor étain)
- ZnO:Al (oxyde de zinc dopé Al)

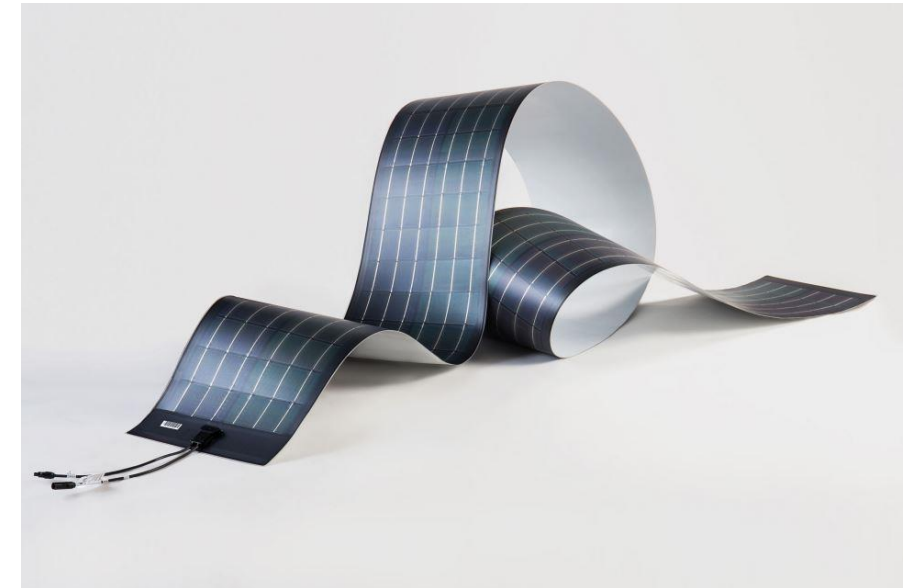


Exemple 4 : evaporation of copper-indium-gallium-selenium alloy

CIGS (copper indium gallium selenium) thin film solar cell



Total thickness $\approx 3 \mu\text{m}$



- ⇒ Flexibility
- ⇒ Lightness
- ⇒ Ease of installation

1 - Introduction

- Overview of deposition processes
- Examples of applications

2 - Sputtering

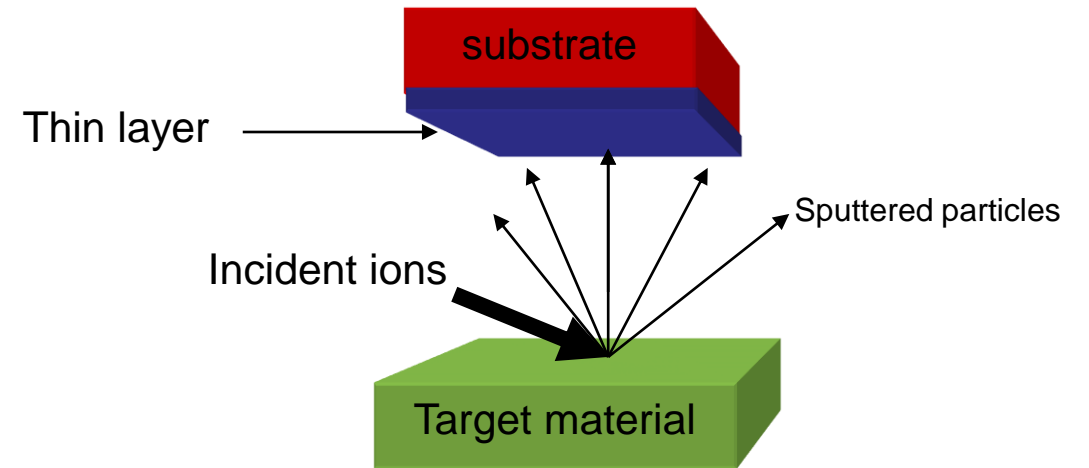
- Principle
- Collisions regimes
- Sputtering yield
- DC and RF systems
- Magnetron
- Hysteresis
- Sputtered films properties
- Systems

3- Thermal evaporation

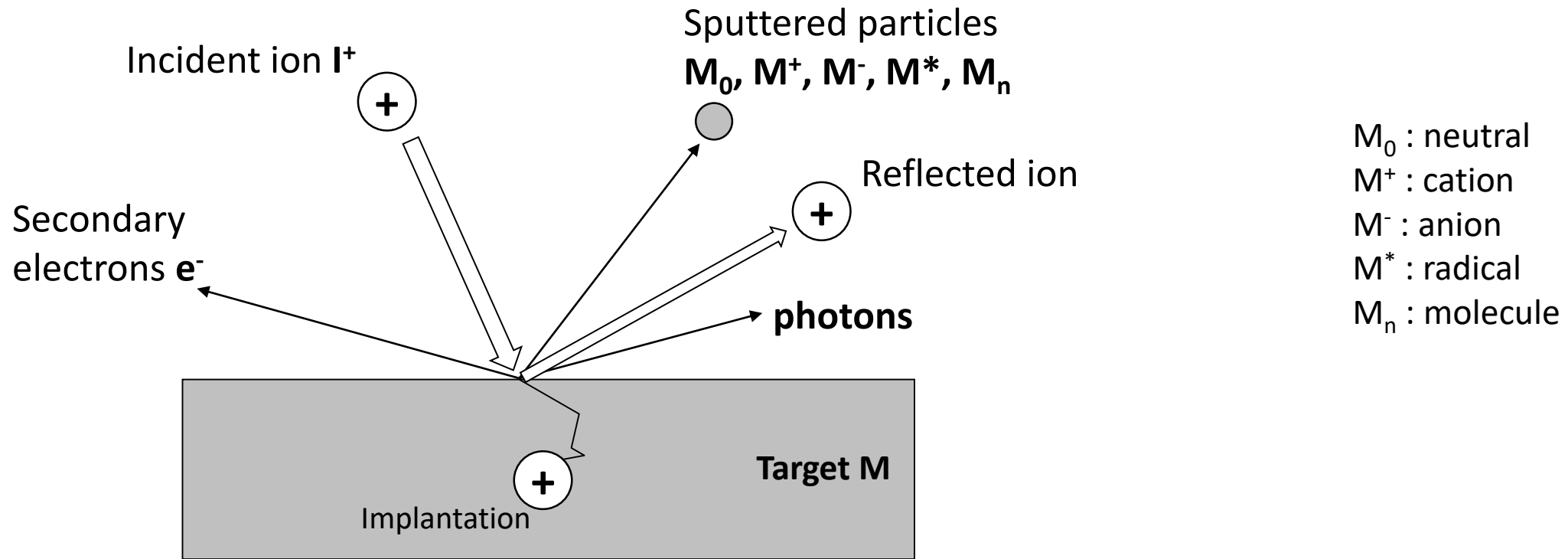
- Principle
- Evaporation sources
- Vapor pressure, atoms flux, mass flux
- Vacuum conditions
- Thickness uniformity
- Thin film growth and microstructure

Sputtering principle

- Vacuum deposition
- Commonly used ions: Ar^+
 - Easy to produce
 - No chemical reaction with any material
 - High atomic mass → important sputtering rate
- Ions energy : 100 eV to keV
- Ions current densities some hundred $\mu\text{A}.\text{cm}^{-2}$ to $10 \text{ mA}.\text{cm}^{-2}$



Ion-matter interaction



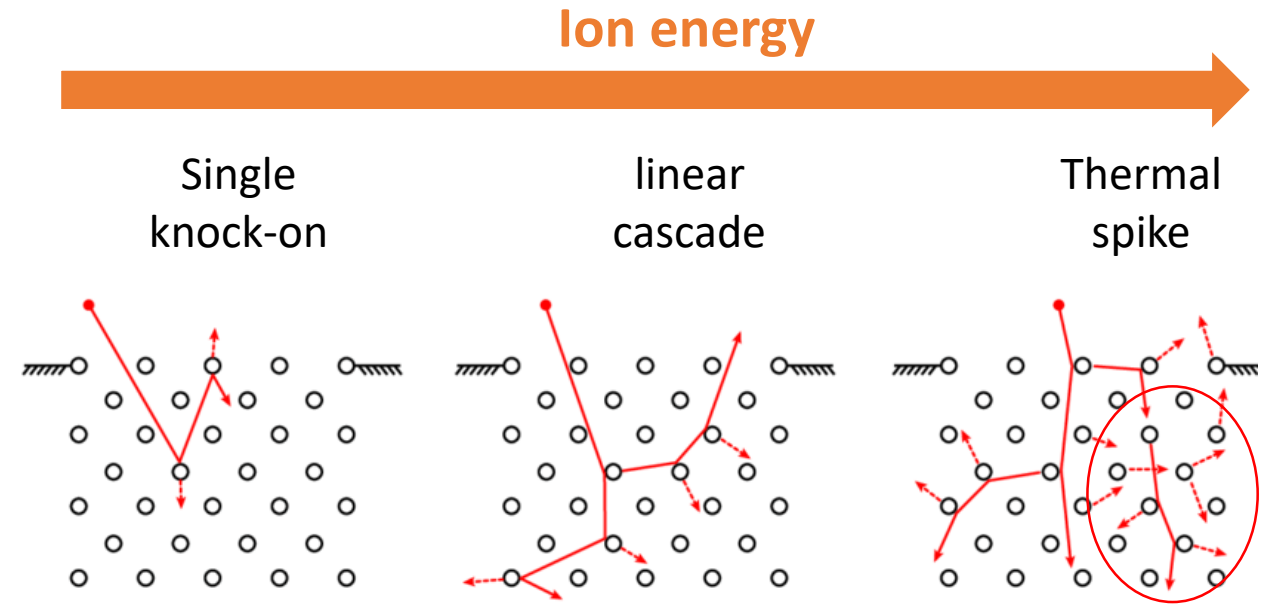
- Sputtered particles are predominantly neutral atomic species (M_0)

Sputtering mechanisms

Sputtering results from a phenomenon of elastic collision between the incident ion and the atoms of the target during which **the incident ion transmits part of its kinetic energy to the atoms**.

Three collision regimes can be distinguished:

- **Single Knock-on** regime
- **Linear cascade** regime
- **Thermal spike** regime



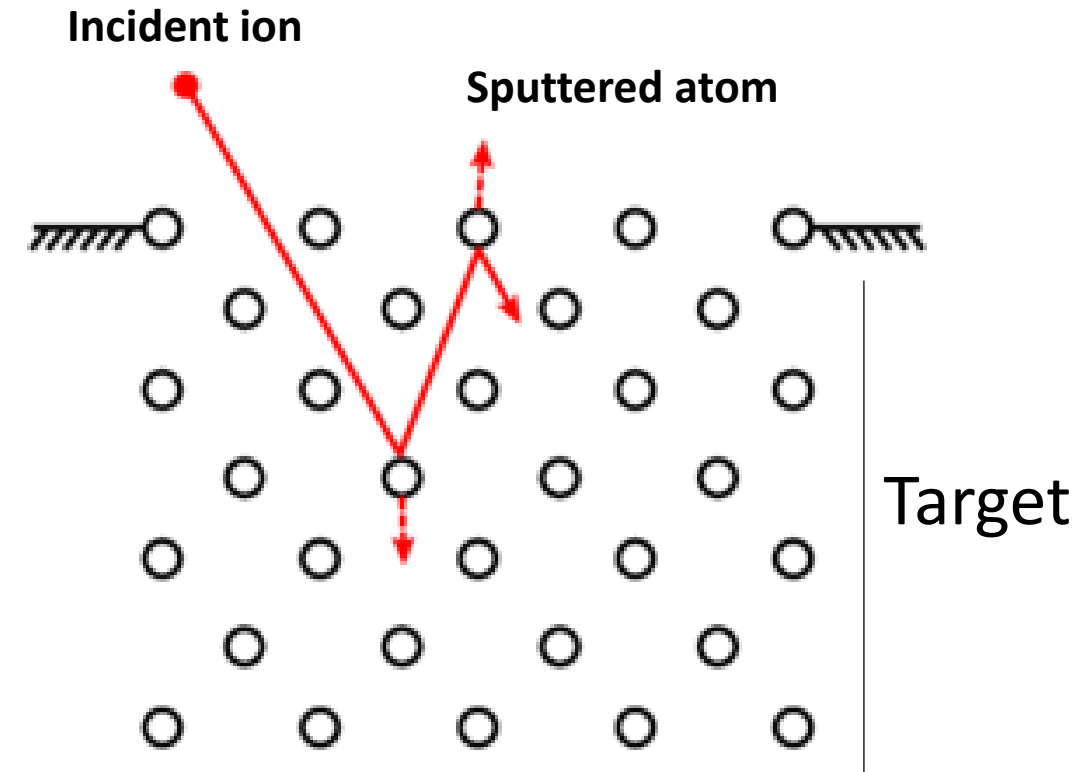
Most of the energy transmitted to the target by the ion beam is transformed into heat

⇒ this heat must be evacuated to avoid melting the target material

⇒ **Necessity to cool the target!**

Single knock-on (low energy)

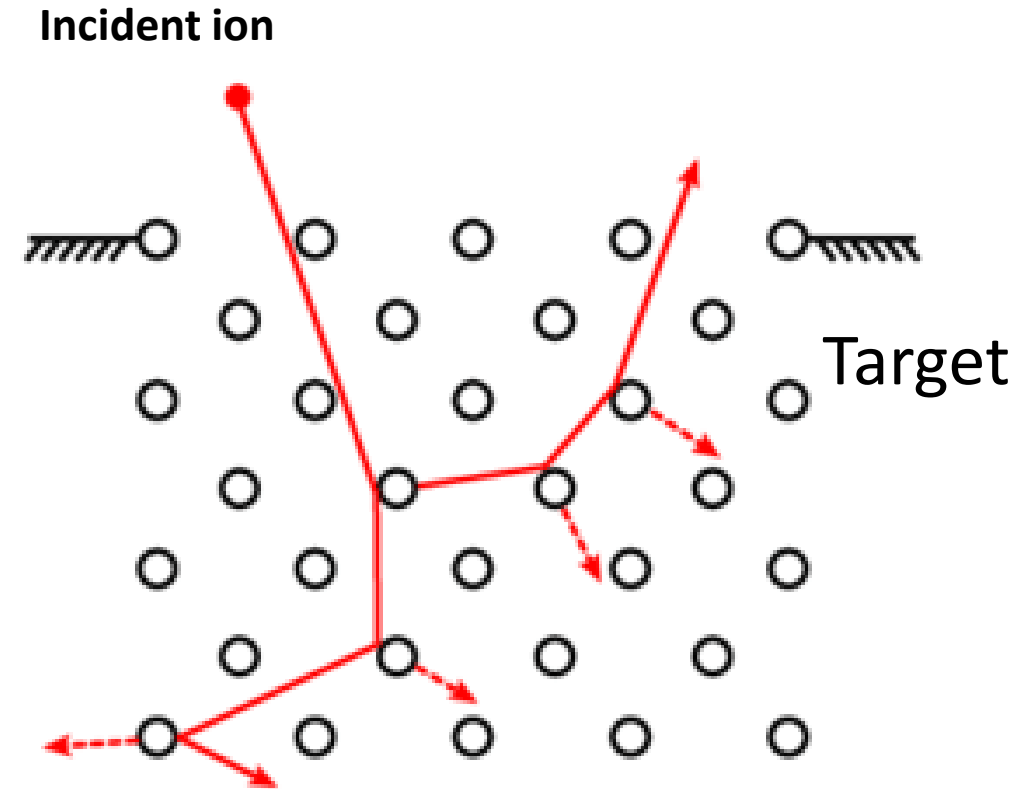
The ion collides with an **atom close to the surface of the target**. This latter acquires sufficient energy to be expelled from its site and leave the surface of the target, but not enough to induce cascading collisions



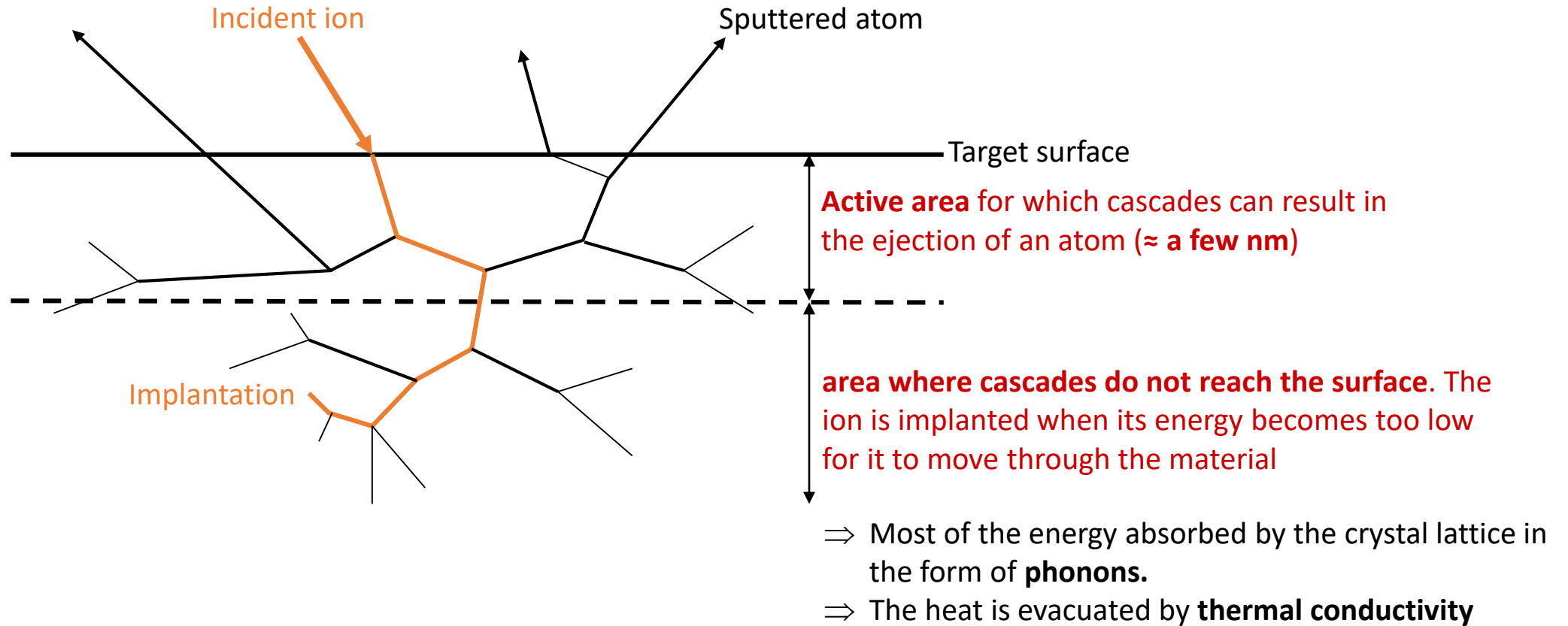
Linear cascade (medium energy)

The energy of the incident ion is large in front of the cohesion energy of the atoms of the target => **hundred of eV**.

The ion collisions with atoms that can be relatively far from the surface. **The atom set in motion can generate a cascade of collisions** between an increasing number of atoms of the target. Some of these collisions can reach the surface of the target and result in the ejection of atoms.



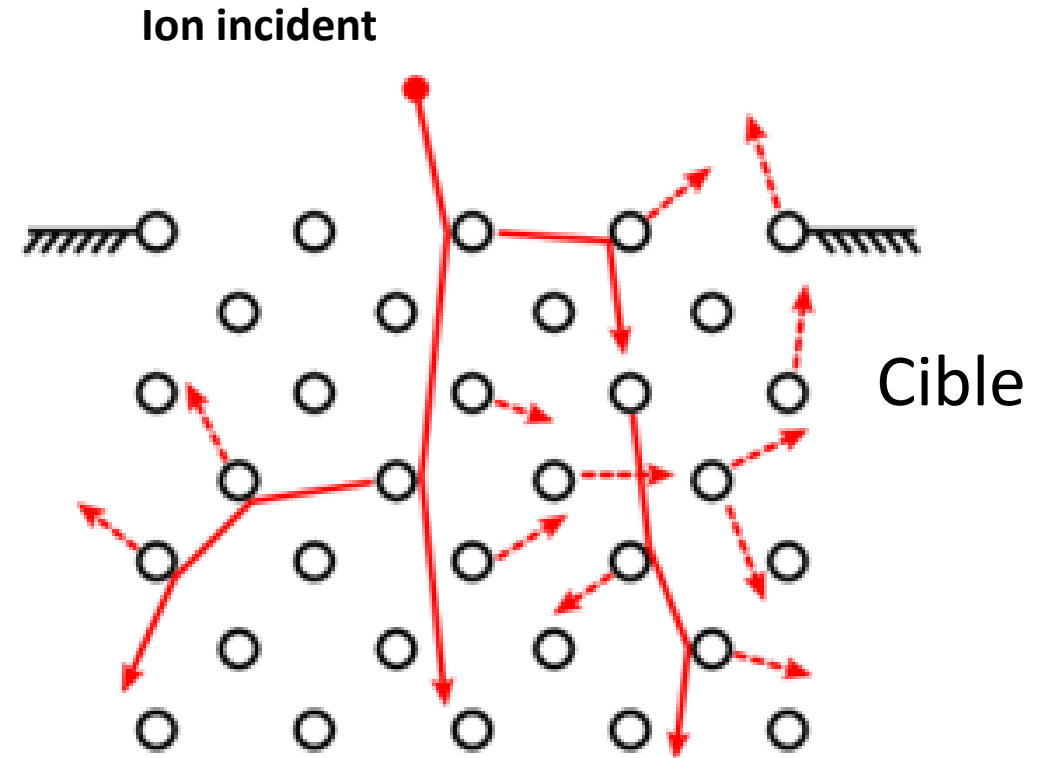
Linear cascade (medium energy)



Thermal spike (high energy)

For ions with high energies (several tens of keV) and whose mass is higher than that of the atoms of the target, **almost all the atoms located in the area of interaction of the ion are set in motion**. There is then a considerable rise in temperature around the point of impact of the ion (thermal spike) because the thermal conductivity of the material is not high enough to evacuate this strong dissipation of energy. Whole **blocks of moving atoms can then be ejected from the surface**.

=> High risk of damaging the target



$$Y = \frac{\text{number of sputtered particles}}{\text{number of sputtered ions}}$$

The sputtering yield depends on:

- the energy of incident ions
- the nature of ions
- the nature of target
- the angle of ions beam with the target

The sputtering yield does not depend on:

- target temperature
- if the beam is ionized or not (sputtering can be carried out with neutral particles as well)

$$Y = \frac{3\alpha}{4\pi^2} \frac{4m_1m_t}{(m_1 + m_t)^2} \frac{E}{U}$$

Ion mass

Ion kinetic energy

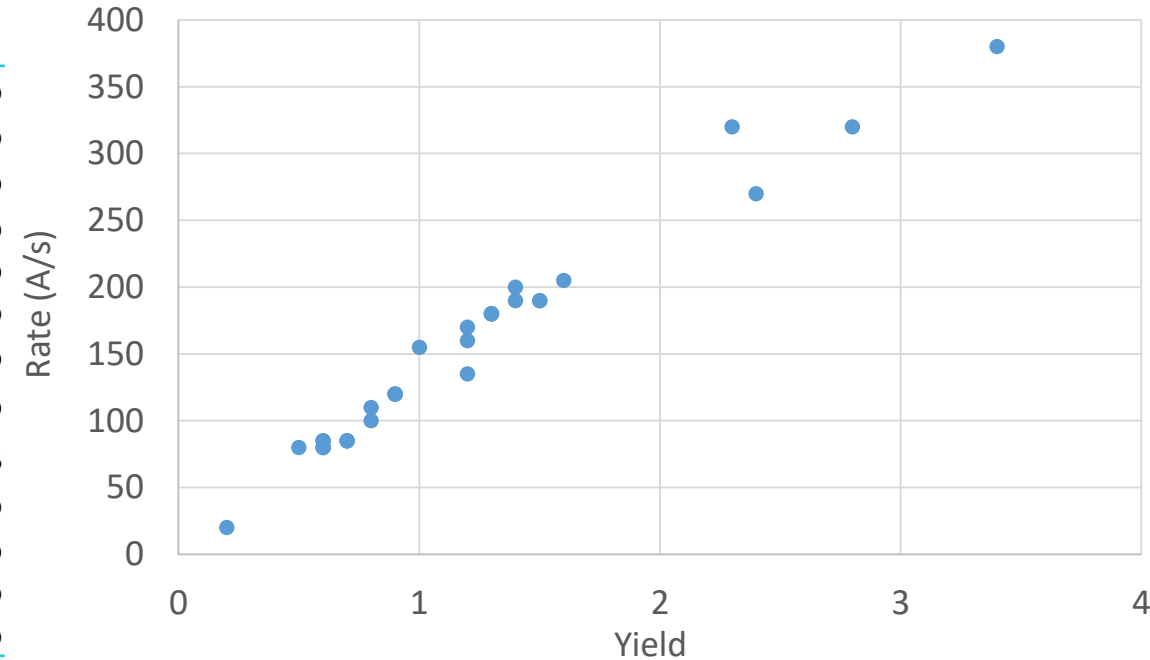
Target atom mass

Target cohesion energy

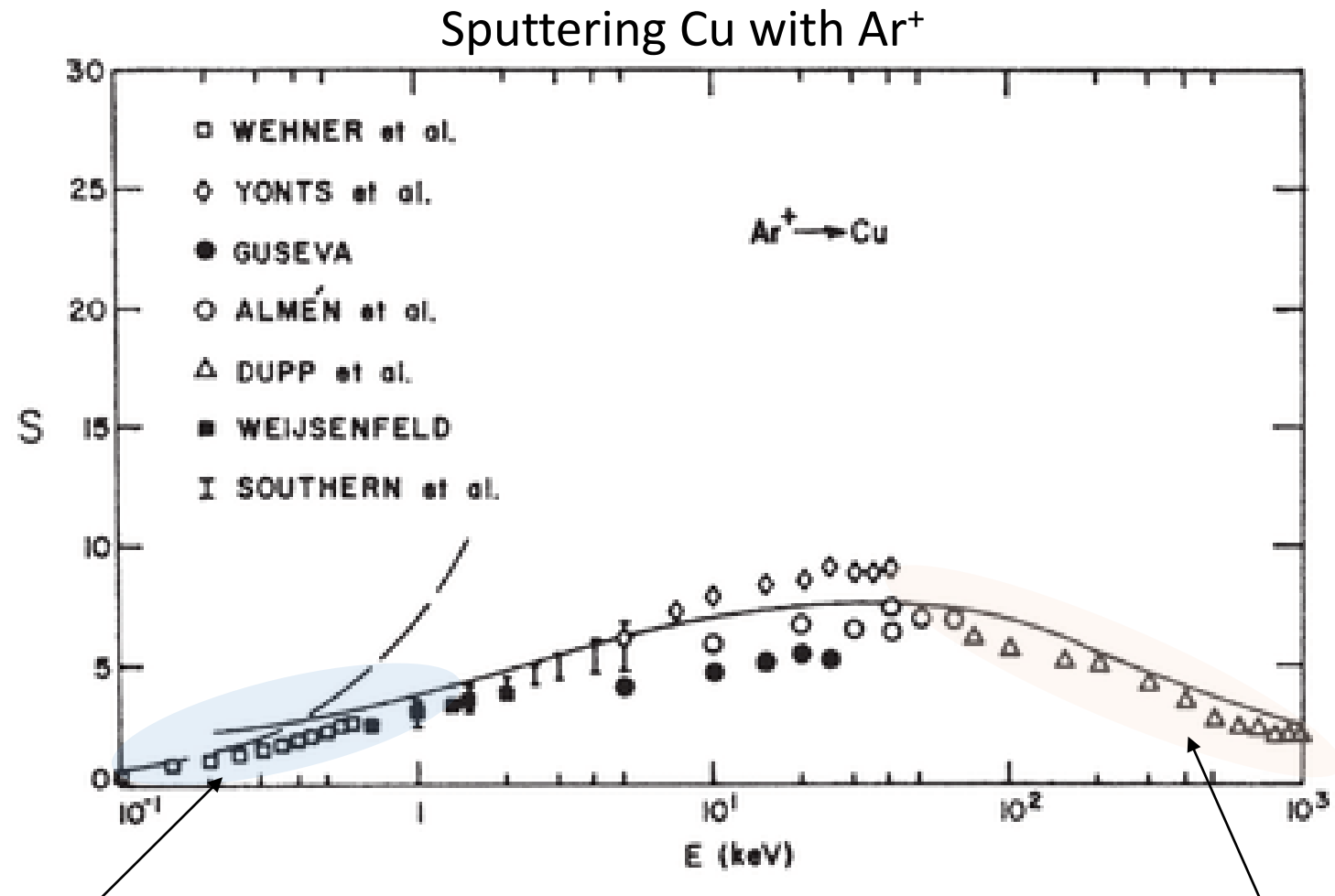
(Sigmund 1969)

Correlation between sputtering yield and film growth rate

Target Material	Density (g/cc)	Yield @ 600 ev	Rate* (Å/sec)	Target Material	Density (g/cc)	Yield @ 600 ev	Rate* (Å/sec)
C	2,25	0,2	20	Cr	7.2	1.3	180
Si	2,33	0,5	80	Fe	7.86	1.3	180
Nb	8,57	0,6	80	Mn	7.2	1.3	180
Ta	16,6	0,6	85	Ru	12.3	1.3	180
Ti	4,5	0,6	80	Co	8.9	1.4	190
W	19,35	0,6	80	Mg	1.74	1.4	200
Y	4,47	0,6	85	Ni	8.9	1.5	190
Th	11,7	0,7	85	Rh	12.4	1.5	190
V	5,96	0,7	85	Pt	21.45	1.6	205
Zr	6,49	0,7	85	Cu	8.92	2.3	320
Be	1,85	0,8	100	Pd	12.02	2.4	270
Hf	13,31	0,8	110	Au	19.31	2.8	320
Mo	10,2	0,9	120	Ag	10.5	3.4	380
Os	22,48	0,9	120				
Re	20,53	0,9	120				
U	19,05	1	155				
Al	2,7	1,2	170				
Ge	5,35	1,2	160				
Ir	22,42	1,2	135				



⇒ The growth rate of the layer is directly related to the sputtering yield

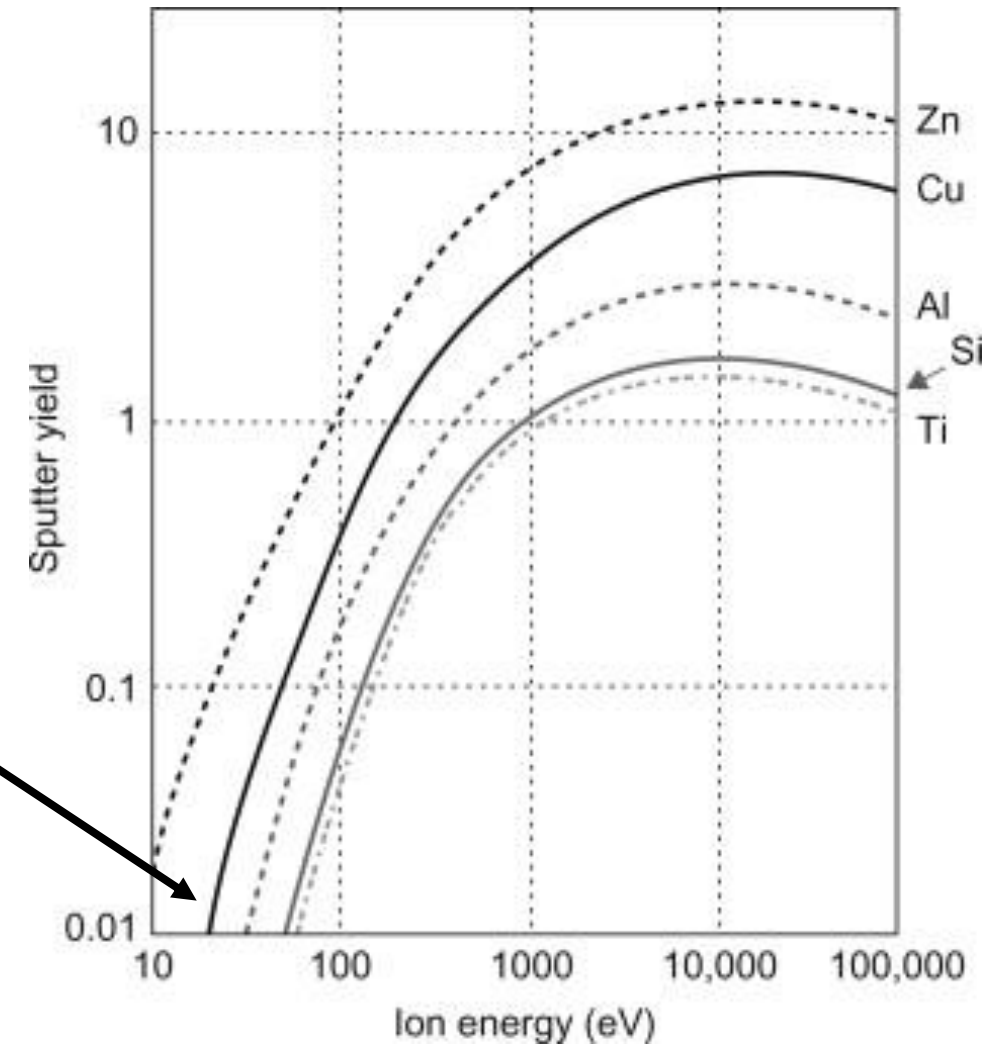


< 1 keV : Typical energies for sputtering. The sputtering yield is almost **linear** with the energy of the ions

Implantation

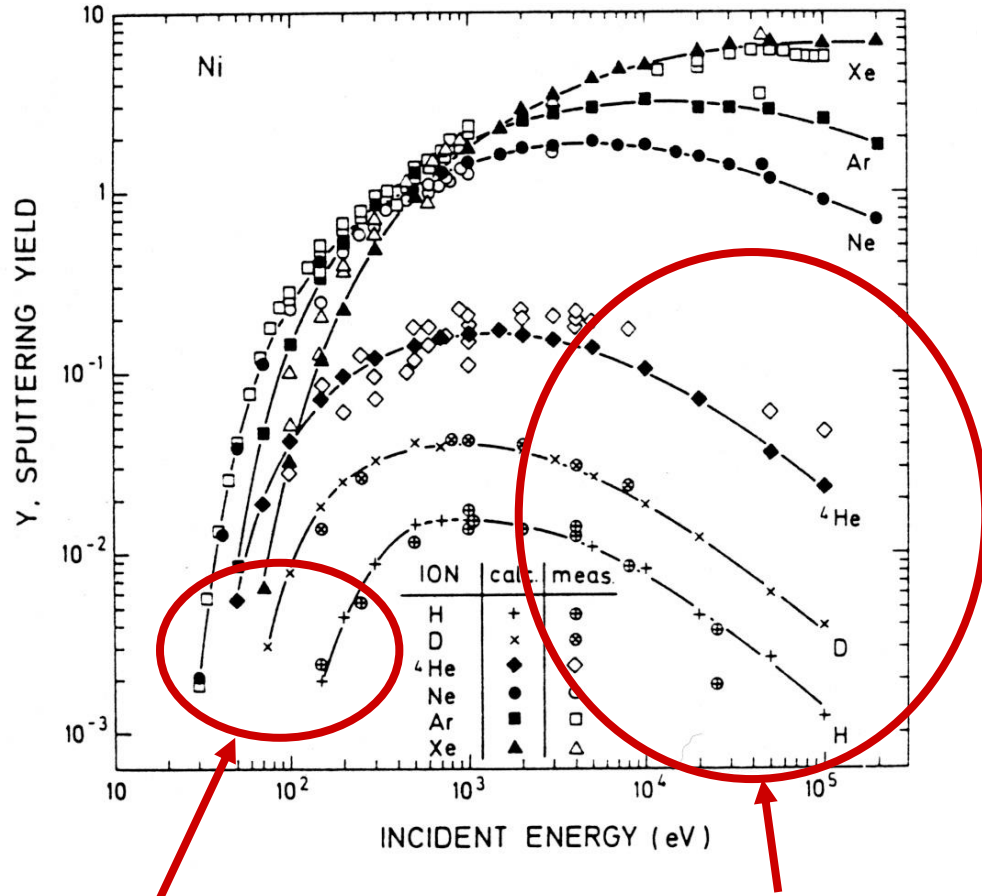
Sputtering threshold

Sputtering threshold = a few eV
=> No sputtering below this threshold



Influence of sputtering parameters on yield (TRIM simulations)

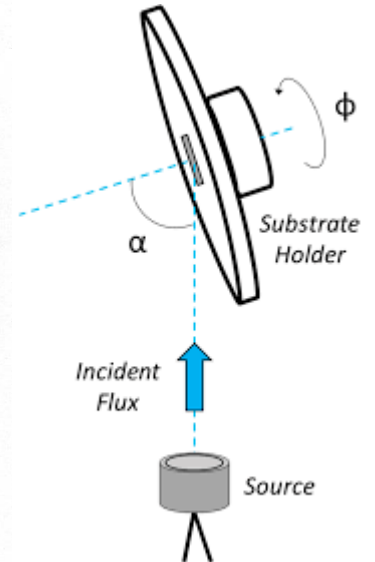
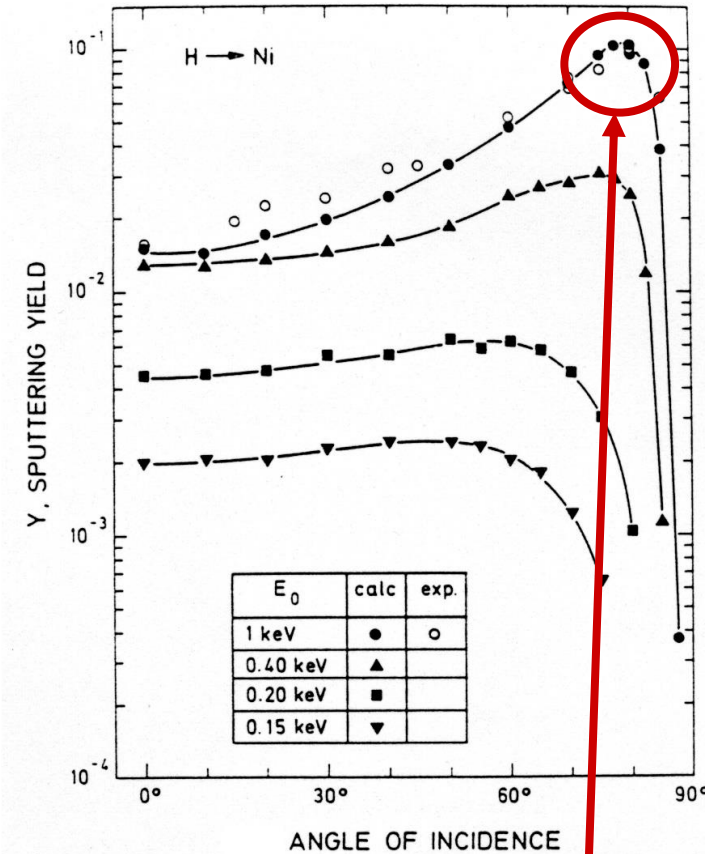
Influence of energy and nature of ions



■ Sputtering threshold E_s

■ Implantation

Influence of incident angle



- Maximum yield is reached for an angle between 60° and 80°
- > 70-80° : ions reflexion and decrease of yield

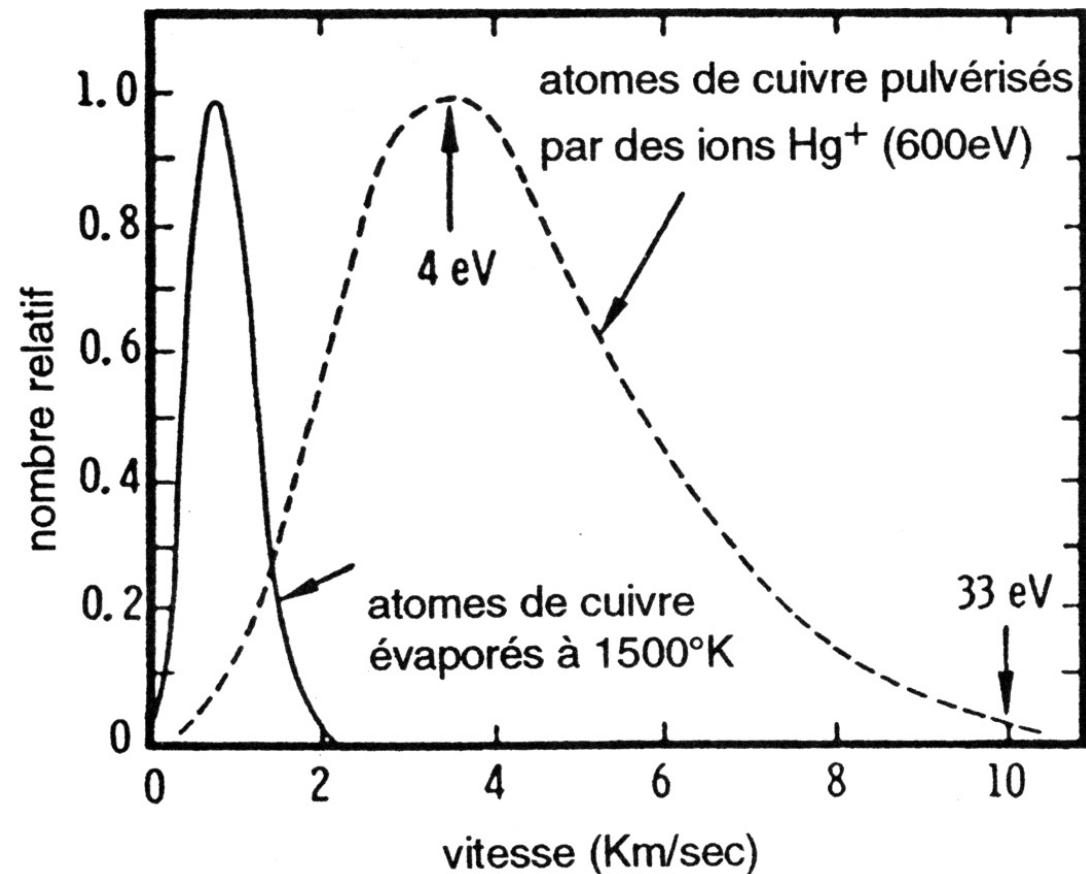
Energy distribution of sputtered atoms

Sigmund's model indicates a distribution proportional to : $\frac{E}{(E + U)^3}$

E : energy of sputtered particles
U : surface binding energy (target)

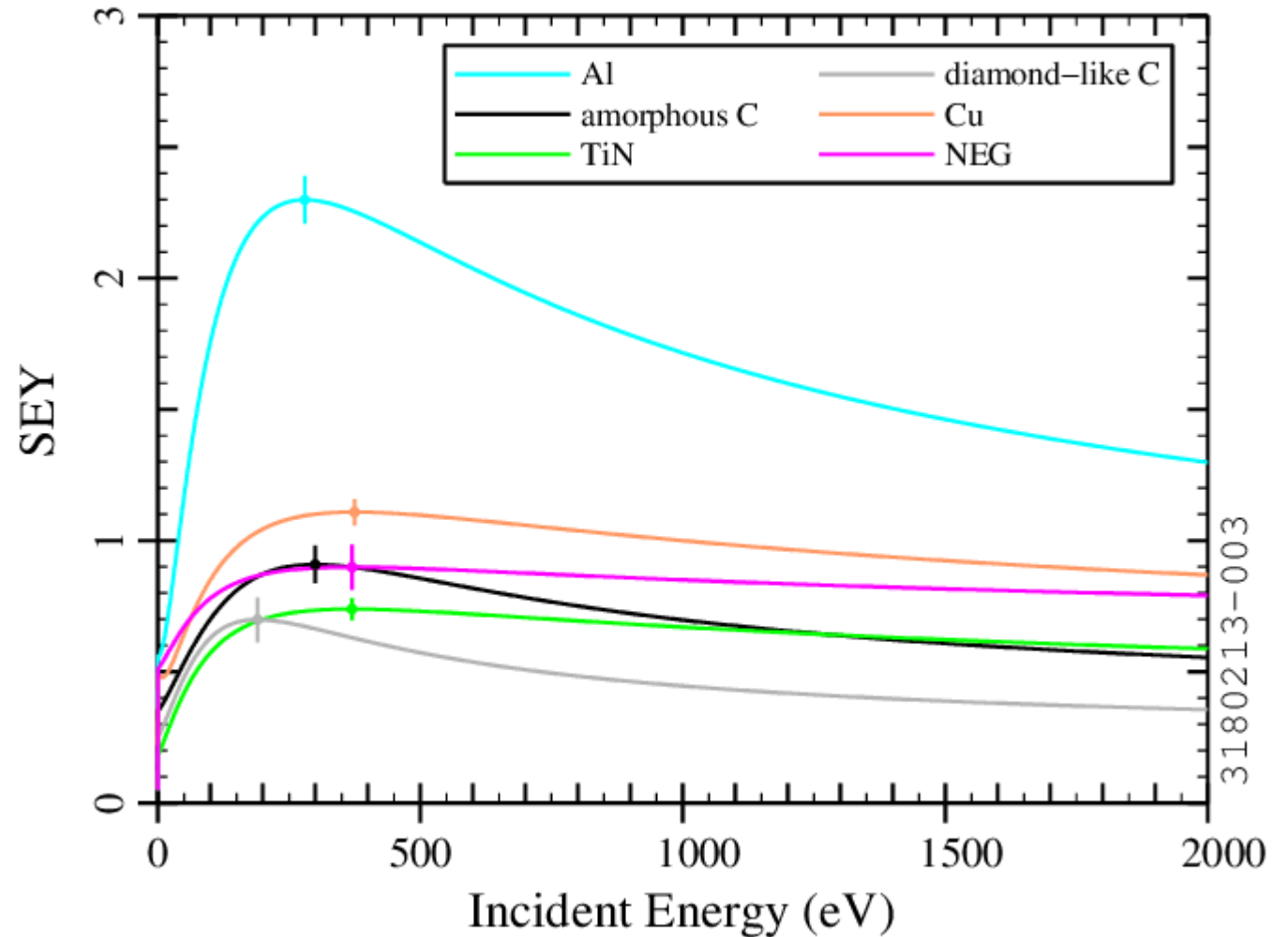
Mean energy of the sputtered atoms:
from **a few eV to a few tens of eV**.

This energy is much higher than that of
evaporated atoms which is a few tenths
of eV.



Secondary Electron Emission Yield (SEE)

- High kinetic energy
- High energy electrons are necessary to maintain the discharge
- Yield is function of:
 - Target and ion nature
 - Chemistry of surface
 - Incident ion energy

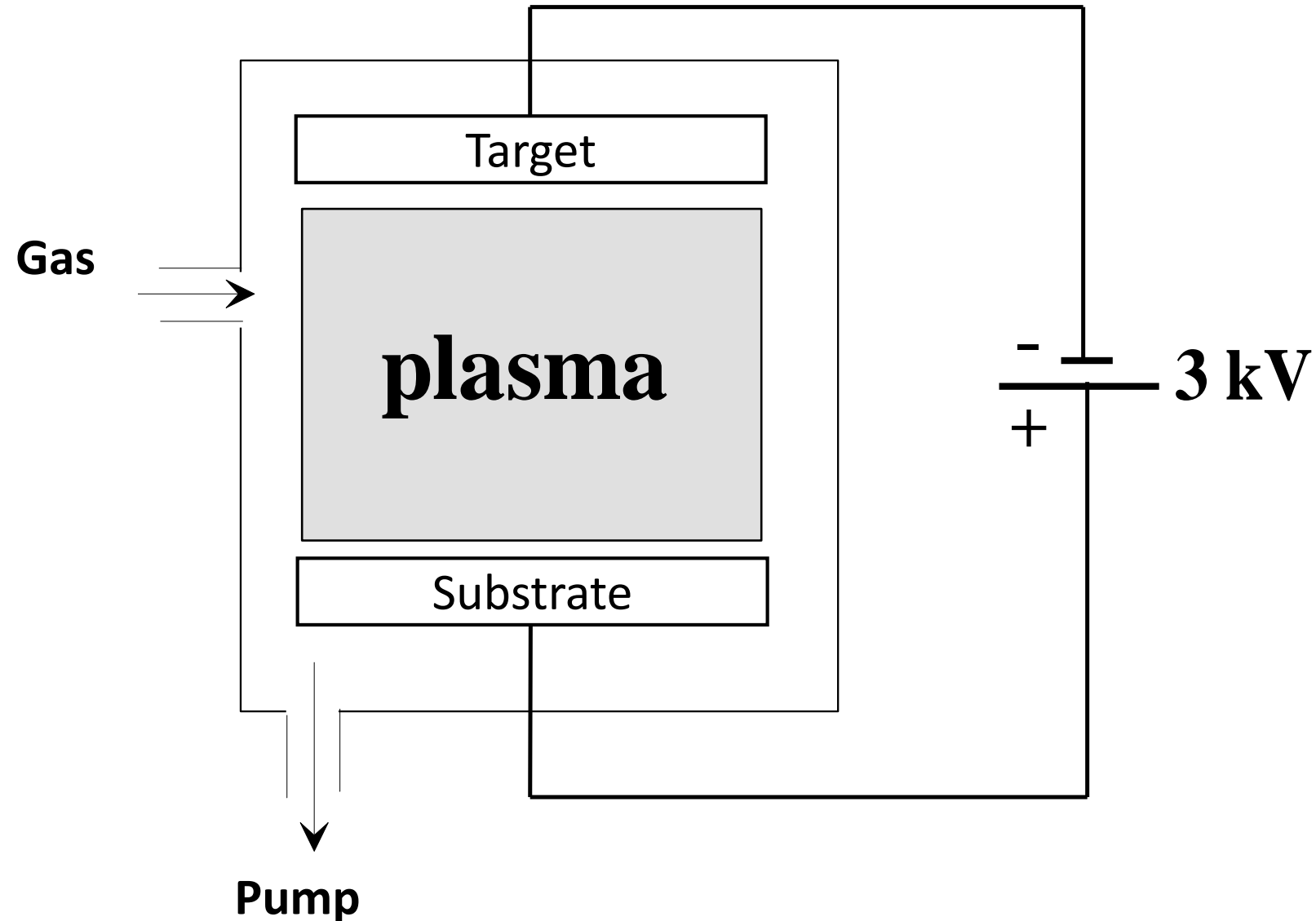


J. Calvey. Measurement and Modeling of Electron Cloud in a Field Free Environment Using Retarding Field Analyzers (2014)

➤ Cathodic sputtering in glow discharge:

- Diode in direct current **(DC)**
 - for conductive materials
 - low deposition rates
- Diode with radio frequency excitation **(RF)**
 - Conductive and insulating materials
 - low deposition rate
- Diode **magnetron** (DC or RF)
 - Higher deposition rate than conventional diodes
- Triode

➤ Ion beam sputtering



Experimental parameters:

- **Substrate temperature**
- **Substrate polarization**
- **DC or RF power supply (target)**
- **Deposition pressure = 0,04 to 0,2 mbar**
- **Gas nature :**

Ar or reactive mixture (Ar/N₂ or Ar/O₂)

- **Distance substrate-target**
- **Target polarization**

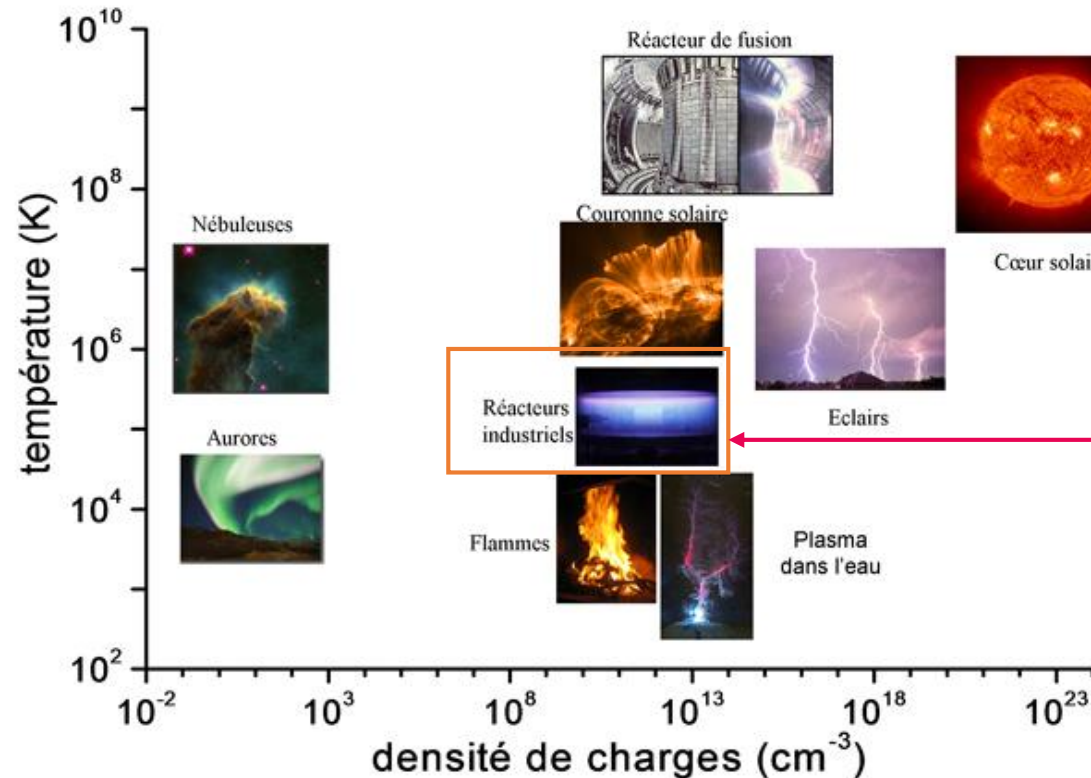
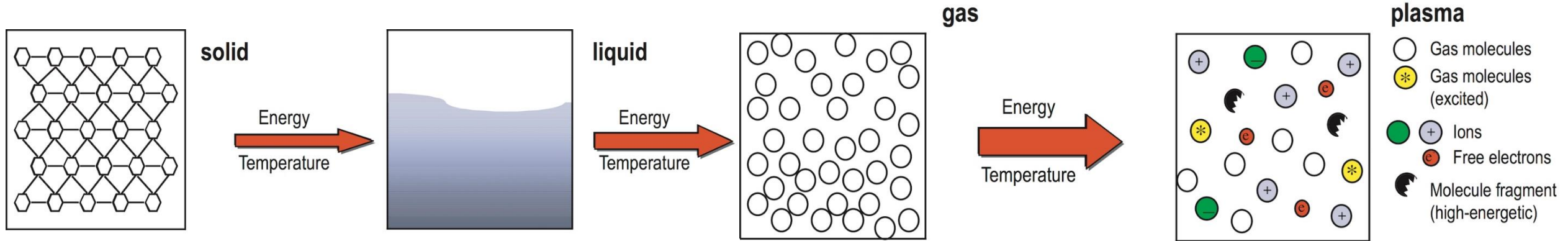
Target current density: $\approx 1 \text{ mA/cm}^2$

Target power density: $\approx 1 \text{ W/cm}^2$

Target voltage: 0,1 to 3 kV

➤ **Deposition rate = 0,1 nm/s to 1 nm/s**

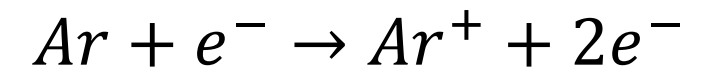
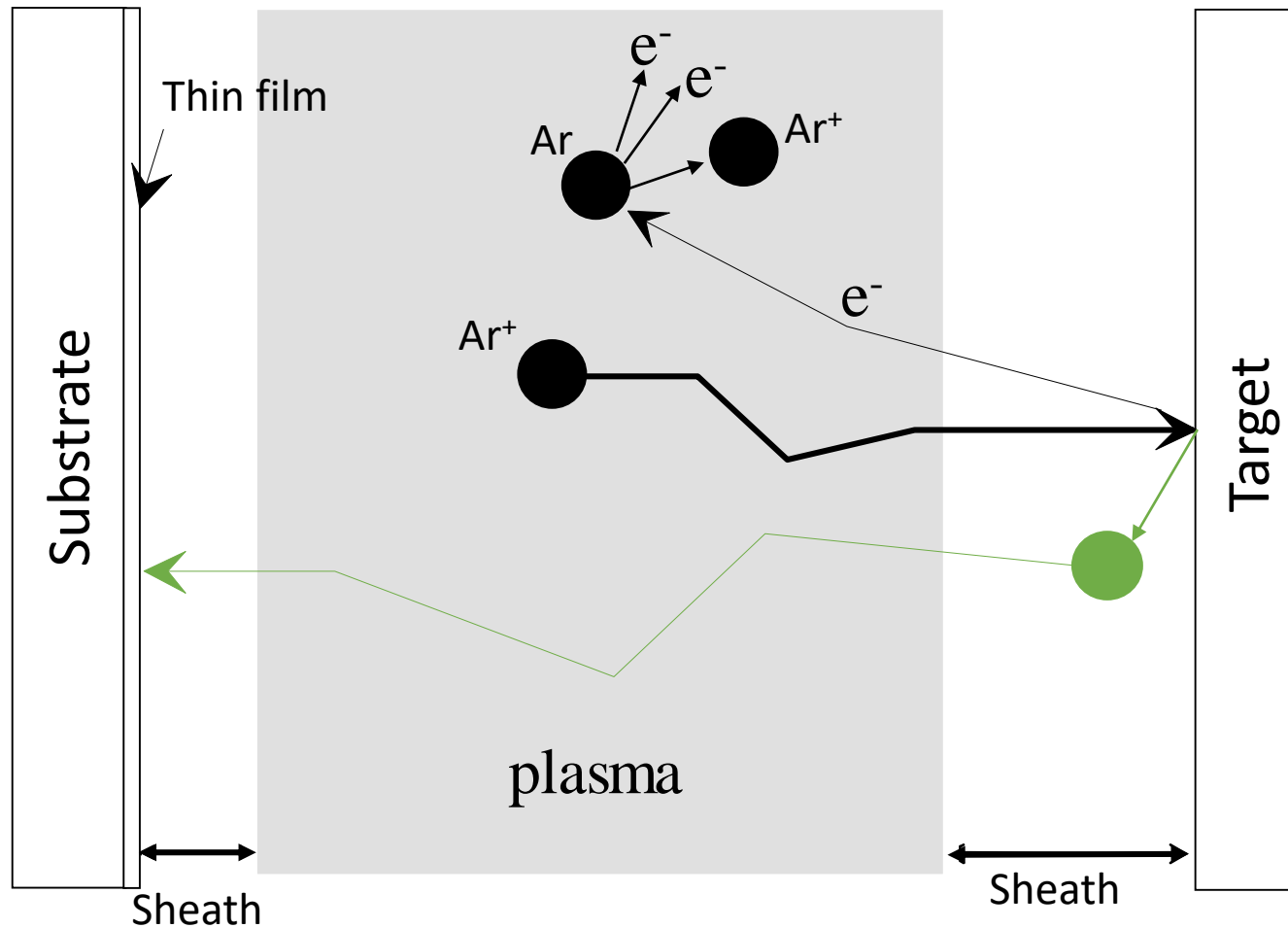
What is a plasma ?



Industrial reactors

- **Low ionisation rate** $R = \frac{n_i}{n_i + n_0} \approx 1\%$
- Plasma species : electrons, ions and neutrals
- Plasma is **neutral** : $n_i = n_e$
- Only electrons respond to RF excitation
 - $T_e > T_i > T_n \Rightarrow$ **out-of-equilibrium plasma**
- Temperature determined by neutrals \Rightarrow near RT \Rightarrow **cold plasma**

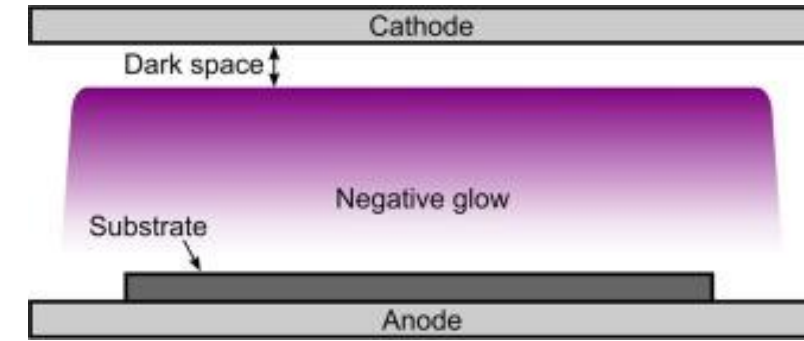
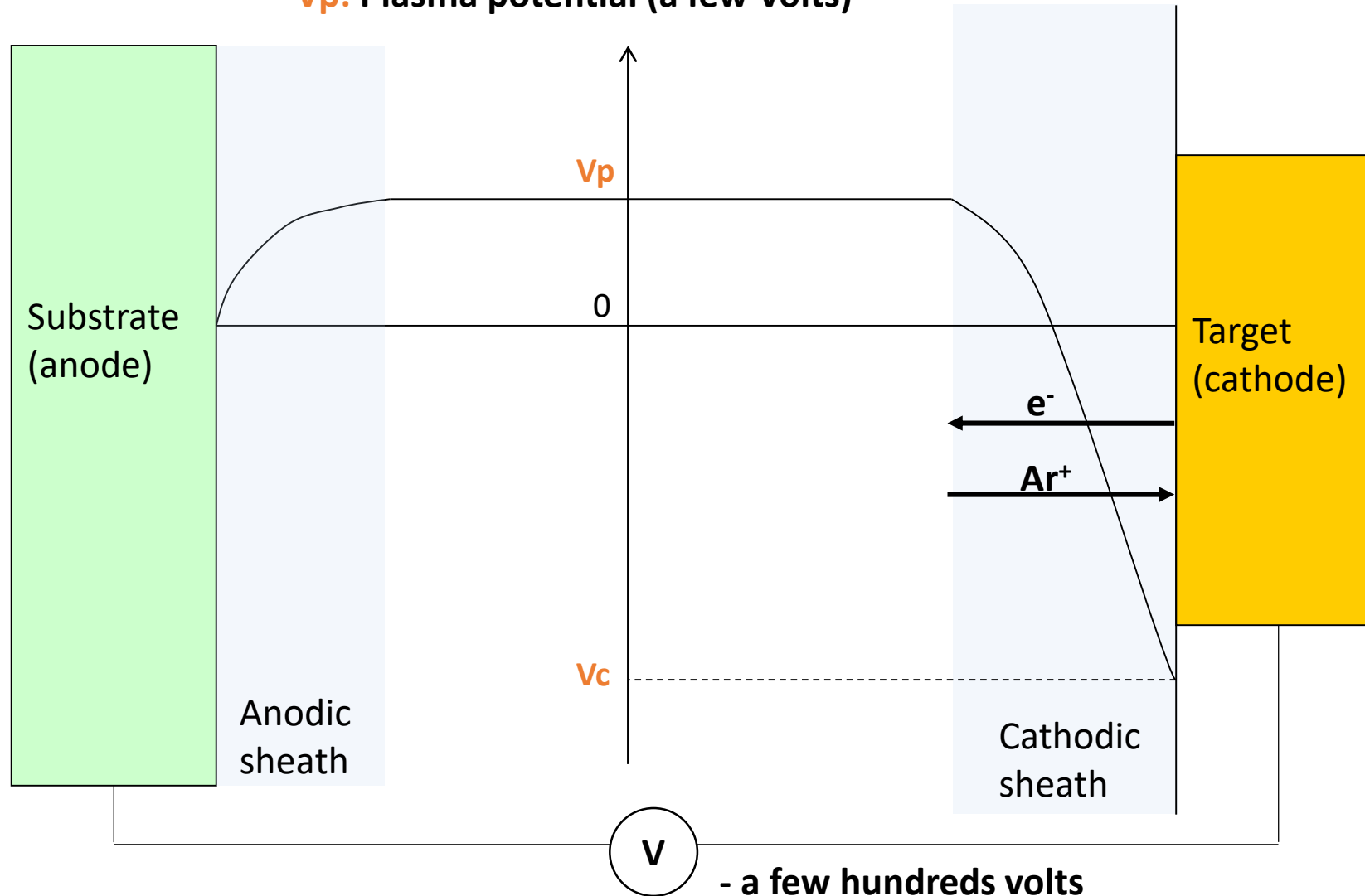
Ionisation cascade due to secondary electrons emission from the target



Potential evolution in a DC discharge

V_c: Potential difference between the anode and the cathode (-500 V to -4000 V)

V_p: Plasma potential (a few Volts)



Ar^{q+} has a kinetic energy of
$$E_{kin} = q(V_p - V_c)$$

Sputtering suitable for a large range of materials:

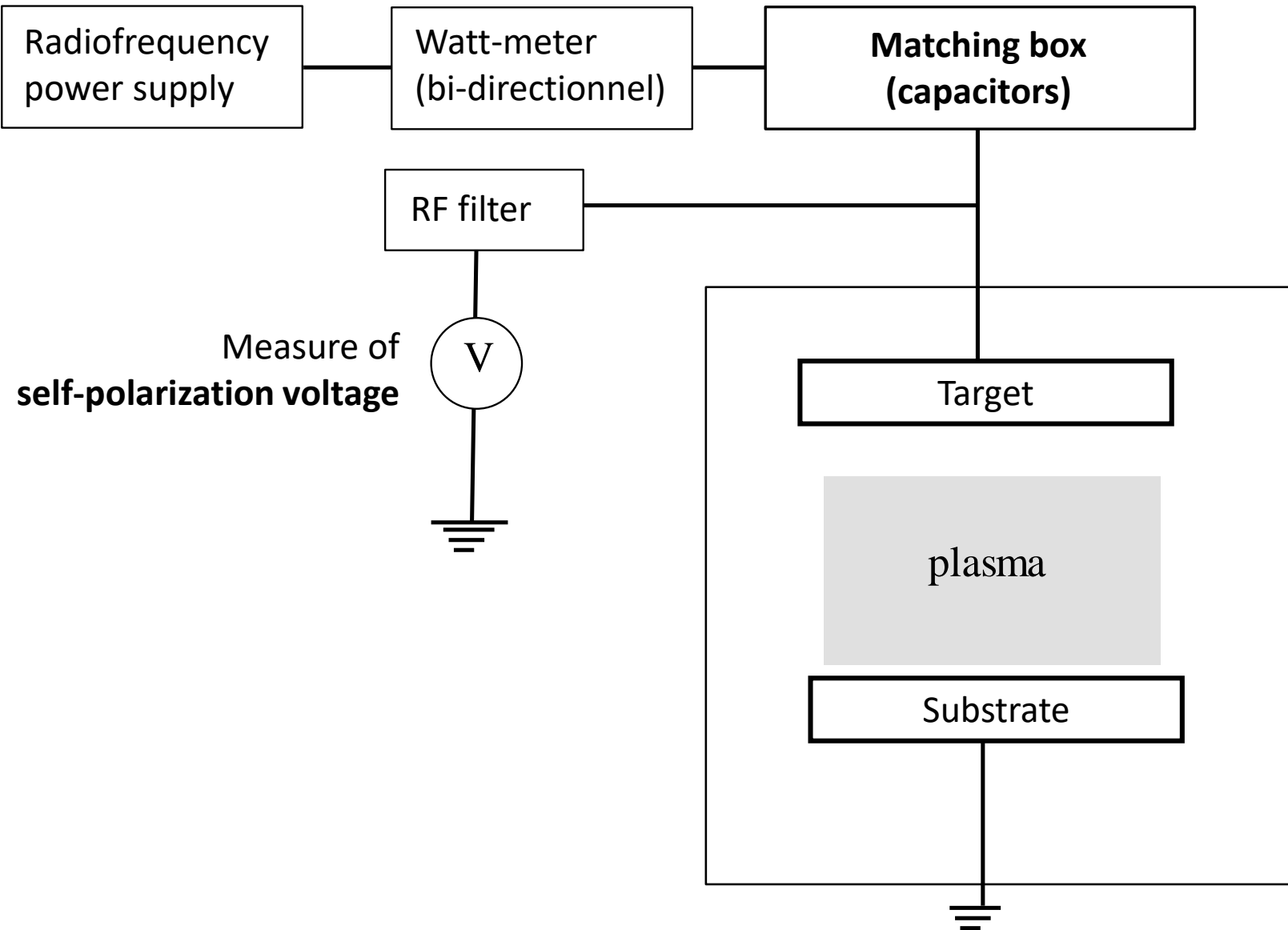
- For **conductors**: DC or RF sputtering
- For **insulators**: DC process not suitable
 - electrical charges transferred by ions cannot be evacuated
 - **RF sputtering necessary**

RF sputtering = industrial radiofrequencies **13,56 MHz** and its harmonics.

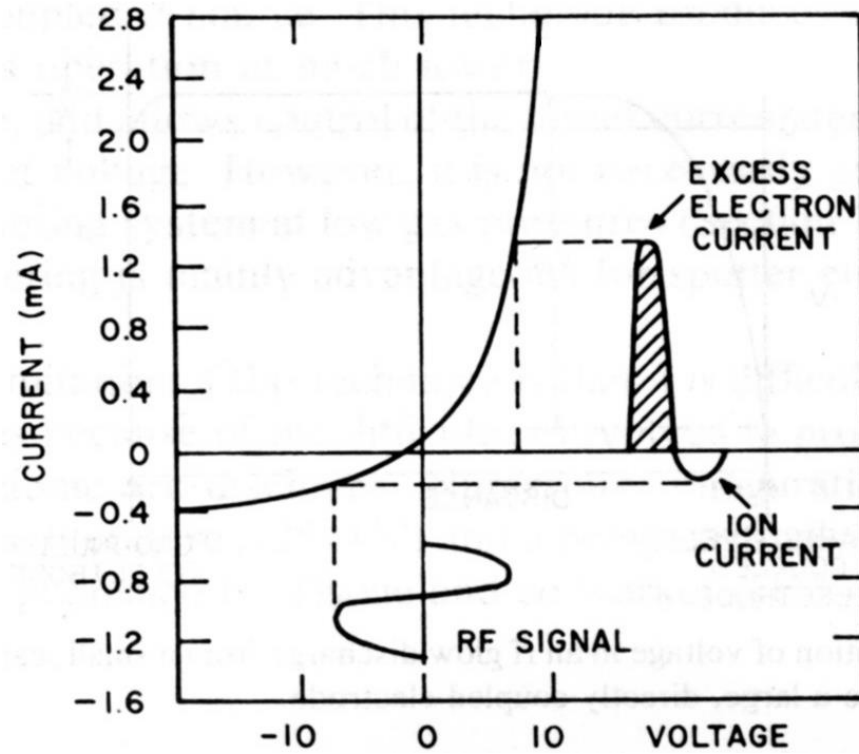
1. For an insulating target (e.g. Al_2O_3) in DC mode, there is no electron current to compensate for the implantation of Ar^+ ions in the target => the target is positively charged and repels the incident ions. **Hence, an insulating target must necessarily be sputtered in RF mode.**
2. At high frequency the electrons in the vicinity of the plasma sheaths oscillate in the electric field with sufficient energy to ionize the atoms, which reduces the dependence of the discharge on the secondary emission of the target => **this allows to lower the discharge pressure to about $2 \cdot 10^{-3}$ mbar**

RF : increased energy of sputtered species

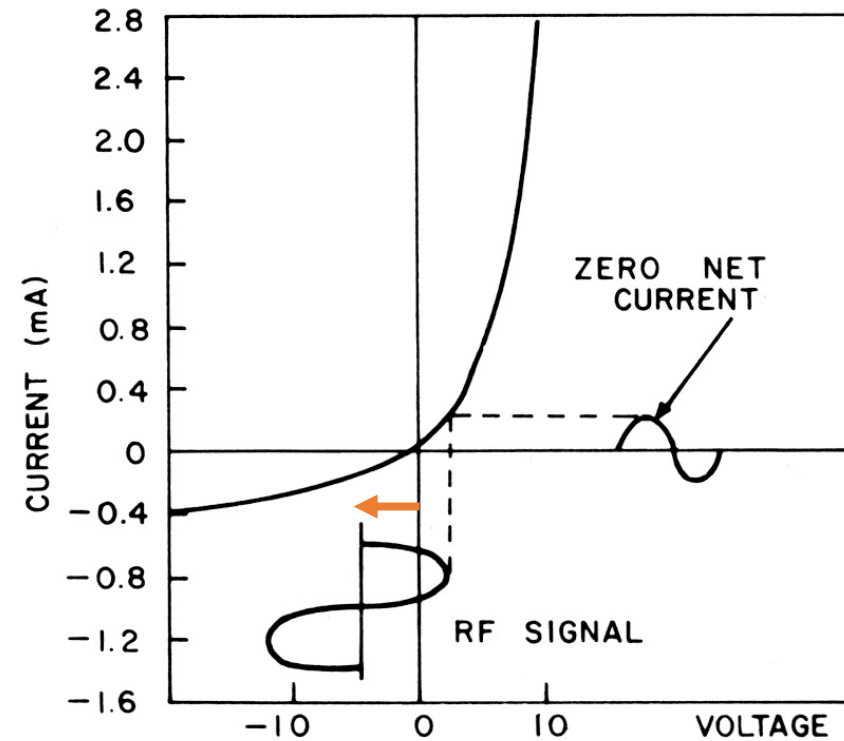
RF sputtering (13,56 MHz)



RF sputtering (13,56 MHz)



Without matching box



With matching box

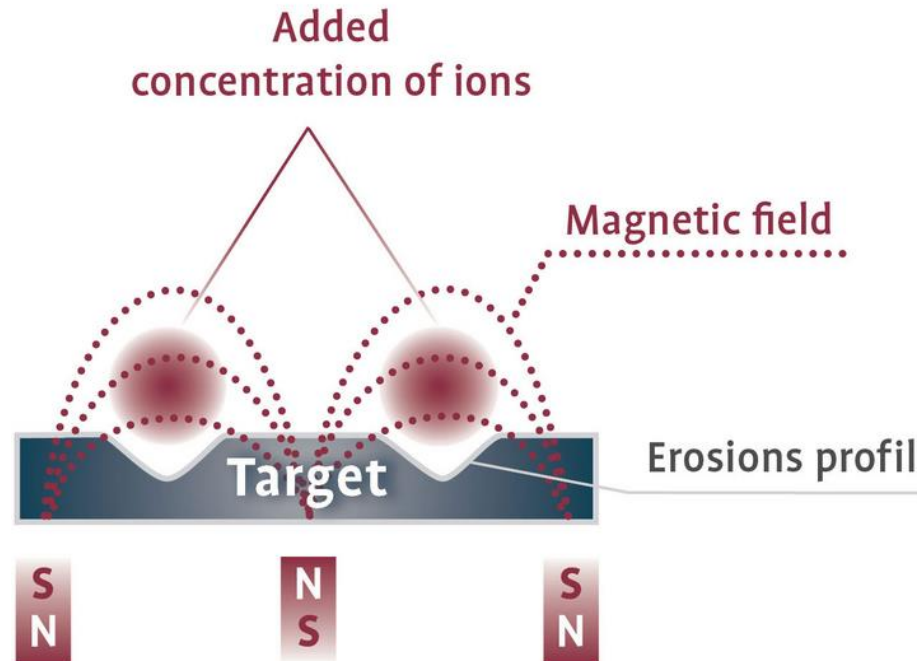
- The target electrode is connected to the RF power-supply via a **capacitor connected in series**.
- A **negative potential**, called **self-polarization potential** appears on the target.
- This potential (typically a few hundred volts negative) allows sputtering of the target, whether it is conductive or insulating.

Standard diode sputtering:

- Pressure \approx **100 mTorr**/Power \approx **1 kV**
 - « High » pressure induces collisions in the plasma for sputtered particles
 - **Decrease of kinetic energy** of particles
 - **Decrease of sputtered particles number and growth rate**
-
- How to decrease the pressure while maintaining a high discharge current?
 - **Trap electrons near the cathode with magnetron sputtering**

Magnetron sputtering

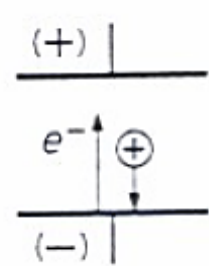
Pressure range
< 20mTorr



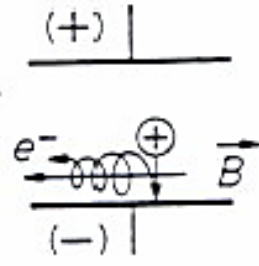
Permanent magnets at the back of the target → coupling with a magnetic field

Magnetron sputtering

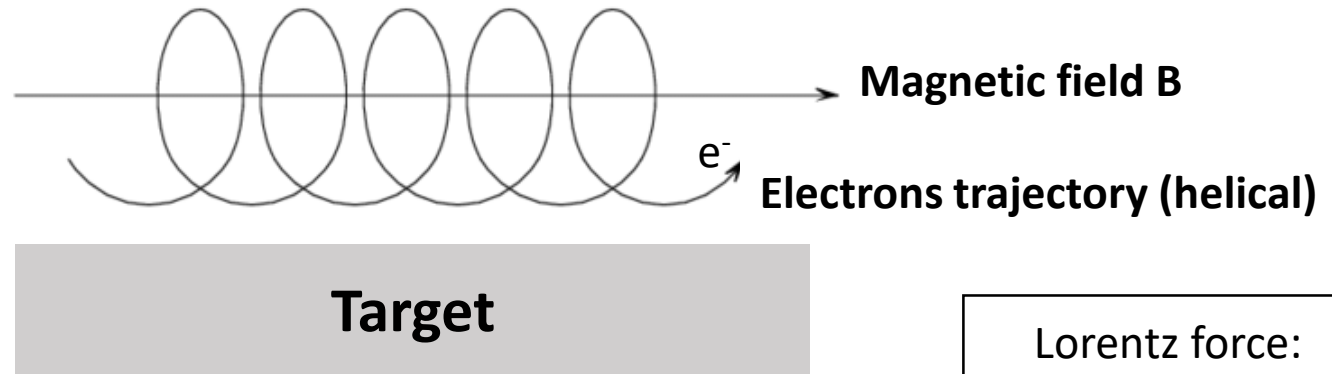
In a conventional DC sputtering system, the discharge is maintained by the secondary electrons emitted by the target. In a **magnetron system**, a **magnetic field parallel to the surface of the target is superimposed on the electric field** so that the electronic trajectories wrap around the magnetic field lines.



Diode system



Magnetron system

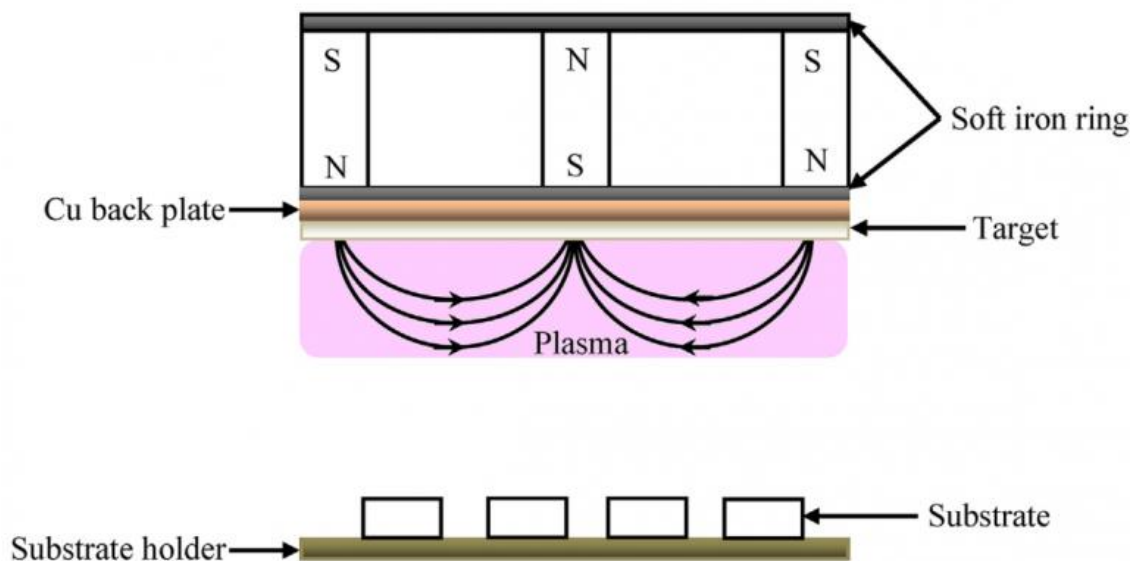


Lorentz force:

$$\vec{F} = -q(\vec{E} + \vec{v} \times \vec{B})$$

- ⇒ **Increase of the trajectories of secondary electrons emitted by the target**
- ⇒ Confinement of the electrons near the surface of the target
 - ⇒ **Higher plasma density near the target**
 - ⇒ Higher Ar⁺ ions currents
 - ⇒ Discharge can be maintained at lower pressures (10⁻³ mbar)
 - ⇒ Higher energy of atoms deposited on the substrate (better film quality)

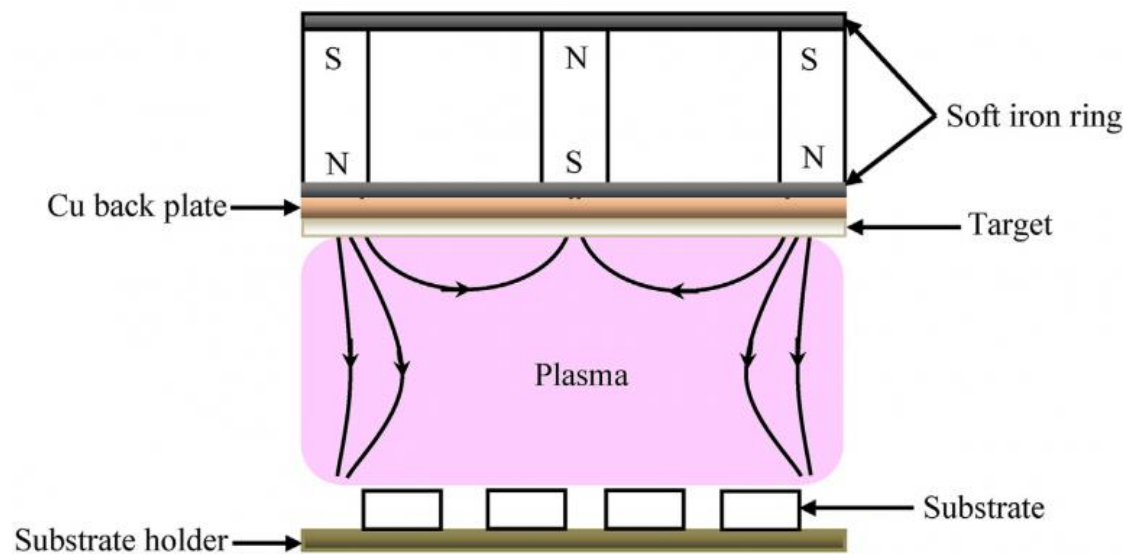
Balanced and un-balanced magnetrons



Balanced magnetron



Plasma localized near the target only. No sputtering of the substrate without polarization

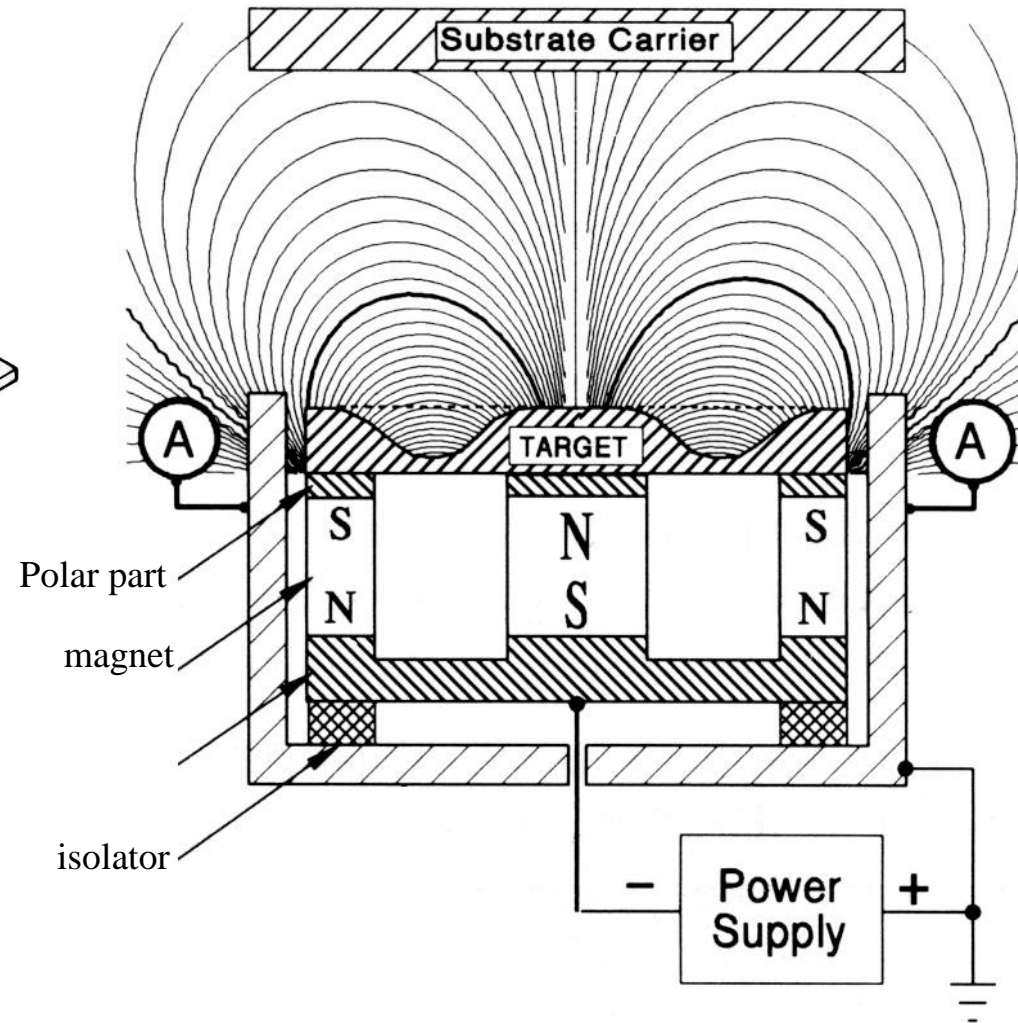
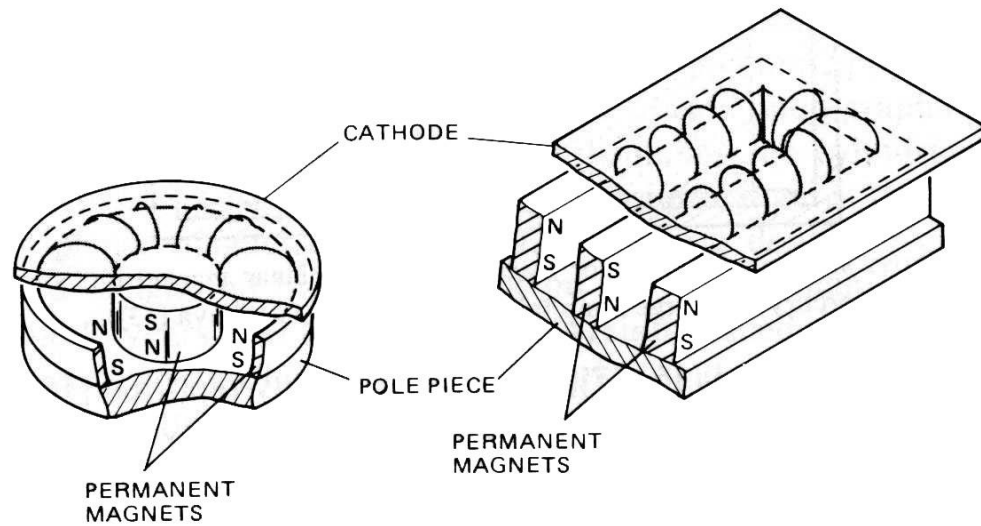


Unbalanced magnetron



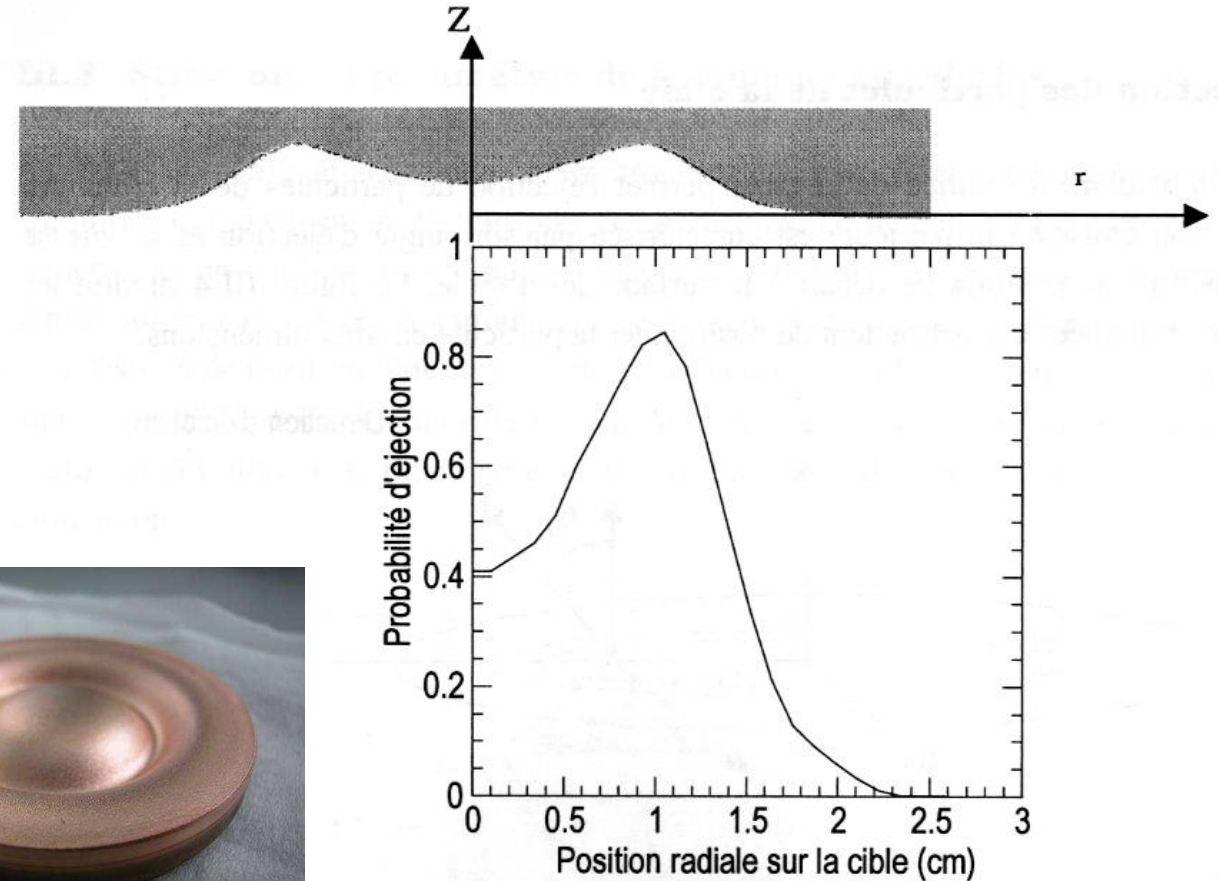
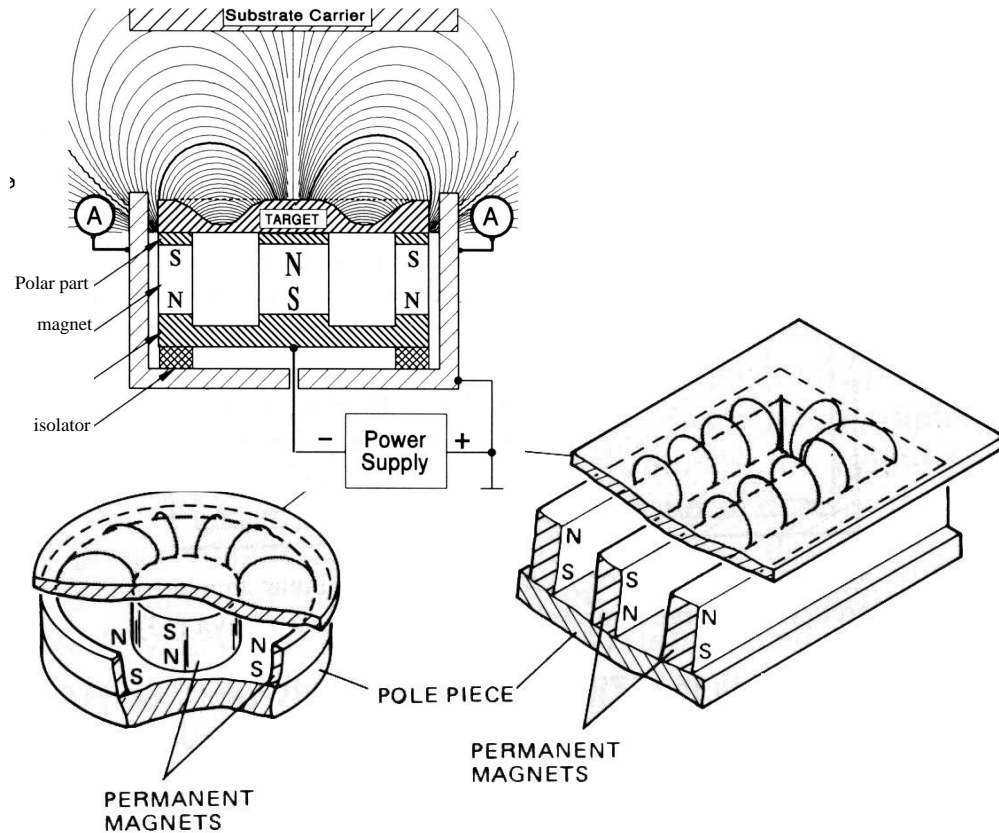
Plasma is delocalized. Ions bombarding the substrate increase the quality of the growing thin film

Structure of a magnetron planar cathode



Structure of a magnetron planar cathode

Erosion is not uniform (Lorentz force is maximum when the magnetic field is perpendicular to the electric field).



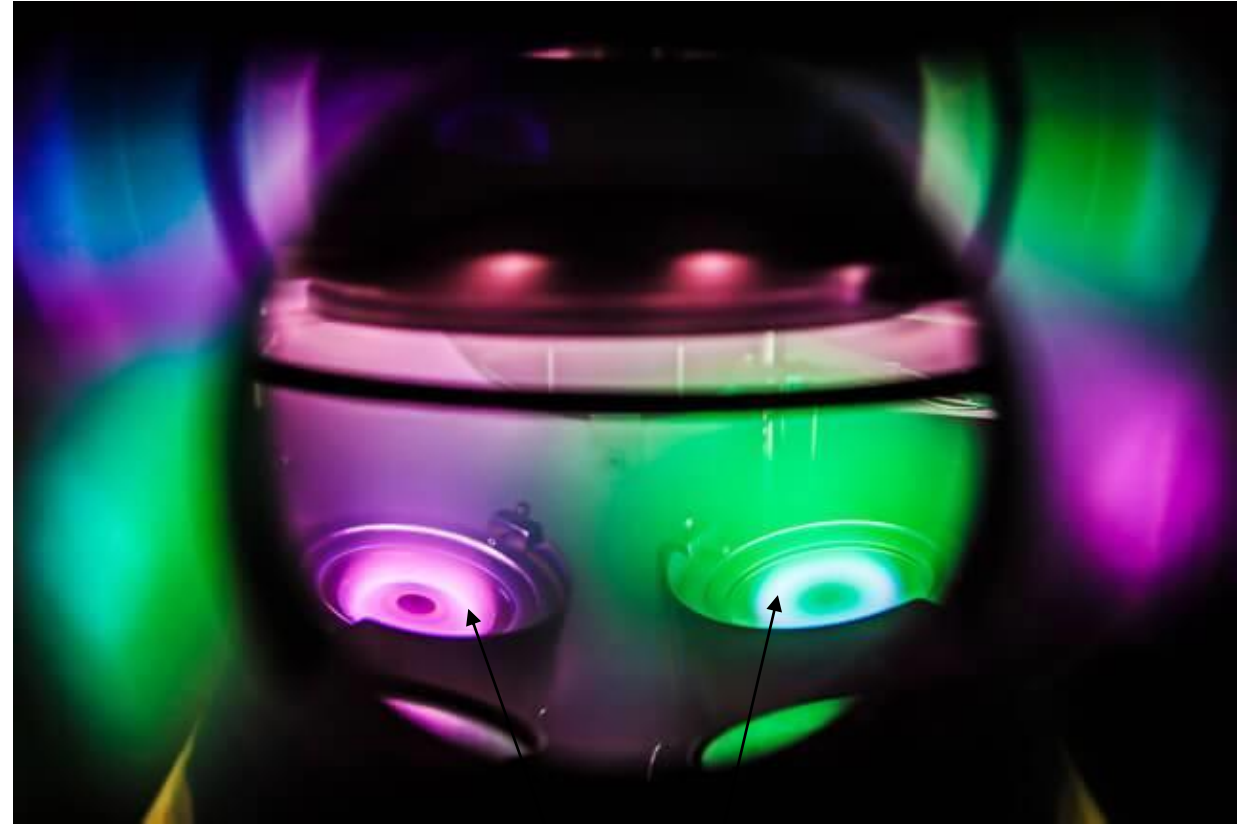
=> There exists magnetrons with moving magnets to move the active zone and allow uniform erosion of the surface of the target.

Magnetron sputtering

DC sputtering



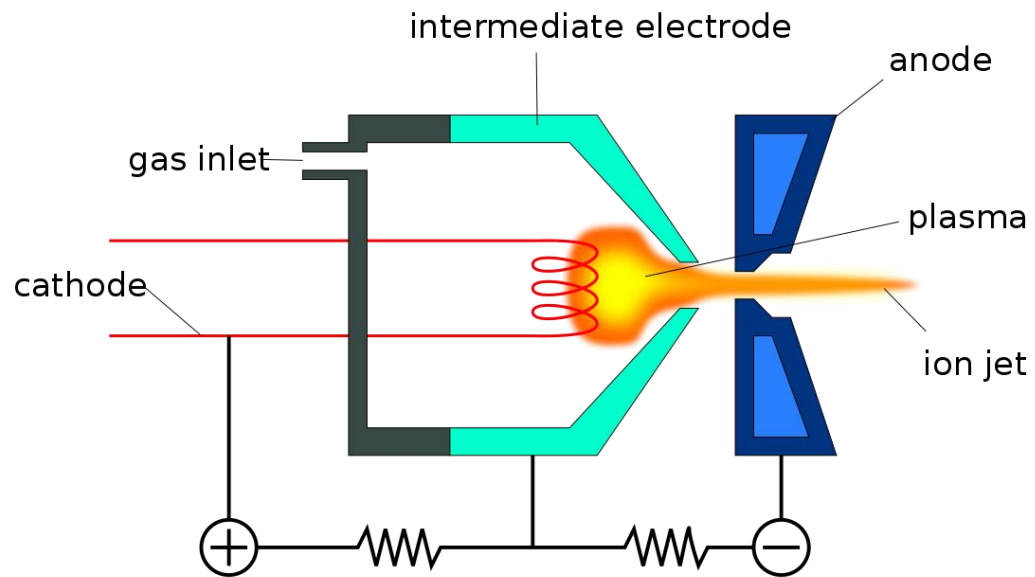
Magnetron DC sputtering



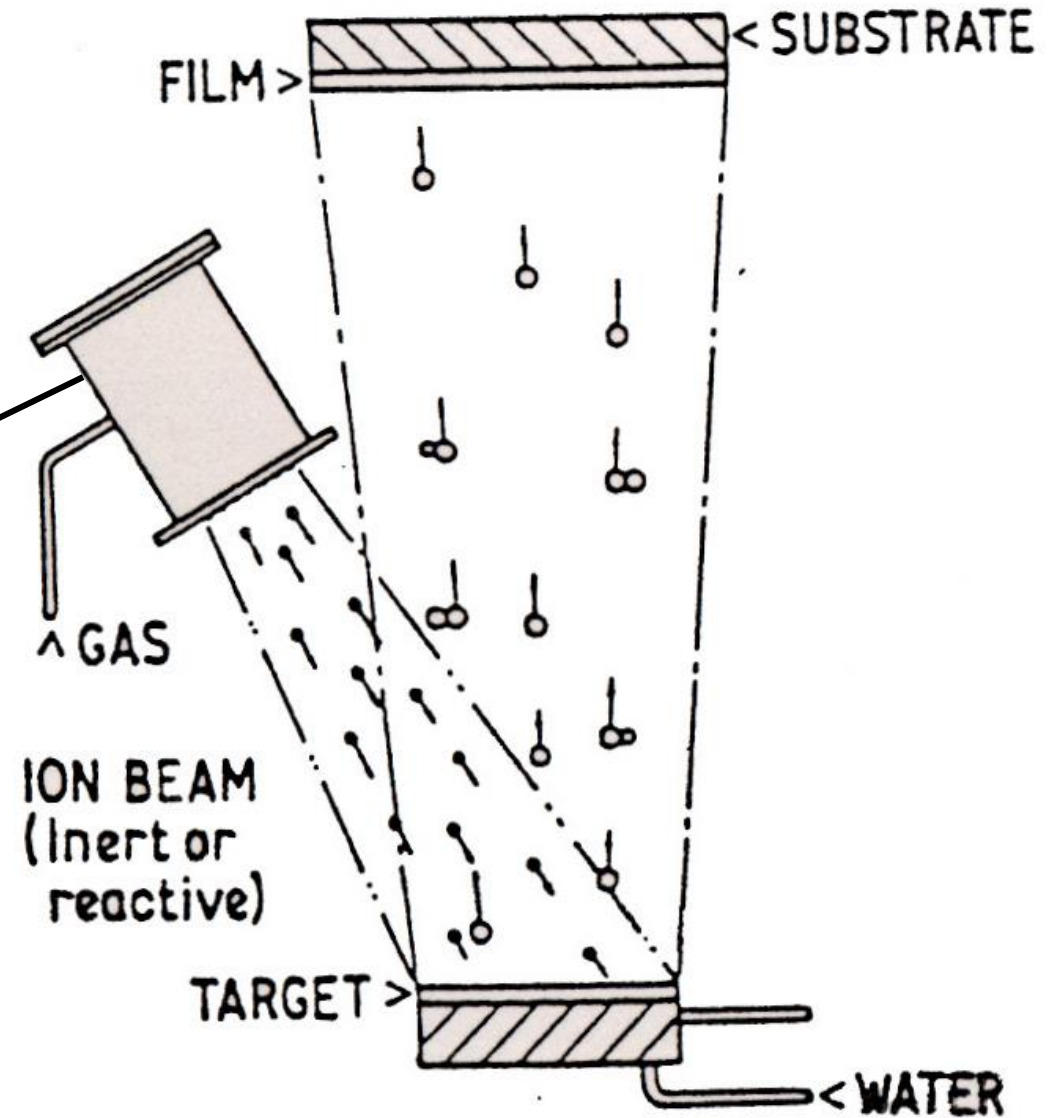
Areas of higher erosion

Ions beam sputtering

- Independent control of ions energy and current
- Deposition can be carried out at very low pressures
- Limitation: higher complexity of implementation



**Ionic
source**

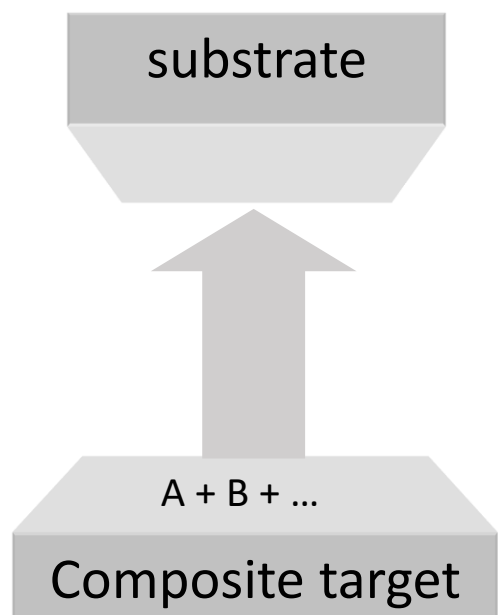


Sputtering of compounds or alloys (ex: ITO for Indium Tin Oxyde)

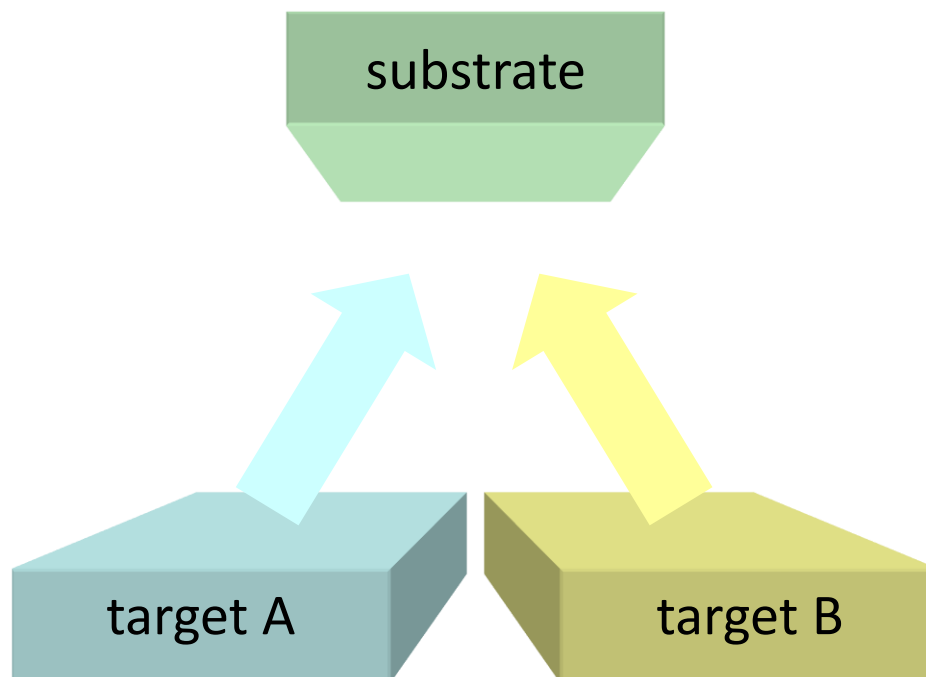
→ **Composite target** (compound or alloy)

Alloys: Zn:Al, Sn:Zn, etc...

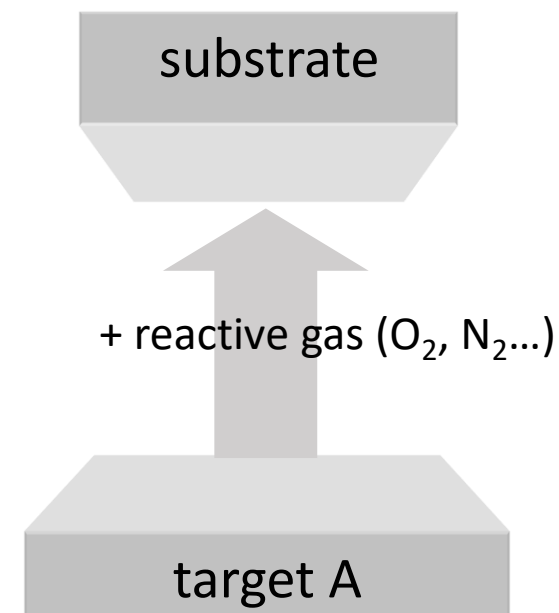
Compounds: TiO₂, ITO, CIGS, etc...

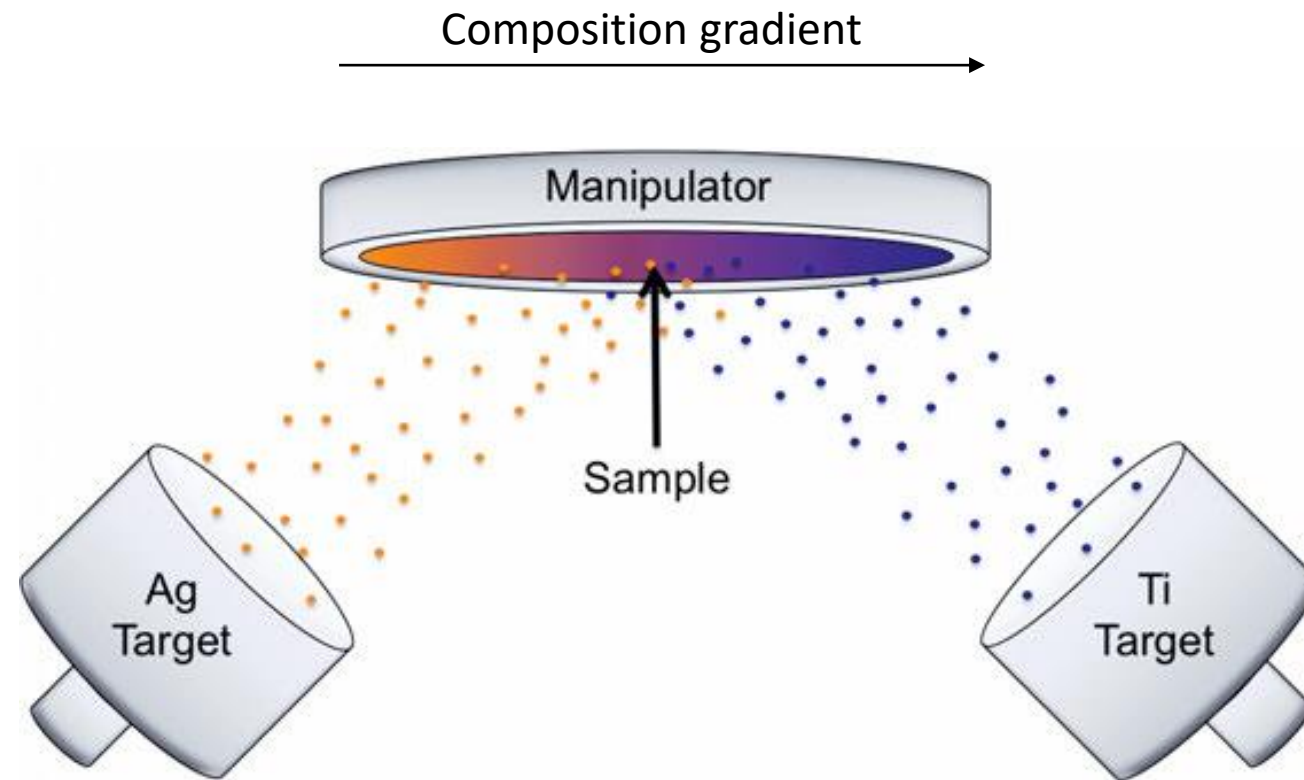


→ **Co-sputtering** of elements

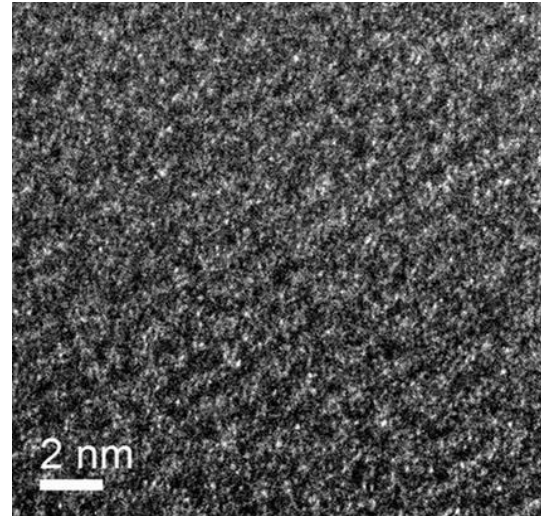
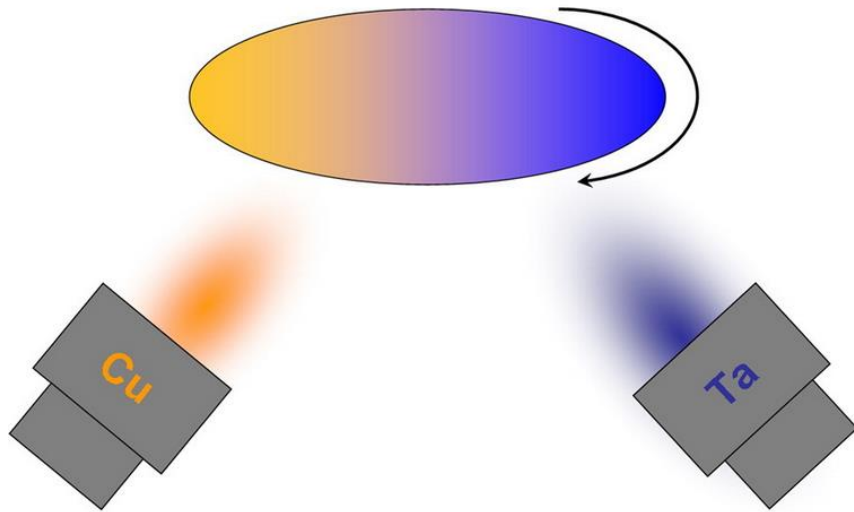


→ **Reactive sputtering**

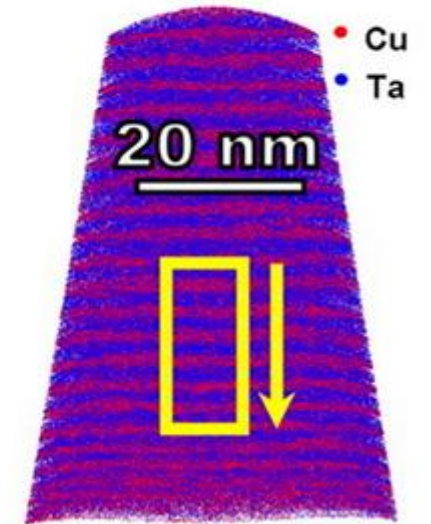




➤ Multilayers deposition



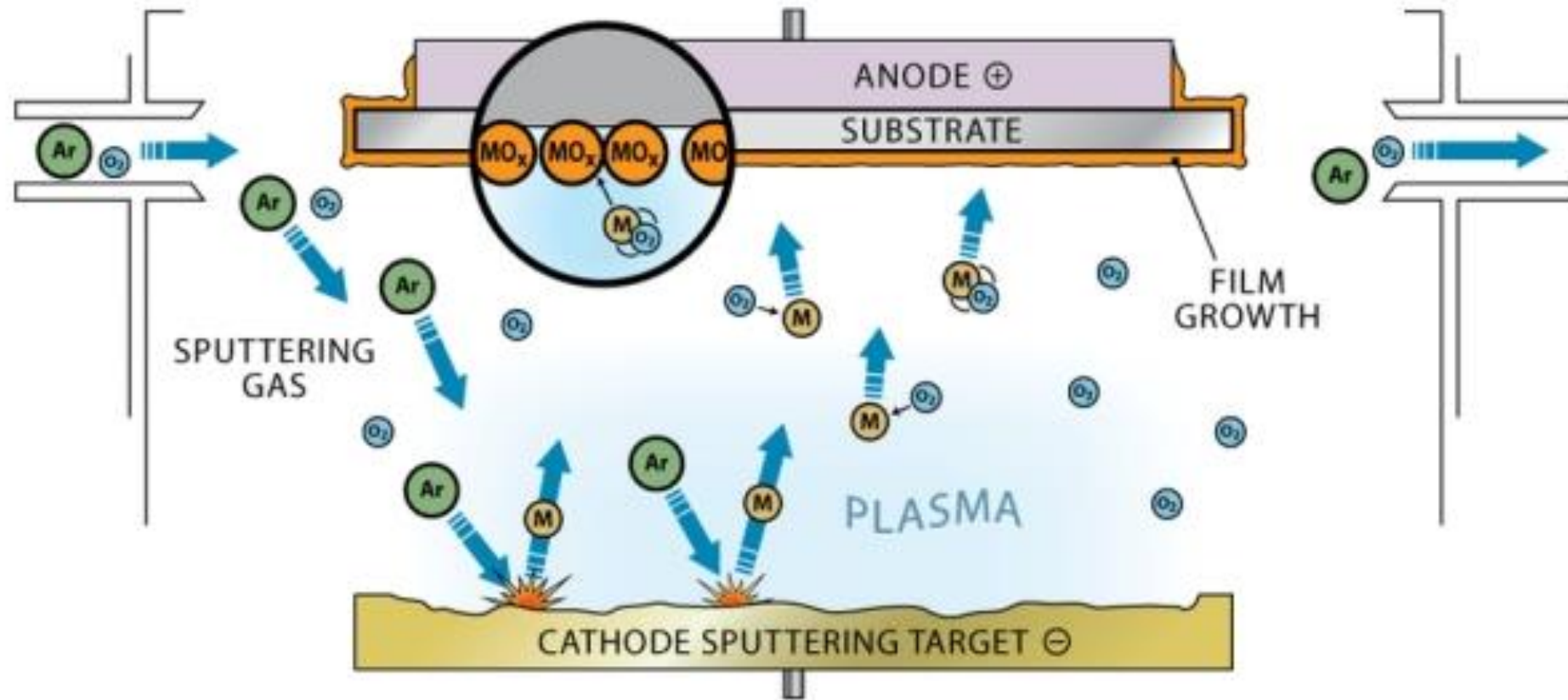
3D reconstruction



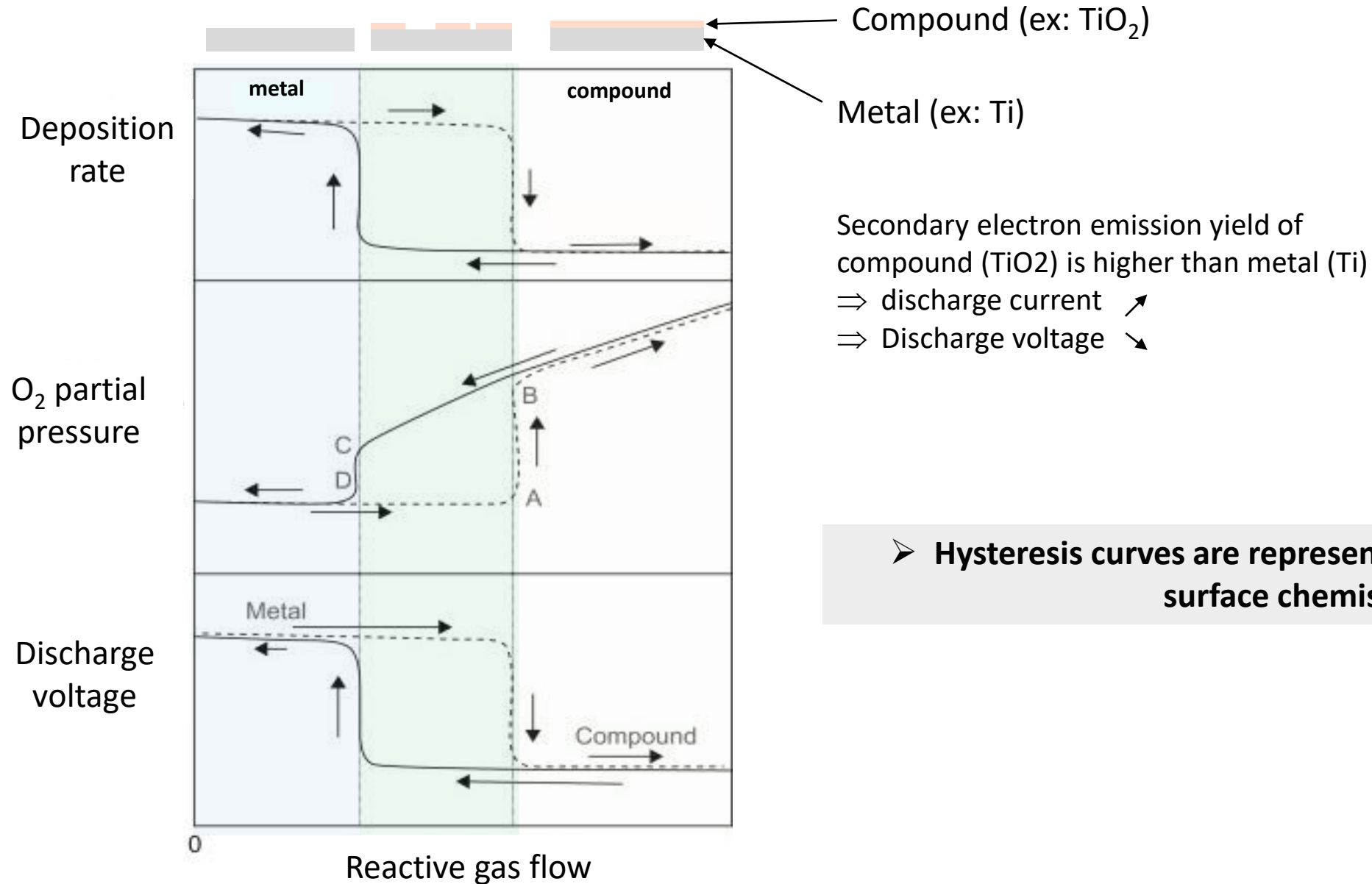
C. Muller, Nanoscale Cu/Ta multilayer deposition by co-sputtering on a rotating substrate. Empirical model and experiment (2016)

Reactive sputtering

Injection of a reactive gas into the discharge: Ar + N_2 , Ar + O_2 , Ar + CH_4 , Ar + C_2H_2 , Ar + H_2S , Ar + SiH_4



Hysteresis curves in reactive sputtering

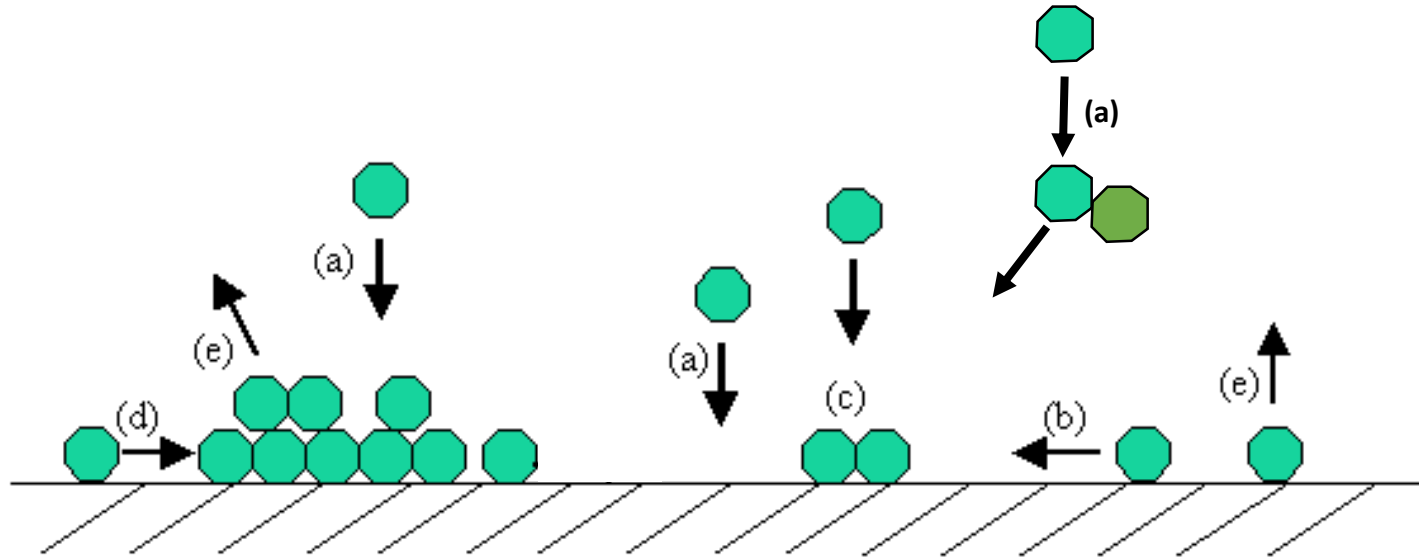


➤ Hysteresis curves are representative of the target surface chemistry

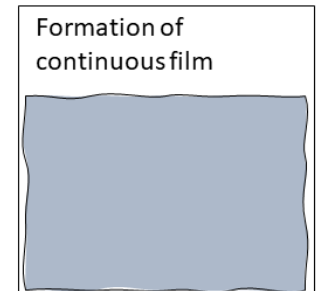
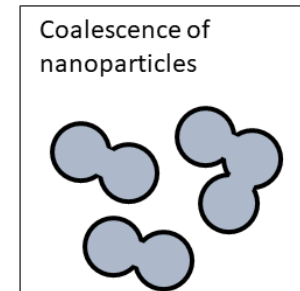
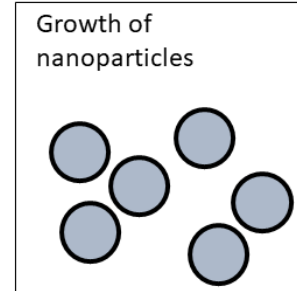
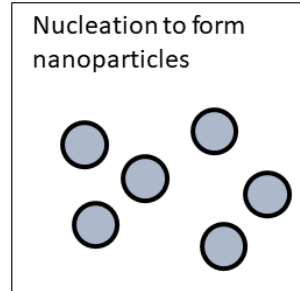
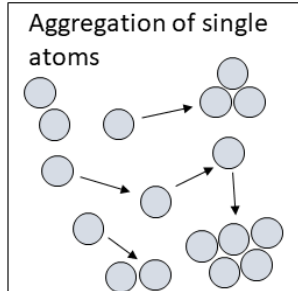
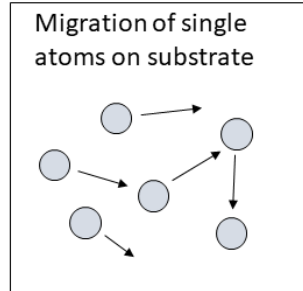
How to control physico-chemistry of materials by sputtering?

- Crystallinity (crystal phase, texturation...)
- Morphology (density, porosity, roughness...)
- Chemistry (composition, oxydation states)

Film growth on substrate surface



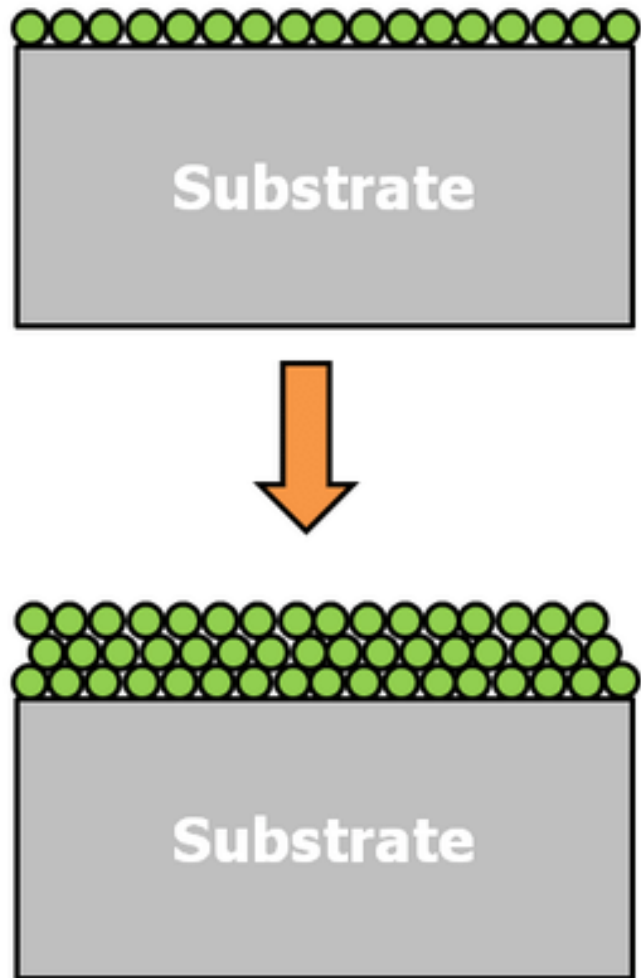
- (a) Transport in vapor phase (collisions)
- (b) Diffusion of ad-atoms at the surface
- (c) Nucleation/formation of clusters
- (d) Coalescence
- (e) Evaporation



Thin films growth modes

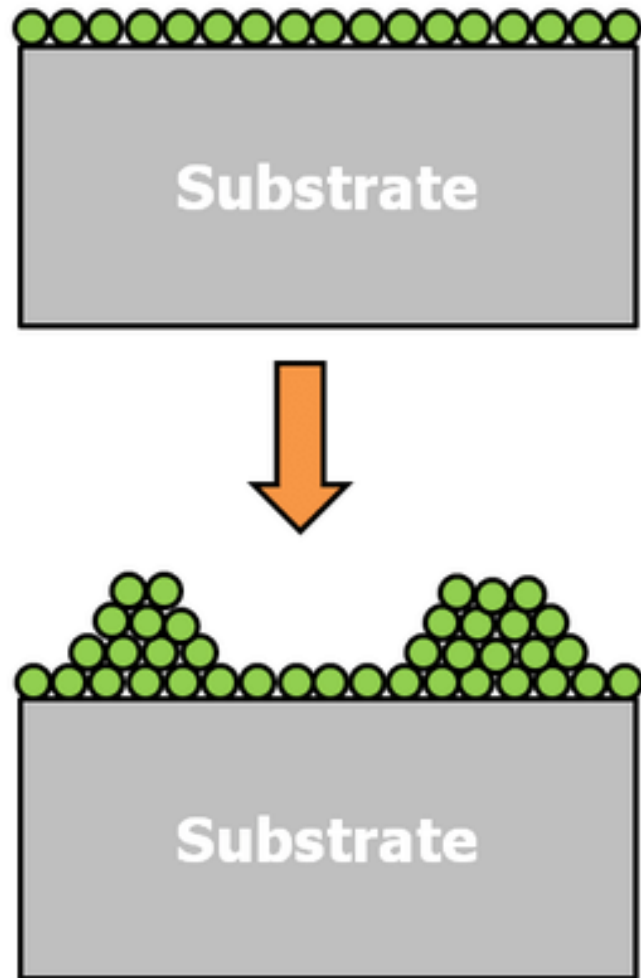
Franck-Van Der Merwe

$$\gamma_{\text{Substrat}} \gg \gamma_{\text{Interface}} + \gamma_{\text{Couche}}$$



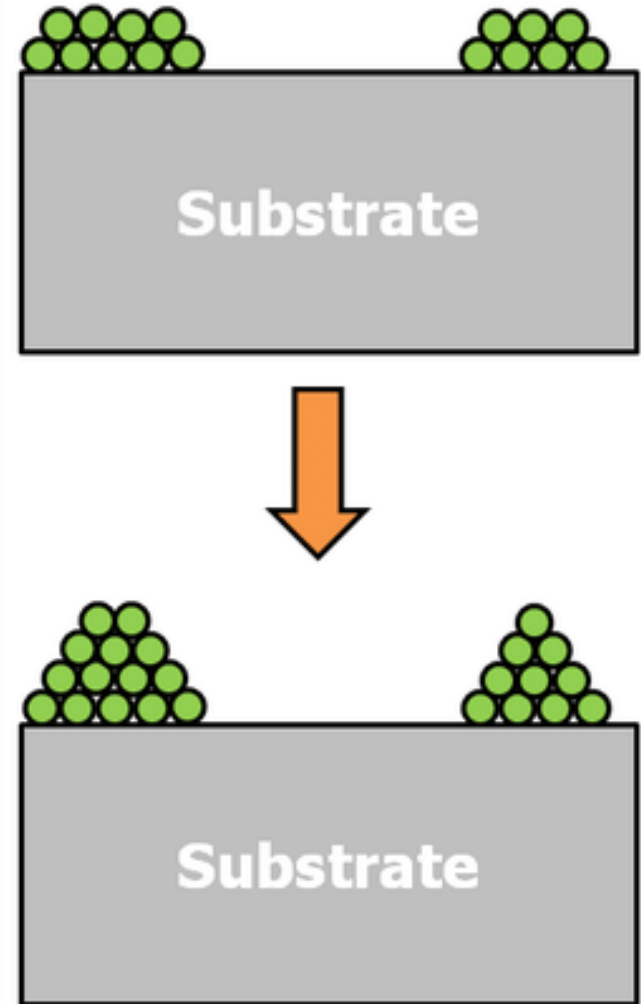
Stranski-Krastanov

$$\gamma_{\text{Substrat}} \approx \gamma_{\text{Interface}} + \gamma_{\text{Couche}}$$



Volmer-Weber

$$\gamma_{\text{Substrat}} \ll \gamma_{\text{Interface}} + \gamma_{\text{Couche}}$$



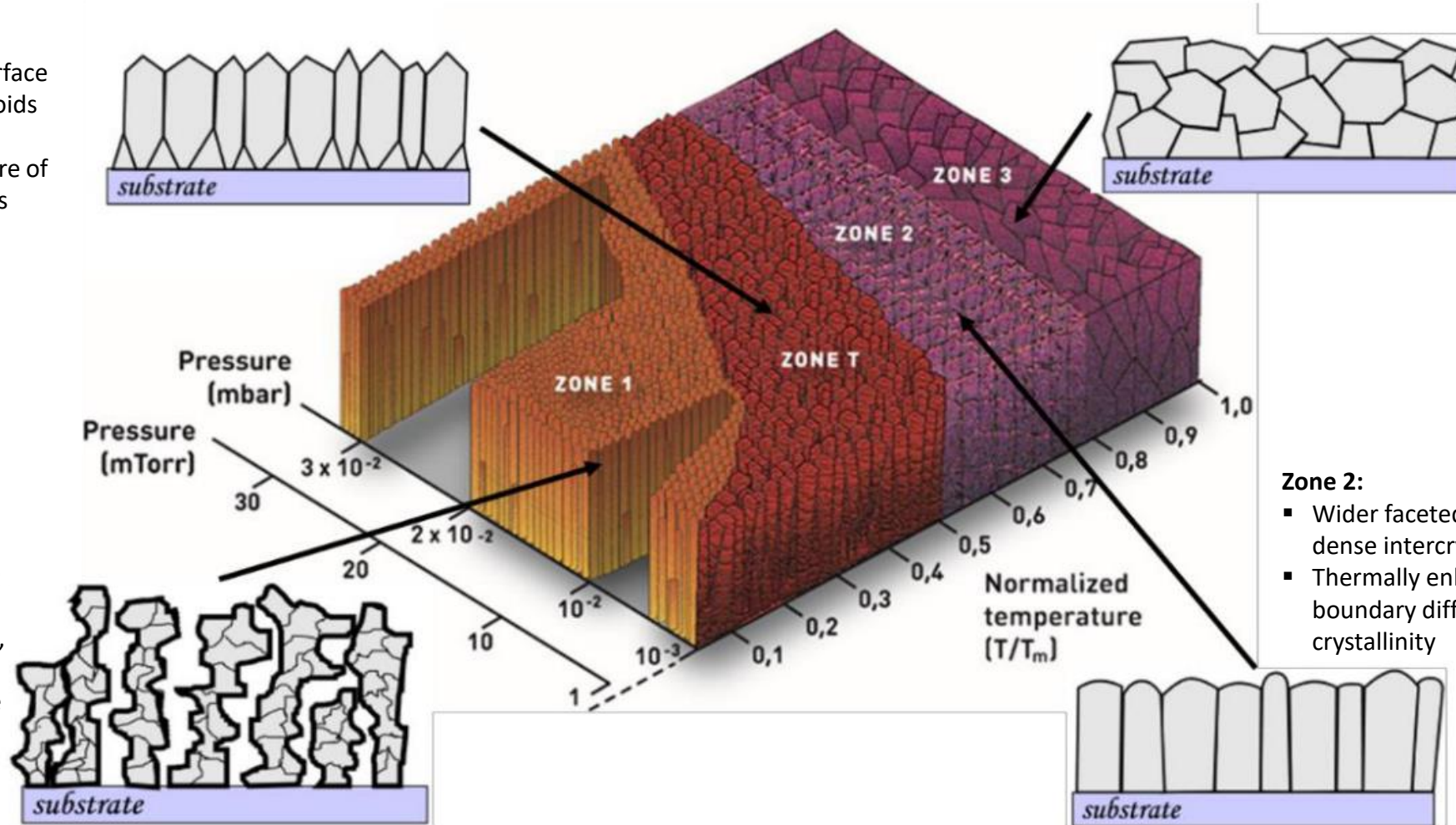
Thornton structure zone model (SZM): pressure-temperature

Zone T:

- Densely packed, poorly defined fibrous grains
- Thermally enhanced surface diffusion begins to fill voids between columns
- Crystallographic structure of columns still amorphous

Zone 1

- Open-voided tapered fibrous structure
- Limited adatom diffusion, yielding amorphous crystallographic structure



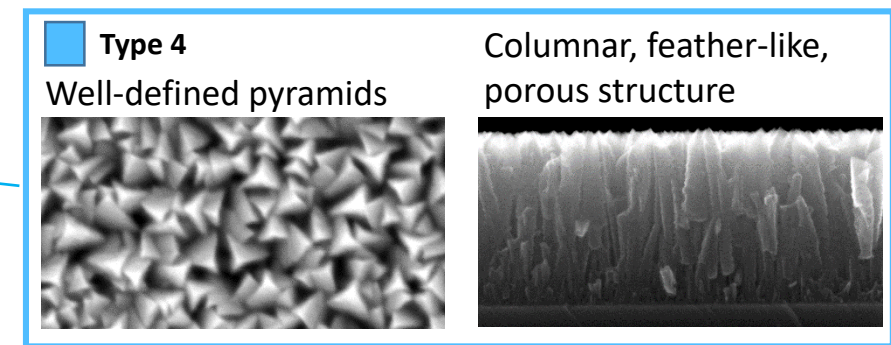
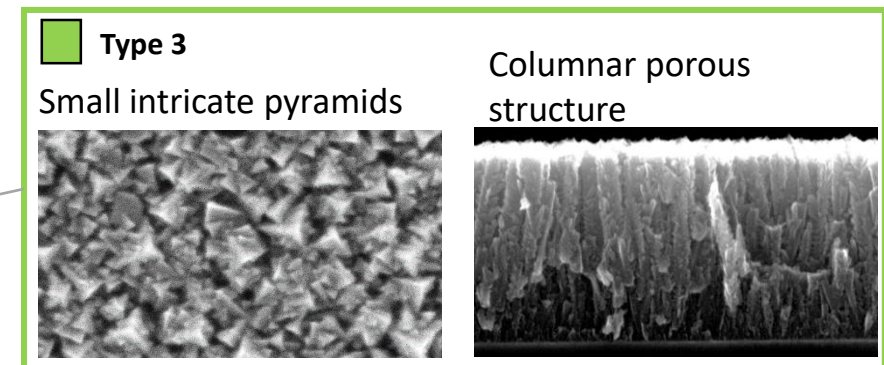
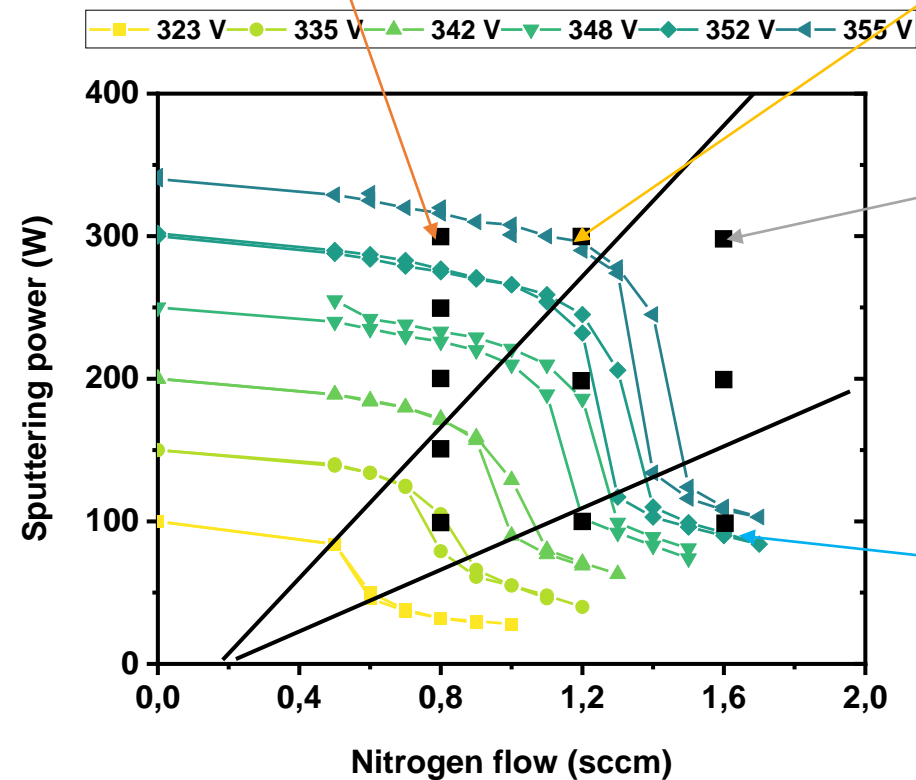
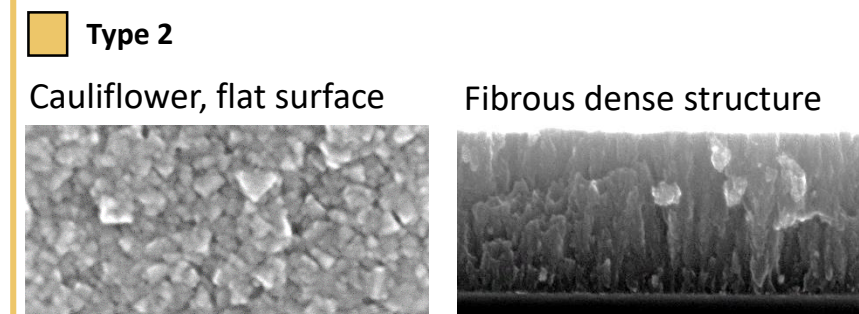
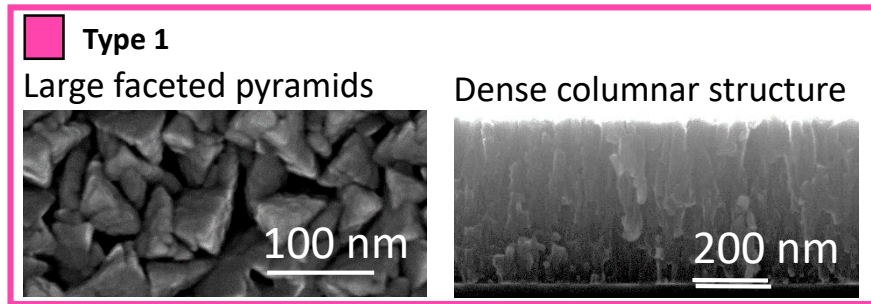
Zone 3

- Recrystallised, near-equiaxed columnar grains
- Bulk and boundary adatom diffusion dominate film structure
- Negligible effect of sputtering pressure on film morphology
- Film properties very similar to bulk material

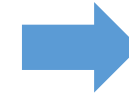
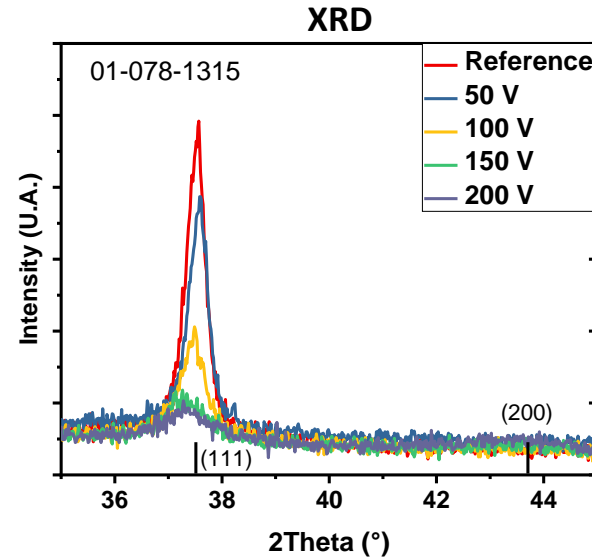
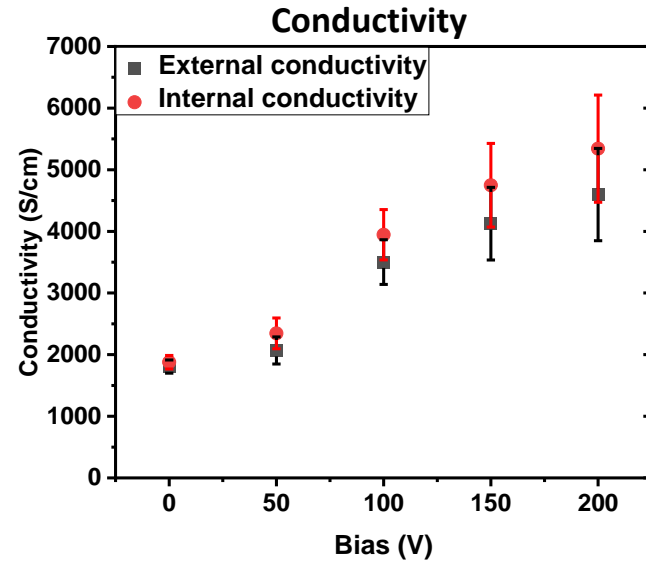
Zone 2:

- Wider faceted columnar grains separated by dense intercrystalline boundaries
- Thermally enhanced surface and grain-boundary diffusion yields higher column crystallinity

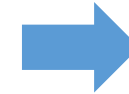
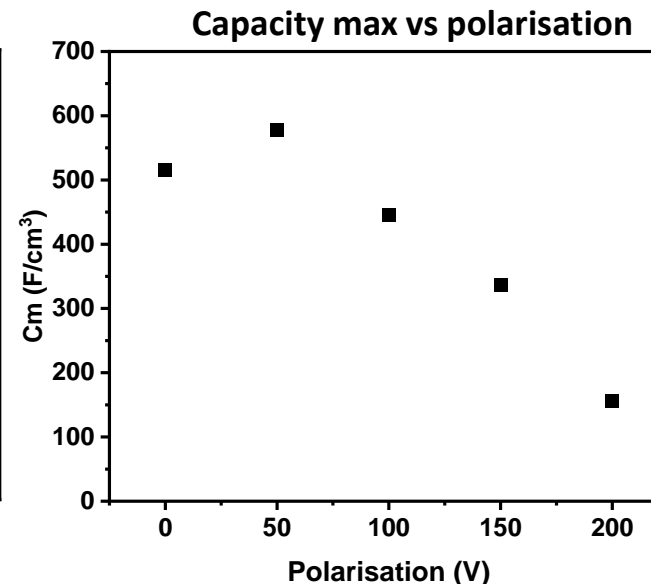
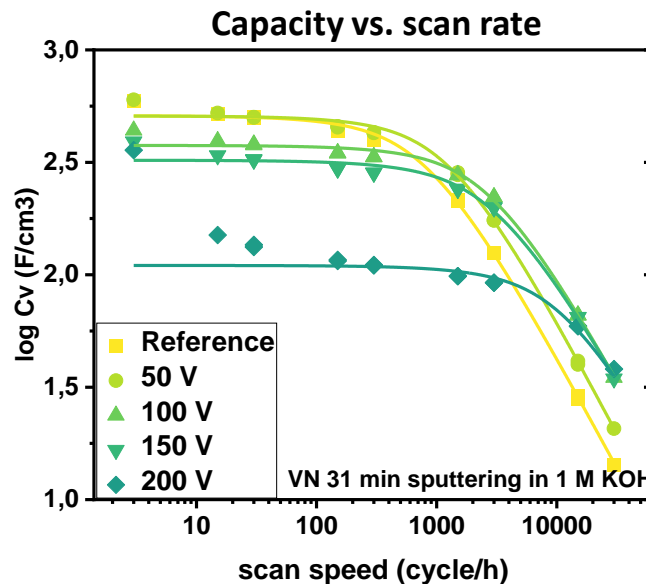
Example 1: VN deposition in reactive mode. Role of **sputtering power** and **nitrogen flow**



Example 1: VN deposition in reactive mode. Role of substrate polarisation



Amorphisation and densification
with increase substrate
polarization (atomic peening)



Decrease capacitance with densification

Example 2: influence of deposition pressure

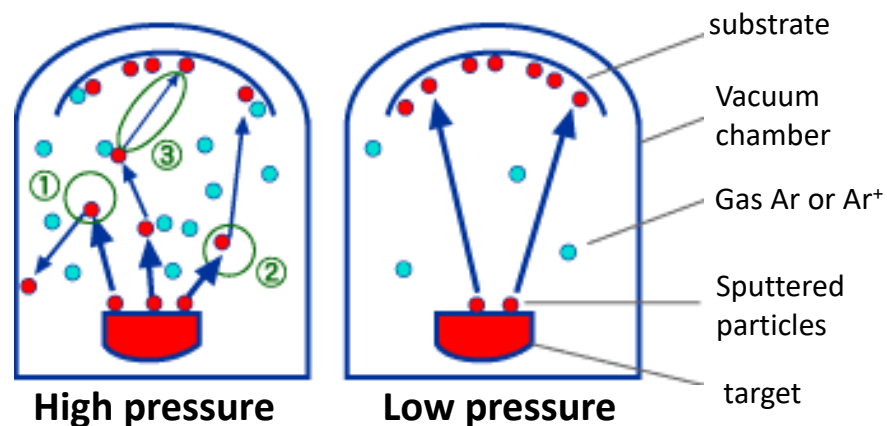
Mean free path λ (cm) $\sim 7 \cdot 10^{-3} / P(\text{mbar})$: average distance over which a moving particle travels before substantially changing its direction or energy, typically as a result of one or more successive collisions with other particles.

If mean free path \ll target-substrate distance

\Rightarrow Thermalization of sputtered species (energy $\sim kT_G$)

If mean free path \geq target-substrate distance

\Rightarrow Energy of sputtered species is maintained until they reach the substrate

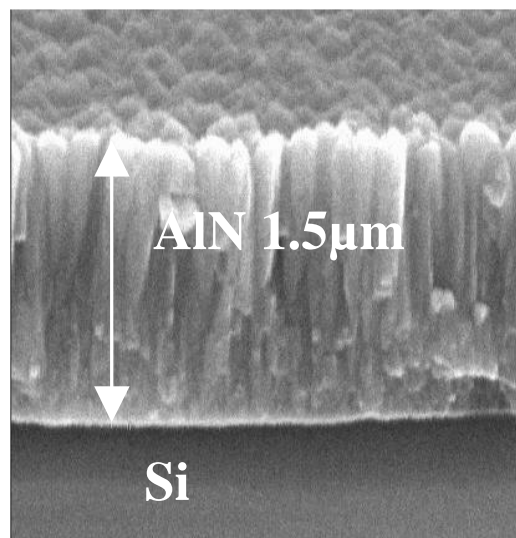
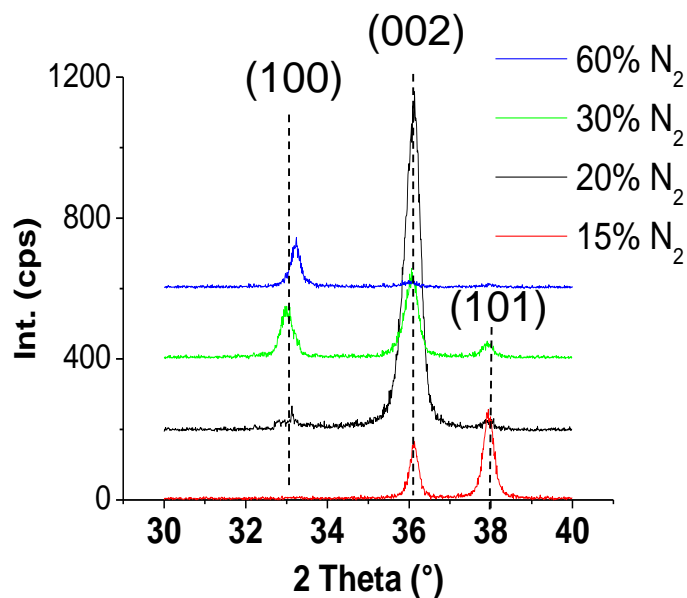


Energy of sputtered particles is preserved at low pressure

Example 2: influence of deposition pressure on AlN films

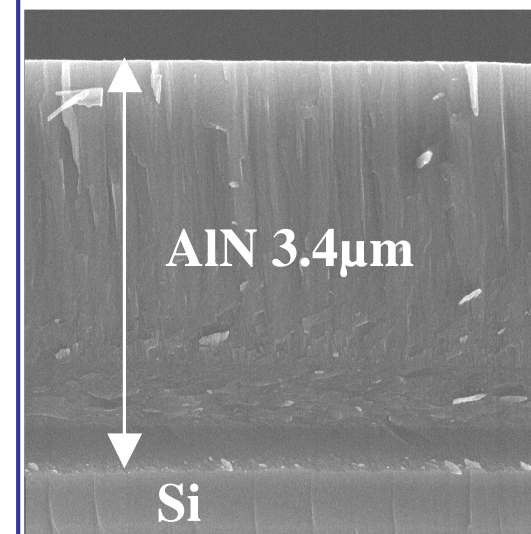
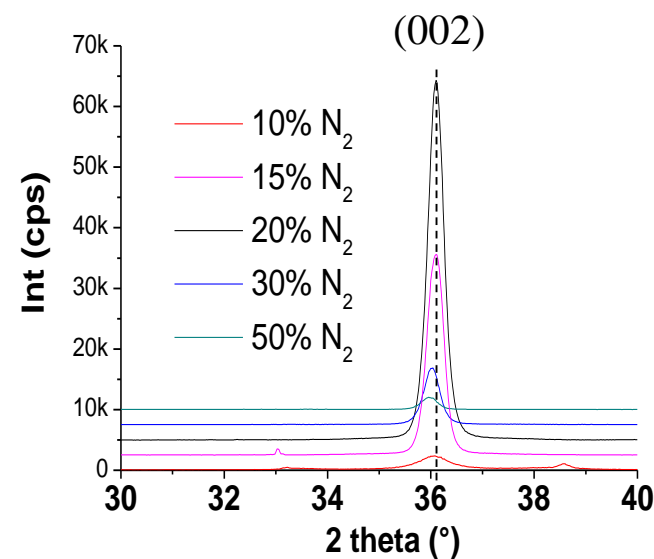
Type 1 (high pressure)

*Selection of crystalline orientation
Grain size # 20 – 30 nm
Contamination [O] # 5 % at.
Tensile stress (0.5 GPa)*

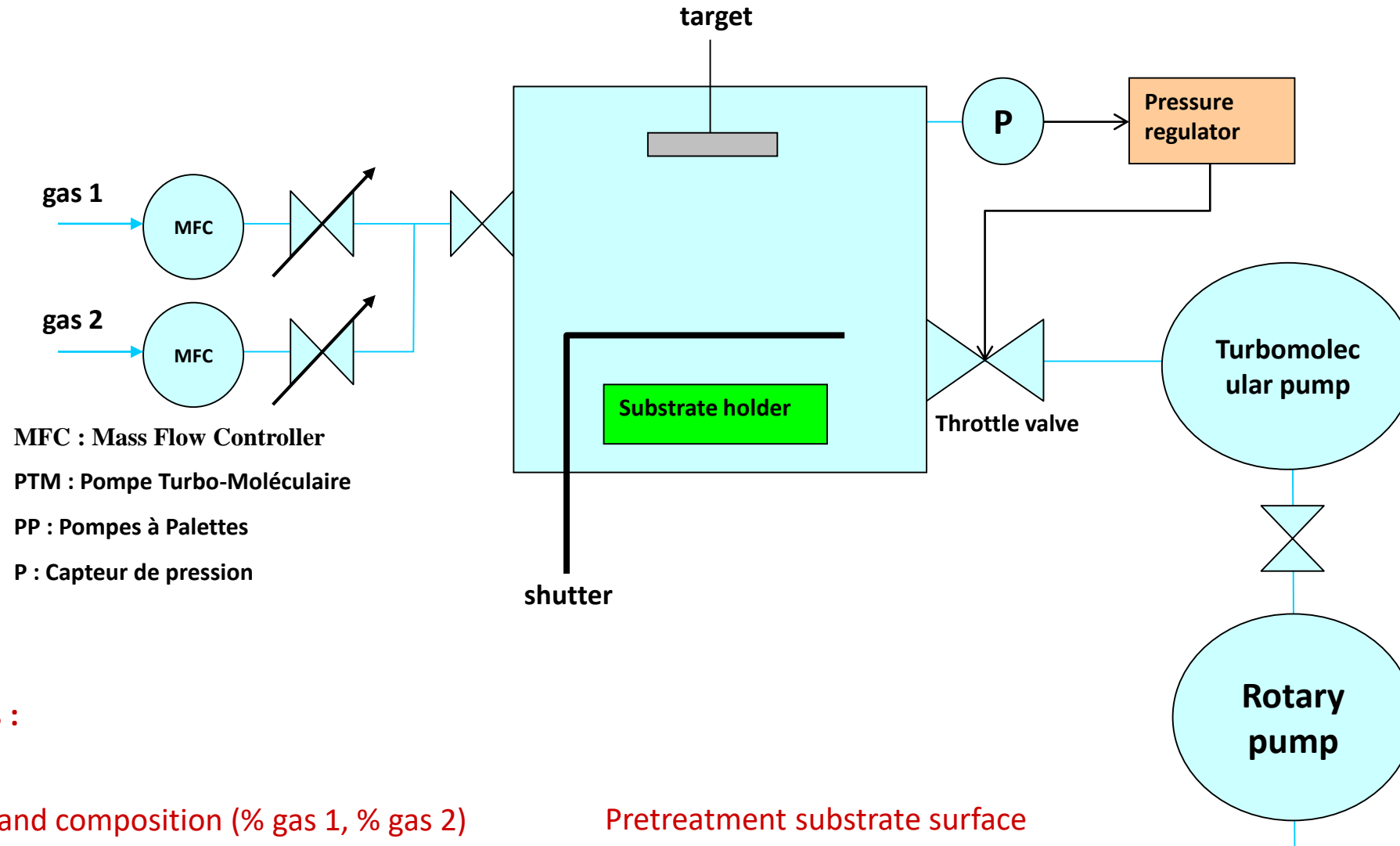


Type 2 (low pressure)

*c (002) Oriented
Grain size # 100 – 150 nm
Contamination [O] # 0.5 % at.
Compressive stress (-1.5 GPa)*



Conventional system for sputtering



Main parameters :

Total pressure

Partial pressures and composition (% gas 1, % gas 2)

Type of excitation of the target (DC, RF)

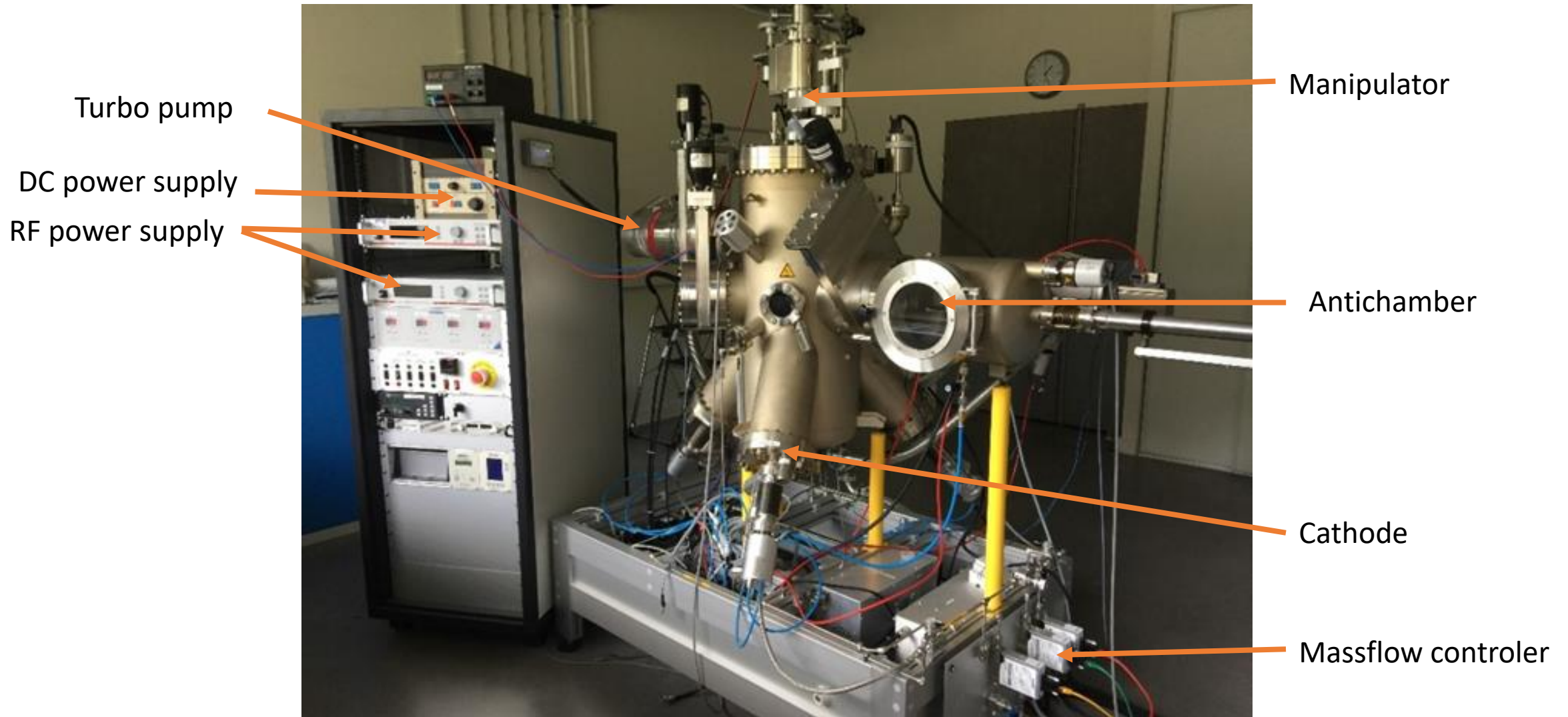
Target power (current – voltage)

Pretreatment substrate surface

Substrate temperature

Substrate polarization (Ion energy, Ion current density)

Confocal three cathode magnetron sputtering in IMN (Nantes)



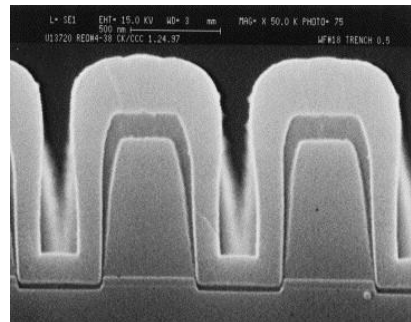
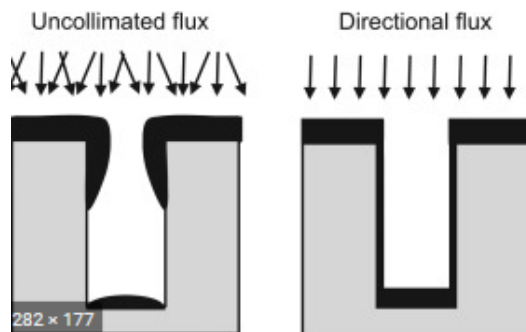
Strong and weak points of sputtering

Strong points:

- deposition of virtually all solid materials
- very stable deposition conditions
- good reproducibility
- good control of thickness
- targets can be changed frequently => ease of use / evaporation where it is necessary to change crucible and recharge
- good adhesion
- well suited to deposition on flat substrates with good uniformity
- the same equipment can be used in DC or RF, with inert or reactive gas

Weak points:

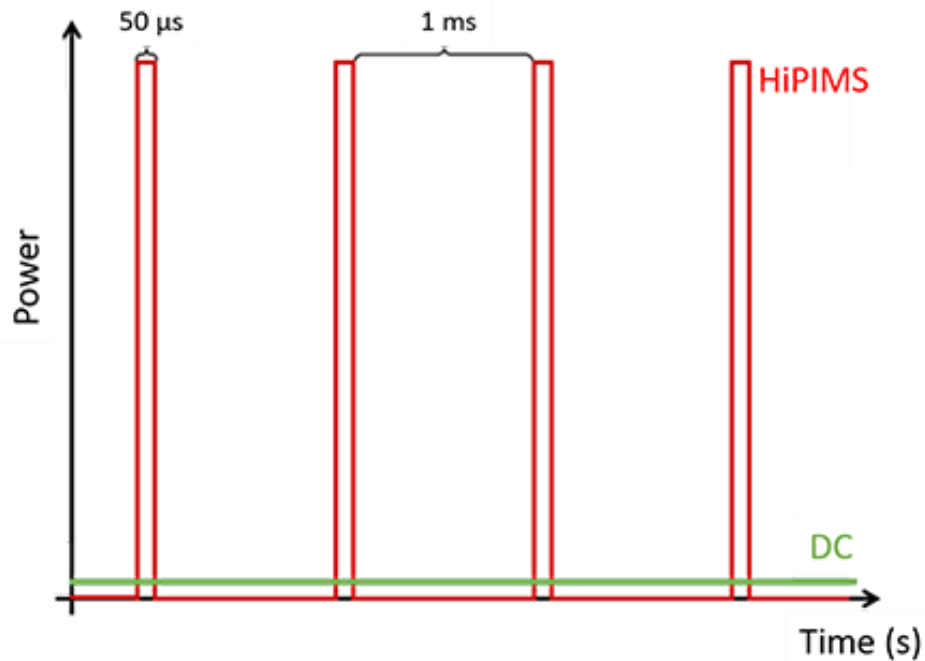
- low deposition rates
- incorporation of Ar^+ into the layer
- not easily suitable for deposition on complex-shaped surfaces



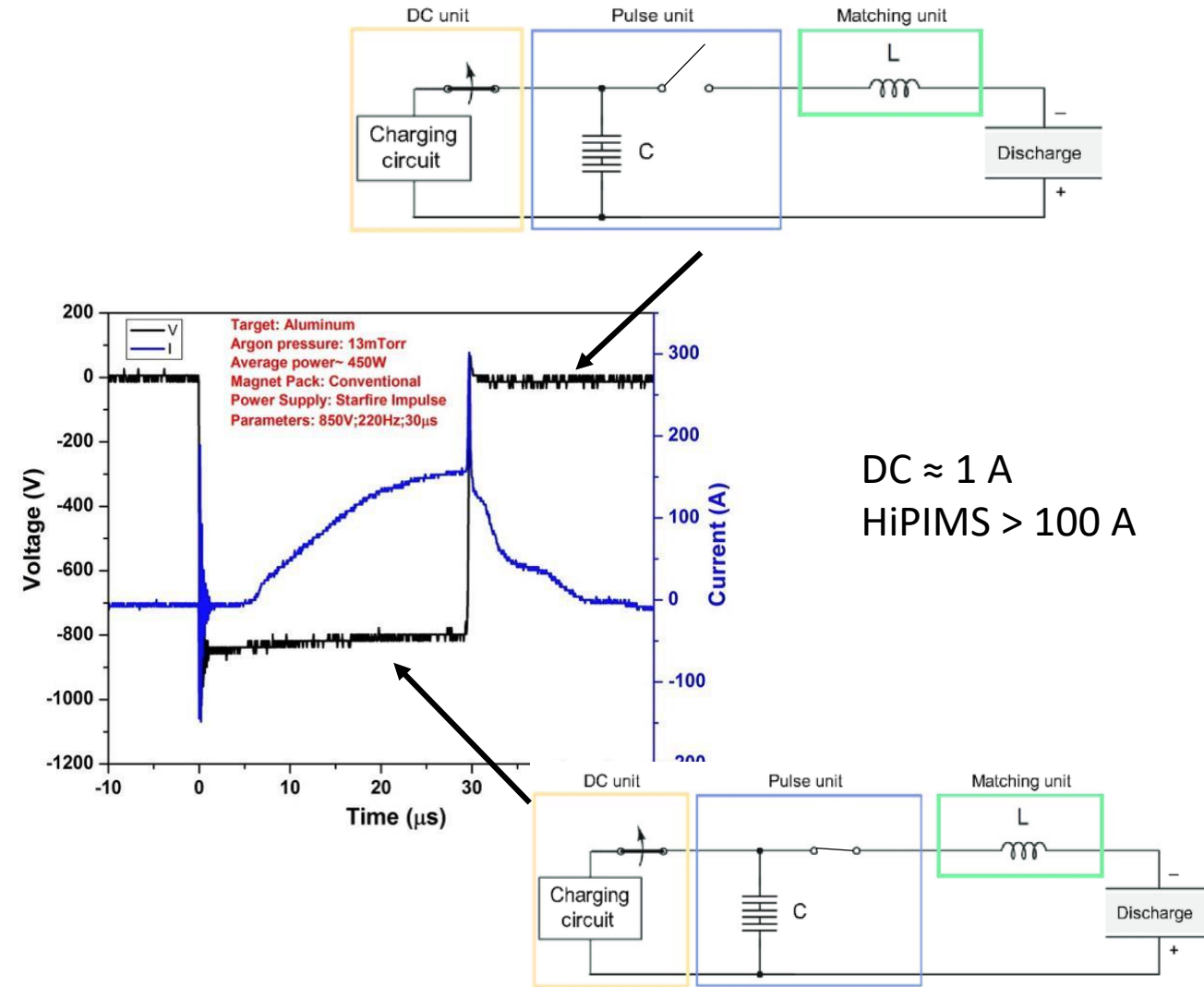
Ionized PVD can improve thin film conformity

High Power Impulse Sputtering (HiPIMS)

Power sequence in HiPIMS and DC



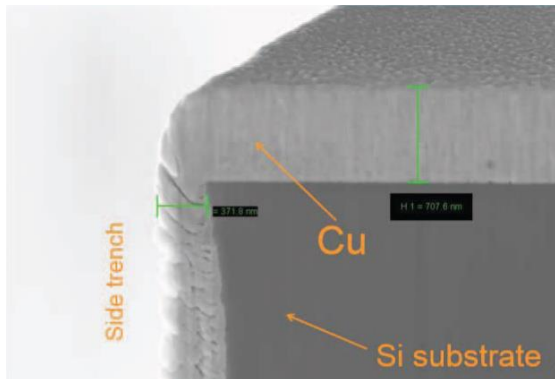
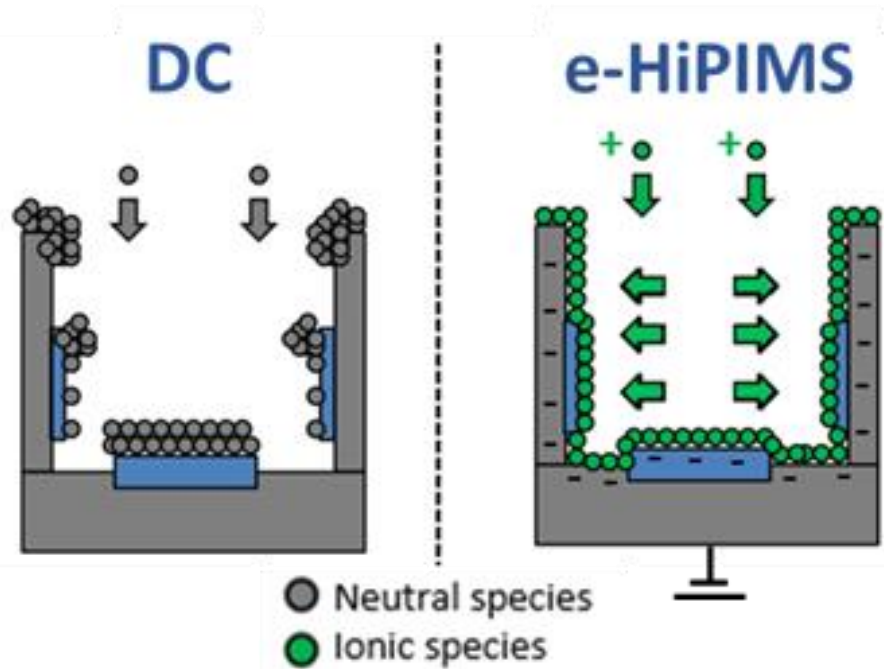
Mean power in HiPIMS similar to DC $\approx 500 \text{ W}$
 \Rightarrow **Limited heating** of the target



- Higher ionisation rate than DC sputtering
- Higher plasma density (10^{19} m^{-3})

High Power Impulse Sputtering (HiPIMS)

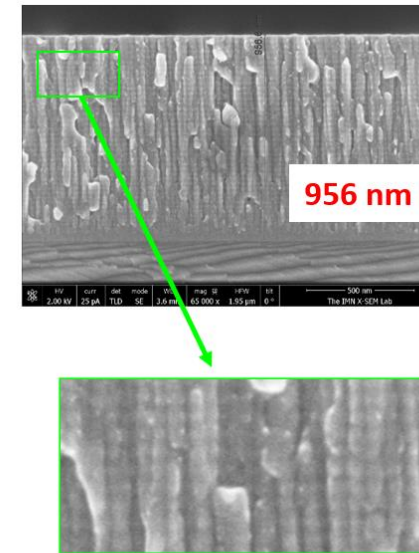
➤ Higher conformity



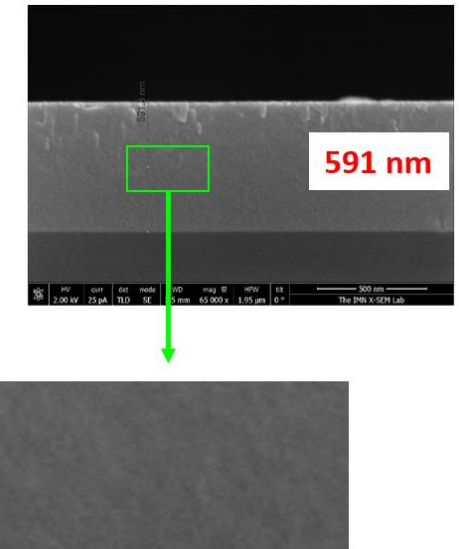
V. Bellido-Gonzalez, "HiPIMS in Full Face Erosion Circular Cathode for Semiconductor Applications"

➤ Denser films

Pulsed DC



HiPIMS



Reactive deposition of TiO₂ from Ti targets at RT onto PET web.

1 - Introduction

- Overview of deposition processes
- Examples of applications

2 - Sputtering

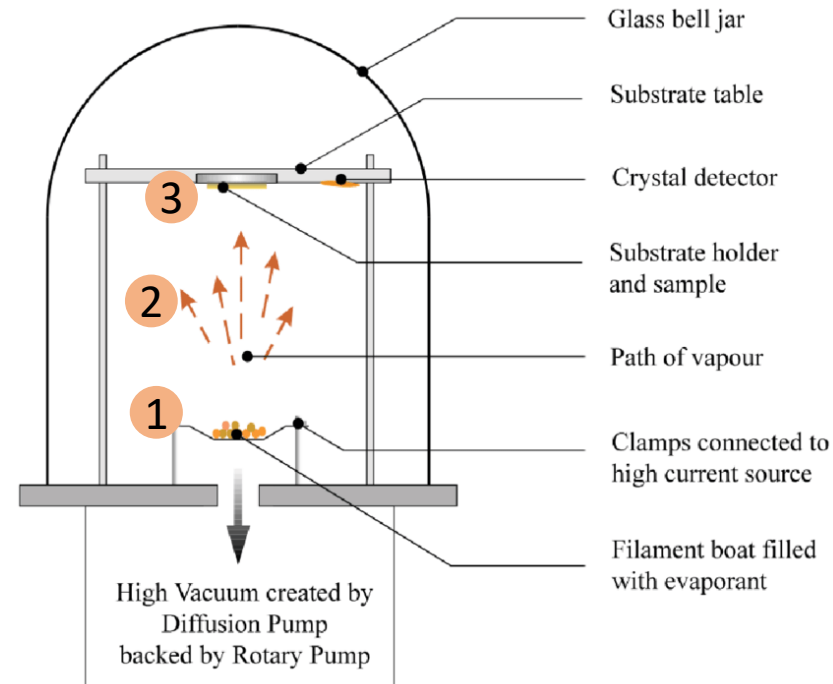
- Principle
- Collisions regimes
- Sputtering yield
- DC and RF systems
- Magnetron
- Hysteresis
- Sputtered films properties
- Systems

3- Thermal evaporation

- Principle
- Evaporation sources
- Vapor pressure, atoms flux, mass flux
- Vacuum conditions
- Thickness uniformity
- Thin film growth and microstructure

Vacuum evaporation principle

The material to deposit is heated in a vacuum chamber. The stream of evaporated species emitted by the material condense on the substrate.

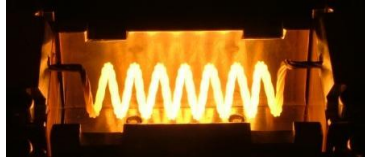


Three steps:

1. Phase change at the evaporation source:
solid \rightarrow liquid (fusion) and then liquid \rightarrow gas (**evaporation**)
or solid \rightarrow gas (**sublimation**)
2. Transport of evaporated species from the evaporation source to the substrate
3. Condensation of vapor on the substrate – **formation of the thin film**

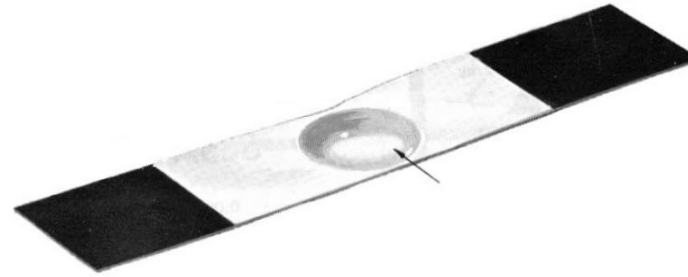
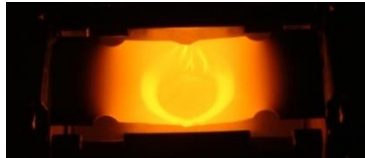
Joule effect

Filament



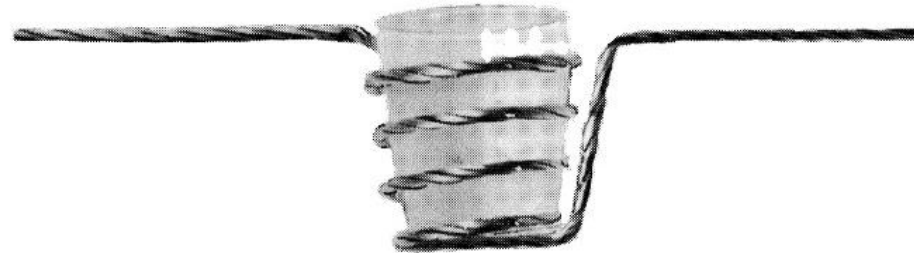
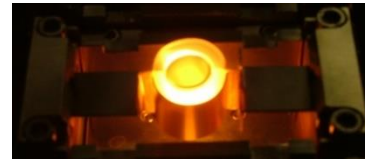
- ⇒ Low loading (lab only)
- ⇒ 50-100 A to 6-20 V

Metallic crucible



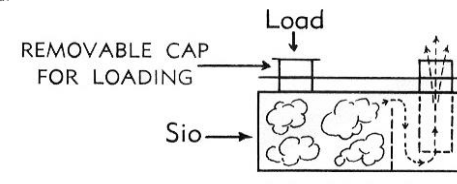
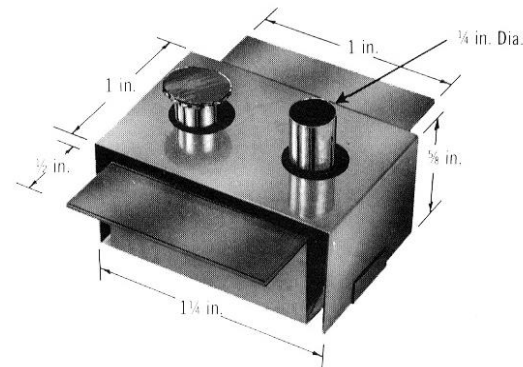
- ⇒ Larger loading but needs higher power
- ⇒ 300-400 A

Ceramic crucible + filament



- ⇒ Avoid reactions between crucible and material to evaporate
- ⇒ Low yield

Sublimation source SiO

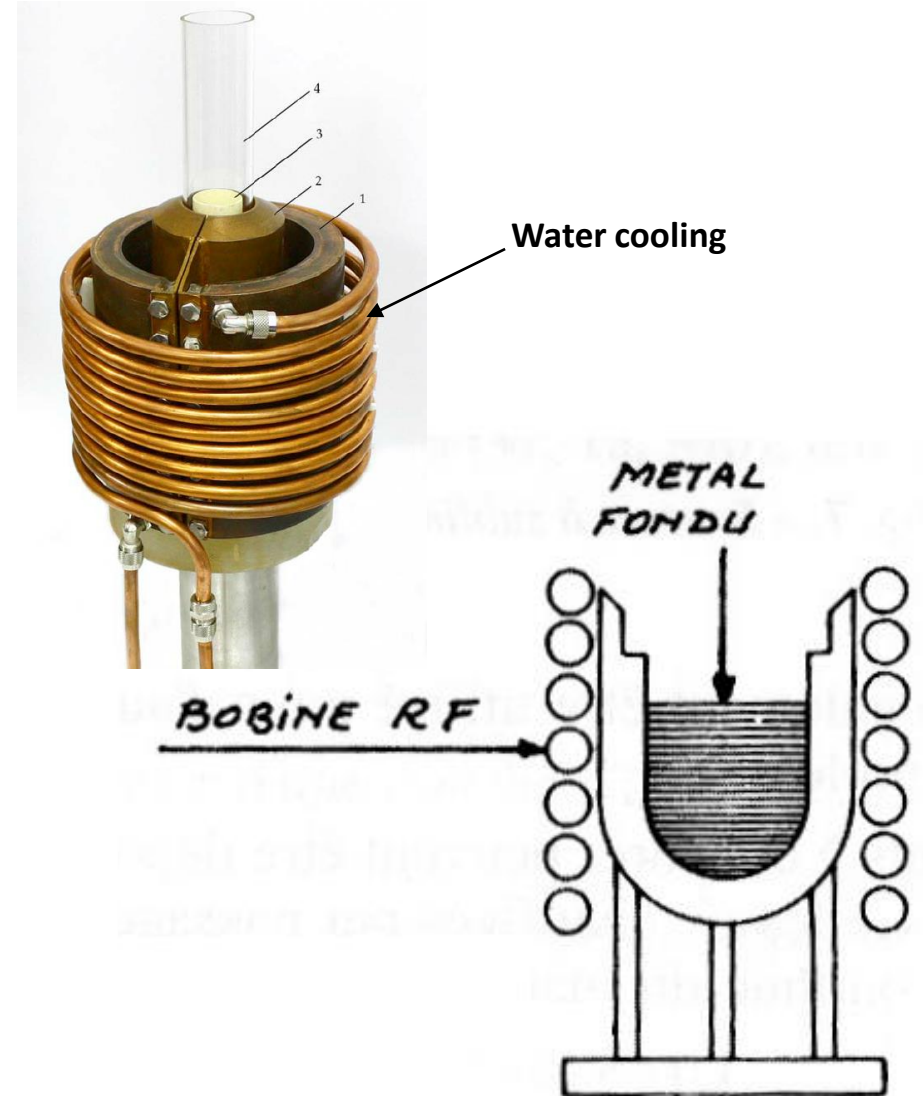


- ⇒ Avoid particle deposits and allows to obtain better quality films for some materials (e.g. SiO)

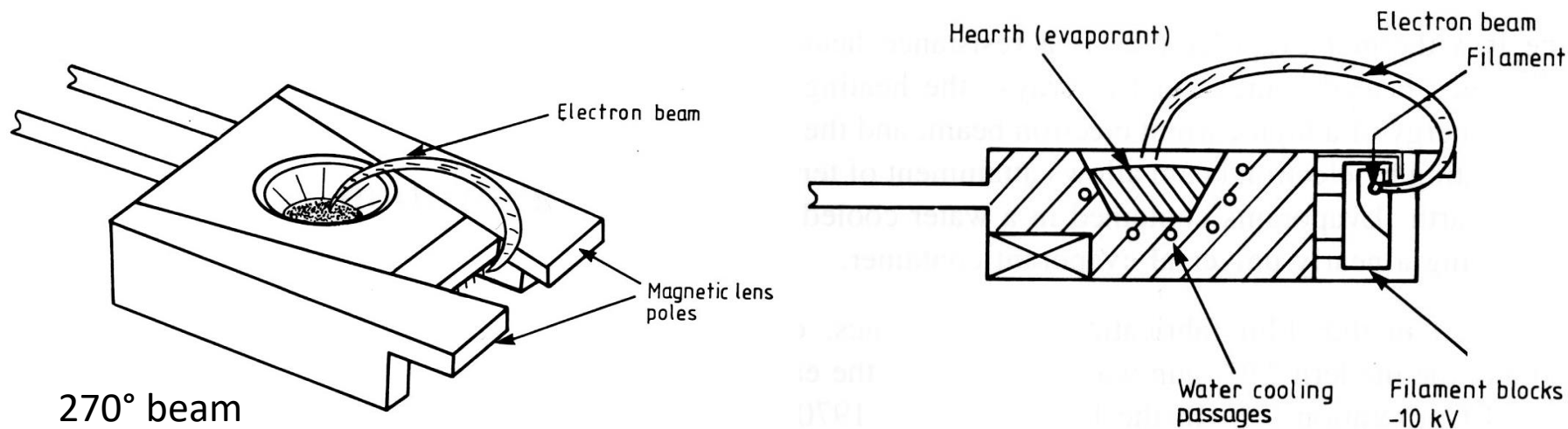
- The material is heated by high-frequency induced currents (skin effect).
- The material to be evaporated **must be electrically conductive**.
- The crucible is made of electrical insulating material: alumina, beryllium oxide, boron nitride... surrounded by a coil traversed by an HF current and cooled by a circulation of water.

Advantages: robustness, **well-suited to high-throughput industrial processes**, possibility of refilling the crucible

Disadvantages: cost, suitable for conductive materials only (metals)

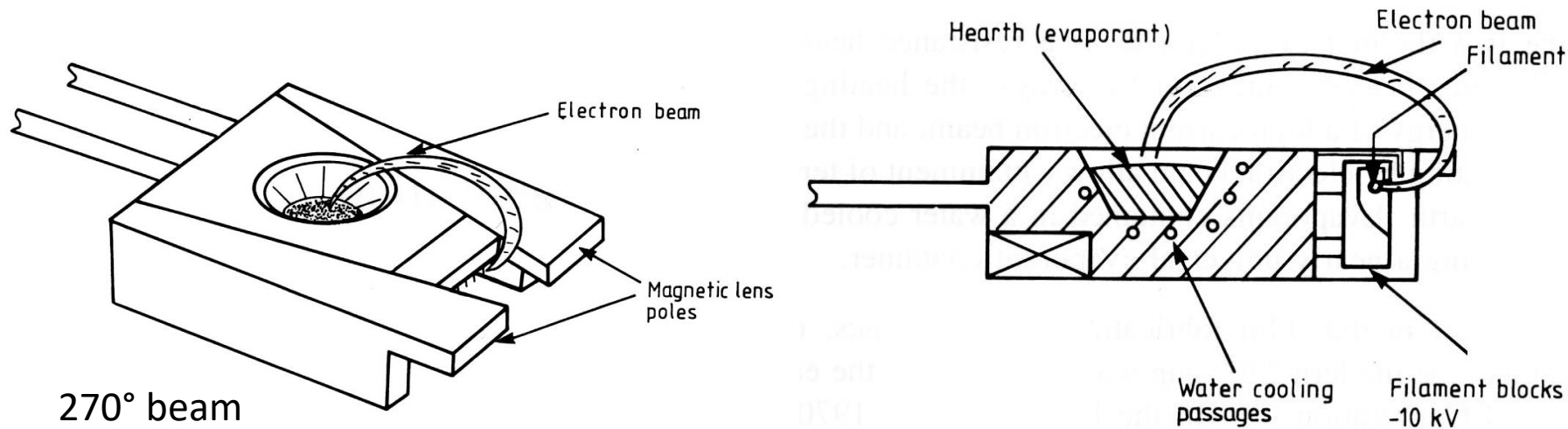


Electron beam



- The **electrons are emitted by thermoelectronic effect** from a tungsten filament heated to 2800 °C.
- They are **accelerated by an electric field and deflected by a magnetic field** towards the material to be evaporated which is placed in a copper crucible cooled by a circulation of water.
- The **material to be evaporated heats up and evaporates at the point of impact of the electron beam**.
- It is possible to carry out a beam scan on the surface of the material to distribute the evaporation.

Electron beam



Advantages: very high evaporation rates ($> 1 \mu\text{m}/\text{min}$), no reaction with the crucible (cold), suited to many materials (refractory metals, insulators), rechargeable crucible, possibility of co-evaporation, easy control of the power and therefore the deposition rate, no contamination due to heating of the crucible.

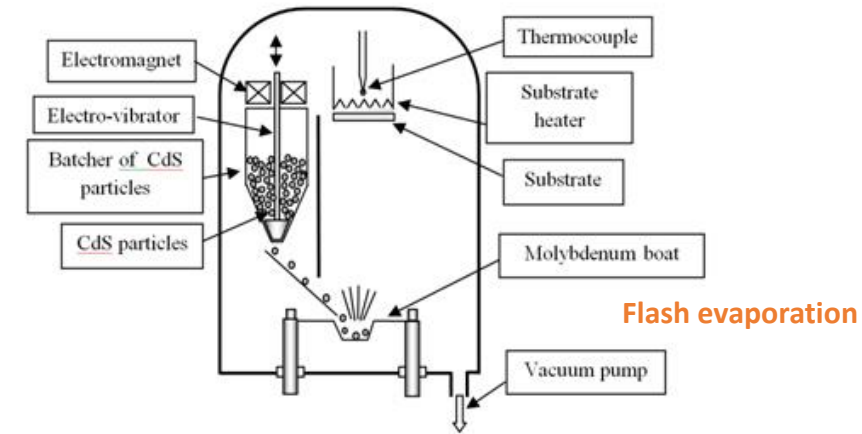
Disadvantages: complexity, cost, fragility of the filament.

Alloys evaporation

Different vapour pressures for the elements of an alloy => **different mass evaporation rates** => **composition of the layer is different from the source material** => flash evaporation or coevaporation can then be carried out.

Flash evaporation

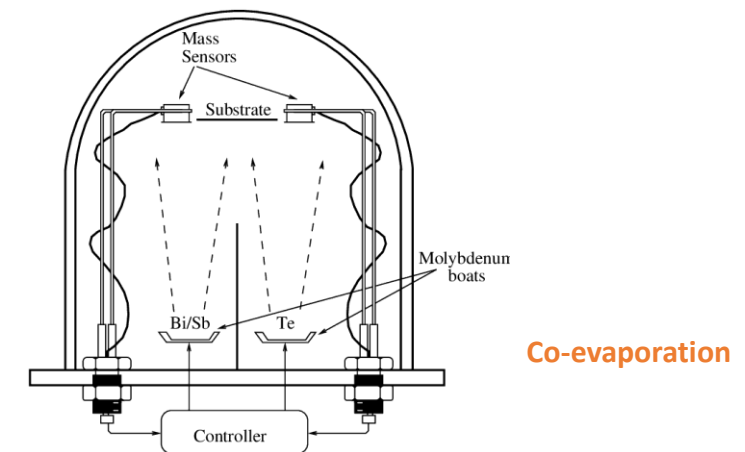
The material to be evaporated is sent continuously in the form of powder
Examples : binary semiconductors AsGa, PbTe, InSb...



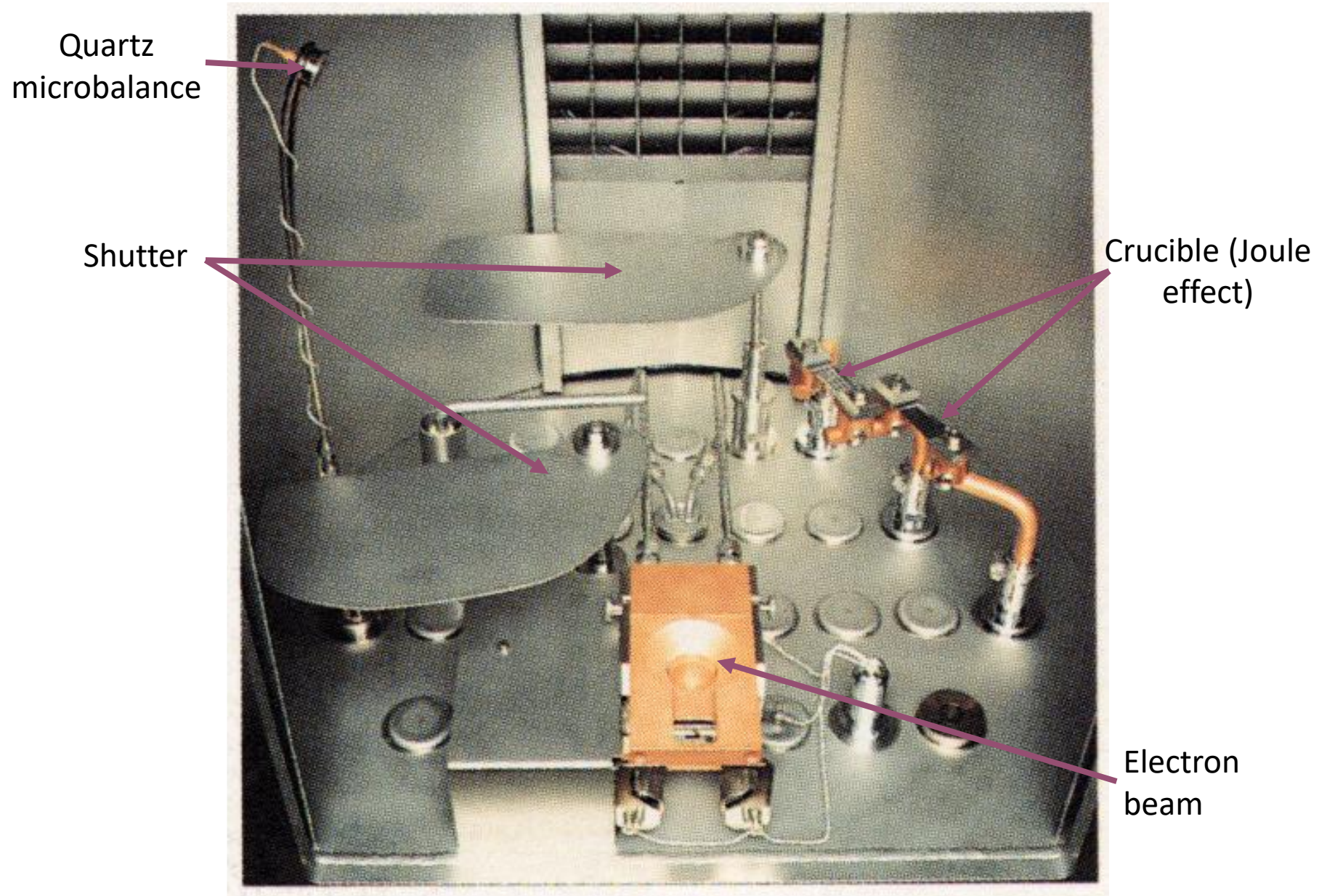
Co-evaporation

As many sources are used as there are elements in the alloy. The deposition rates of each of the evaporation sources can be adjusted to obtain the desired composition.

Example: CIGS solar cells



Evaporation system



Vapor pressure P_v

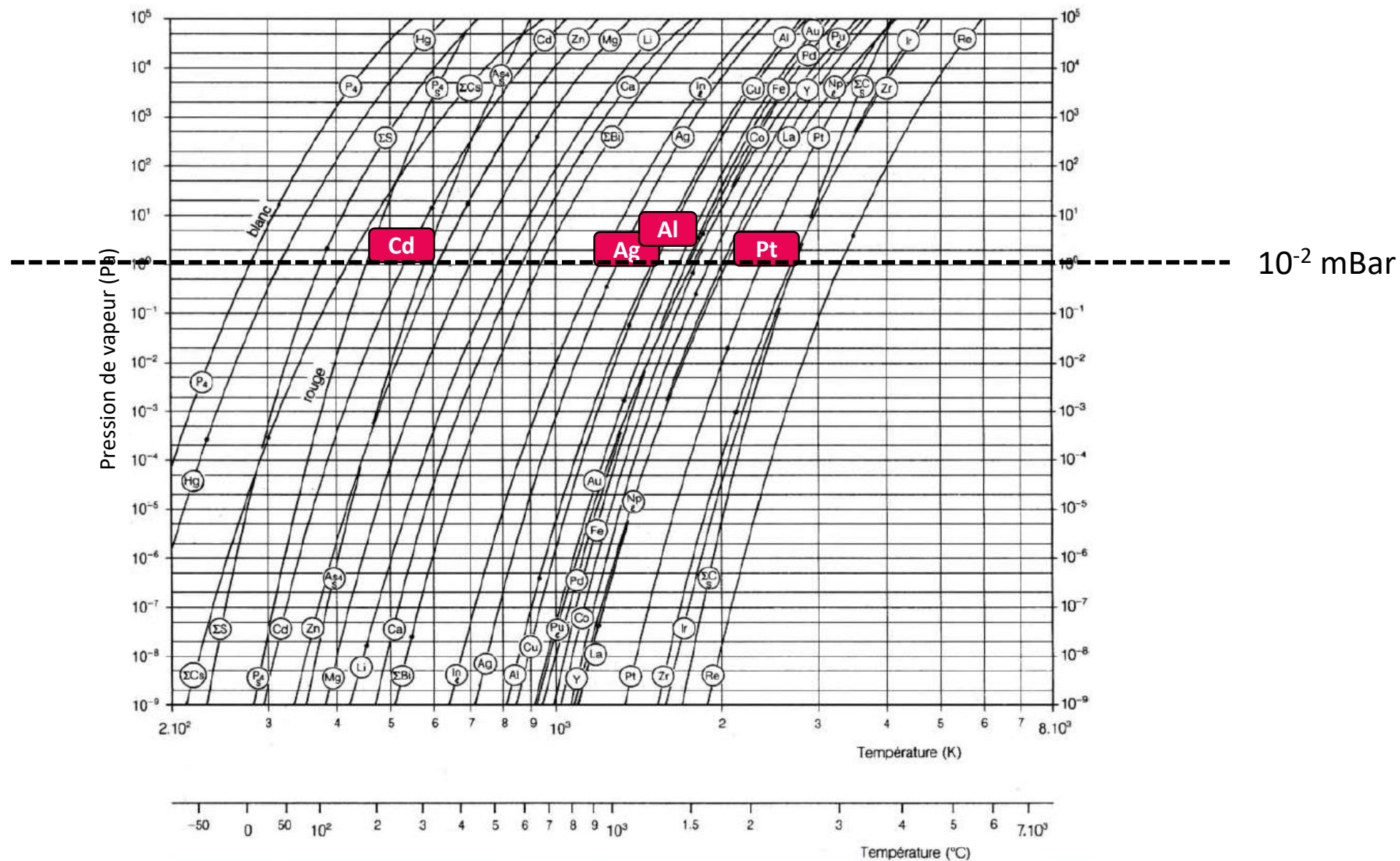
P_v : vapor pressure in equilibrium with the solid or liquid phase. This pressure determines the flux of gas emitted by the material to be evaporated at a given temperature.

The vapor pressure depends on the temperature, its variation is given by the Clapeyron relation:

$$\text{Log}(P_v) = A - \frac{H}{RT}$$

A	constant (characteristic of the material)
H	vaporisation heat (J)
R	ideal gas constant, $R = 8,31 \text{ J/K}$
T	absolute temperature of the material (K)

Vapor pressure of materials



Vapour pressures of at least 10^{-2} mbar must be achieved to obtain significant evaporation mass rates.

Element	Al	Ag	Au	Sn	W*	Ta*	Mo*	C*
Température (°C) $P_v = 10^{-2}$ Torr $= 1,33 \cdot 10^{-2}$ mbar	1150	1047	1460	1250	3230	3060	2350	2460



These materials are not easily evaporable => used as crucibles

Evaporated flux Φ_e and deposited flux Φ_d

Number of atoms emitted by the evaporation source per unit of time and area ($\text{m}^{-2}.\text{s}^{-1}$).

Φ_e depends directly on the vapor pressure of the material to be deposited at crucible temperature.

$$\Phi_e = \frac{P_v}{\sqrt{2\pi m k T}}$$

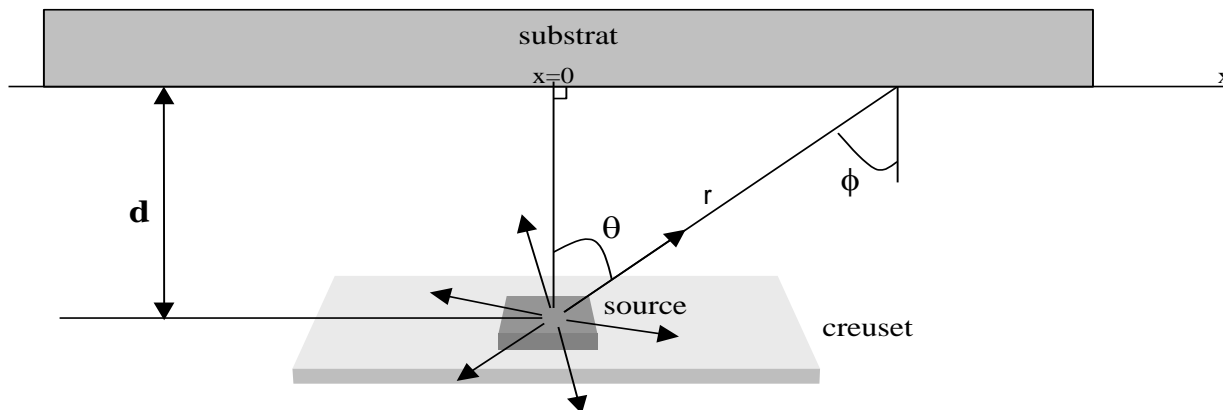
Φ_e : evaporated flux

P_v : vapor pressure (Pa)

m : particle mass (kg)

k : Boltzmann constant, $k = 1,38.10^{-23} \text{ J.K}^{-1}$

T : absolute temperature (K)



Deposited Φ_d flux can be calculated from evaporated flux Φ_e :

$$\Phi_d = \frac{s\Phi_e}{\pi r^2} \cos(\theta) \cos(\phi)$$

Mass flow at the substrate Γ_d

Deposited mass at the substrate per unit area and unit time:

$$\Gamma_d = m. \Phi_d$$

Γ_d depends on:

- the flux emitted by the evaporation source
- the size and geometry of the source
- the position and orientation of the substrate relative to the source

Growth rate:

$$v_d = \alpha \frac{\Gamma_d}{\rho_{cm}}$$

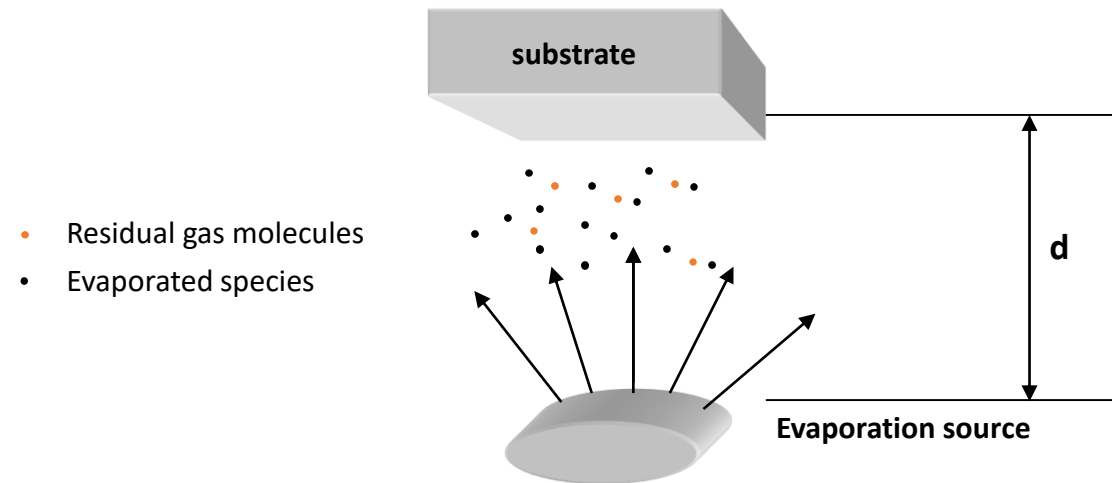
α

Sticking coefficient

ρ_{cm}

density of the thin film material (< than bulk)

Condition 1 \Rightarrow Mean free path $\lambda \gg$ source – substrate distance d



If this condition is fulfilled, the atoms move in a straight line from the source to the substrate

\Rightarrow No collisions with residual gas molecules and limited contamination (oxydation)

Mean free path: $\lambda = \frac{1}{\sqrt{2}n\pi D^2} = \frac{kT}{\sqrt{2}P\pi D^2} \Rightarrow \lambda \propto \frac{T}{P_{gr}}$ P_{gr} : Residual gas pressure

If we choose $\Rightarrow \lambda > 100d$

$$\Rightarrow \frac{kT}{\sqrt{2}P_{gr}\pi D^2} > 100d$$

$$\Rightarrow P_{gr} < \frac{kT}{\sqrt{2} * 100d\pi D^2}$$

For atoms diameter $D = 0,3 \text{ nm}$ at 300 K and $d = 10 \text{ cm}$

➤ $P_{gr} < 10^{-3} \text{ Pa} = 10^{-5} \text{ mbar} \Rightarrow$ **Secondary vacuum needed**

Vacuum conditions

Condition 2 : To reduce impurities, the flux Φ_{gr} of residual gas molecules must be much lower than the flux Φ_d of the evaporated species arriving at the surface of the substrate during deposition:

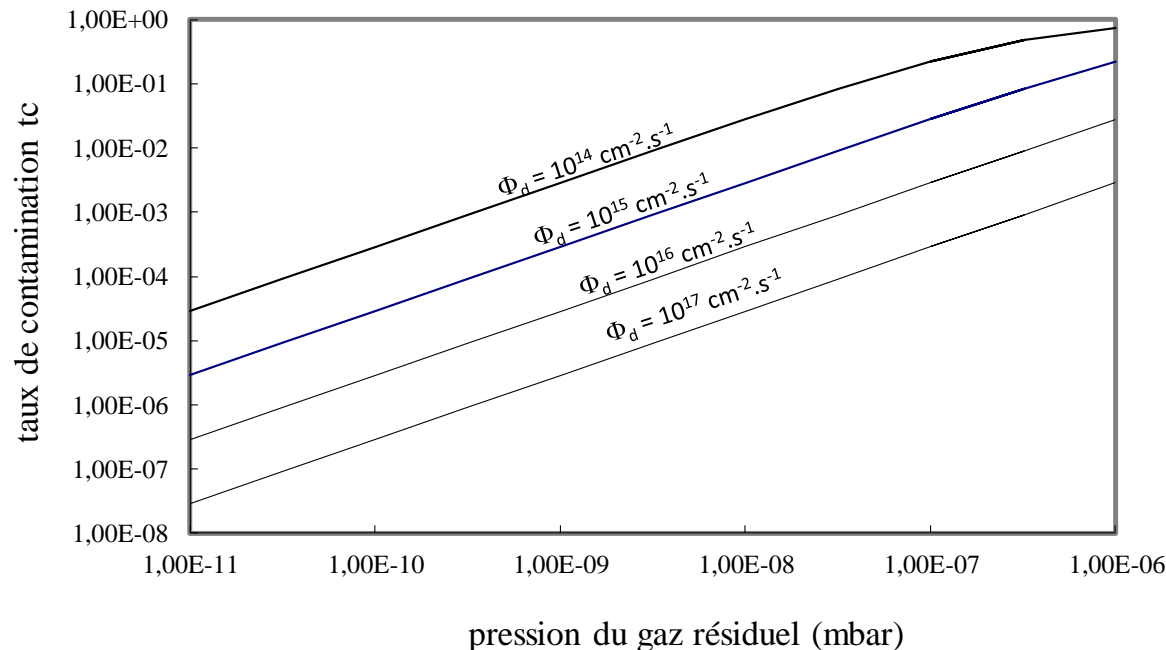
$$\Phi_{gr} \ll \Phi_d$$

Contamination coefficient t_c :

$$t_c = \frac{\Phi_{gr}}{\Phi_{gr} + \Phi_d}$$

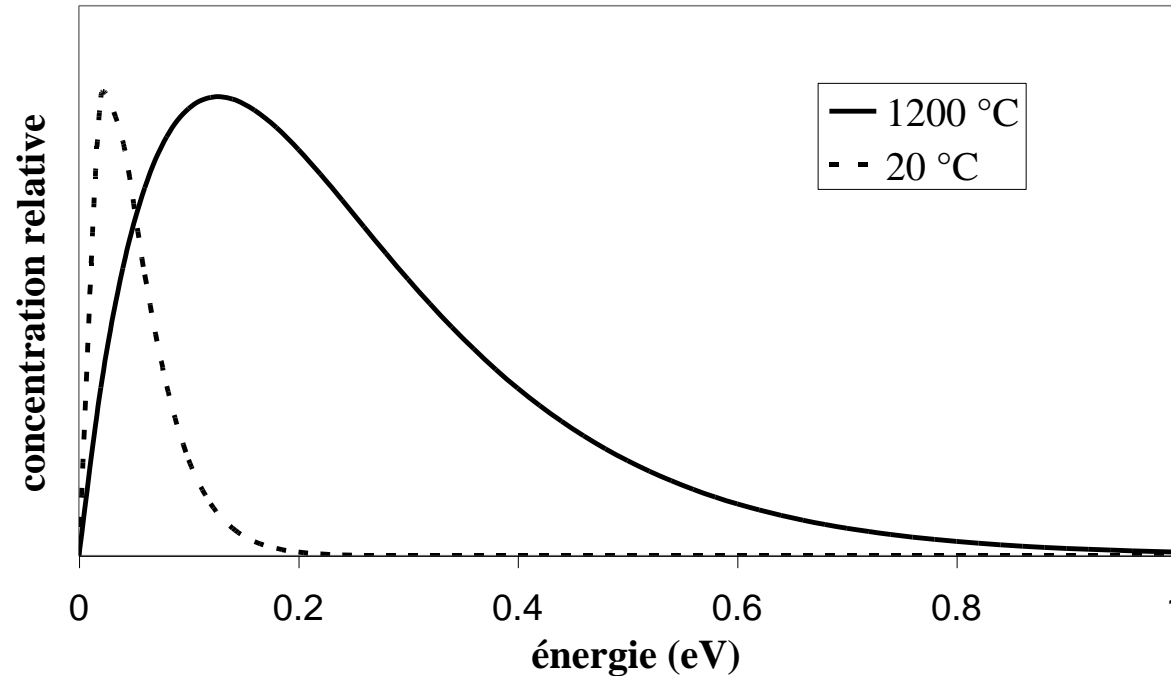
flux Φ_{gr} depends on residual gas pressure P_{gr} in the reactor:

$$\Phi_{gr} = \frac{P_{gr}}{\sqrt{2\pi mkT}}$$



Obtaining very low contamination rates imposes very **high vacuum or even ultra-high vacuum conditions**.

Maxwell distribution:



The average kinetic energy of these species corresponds to the thermal energy supplied by the evaporation source:

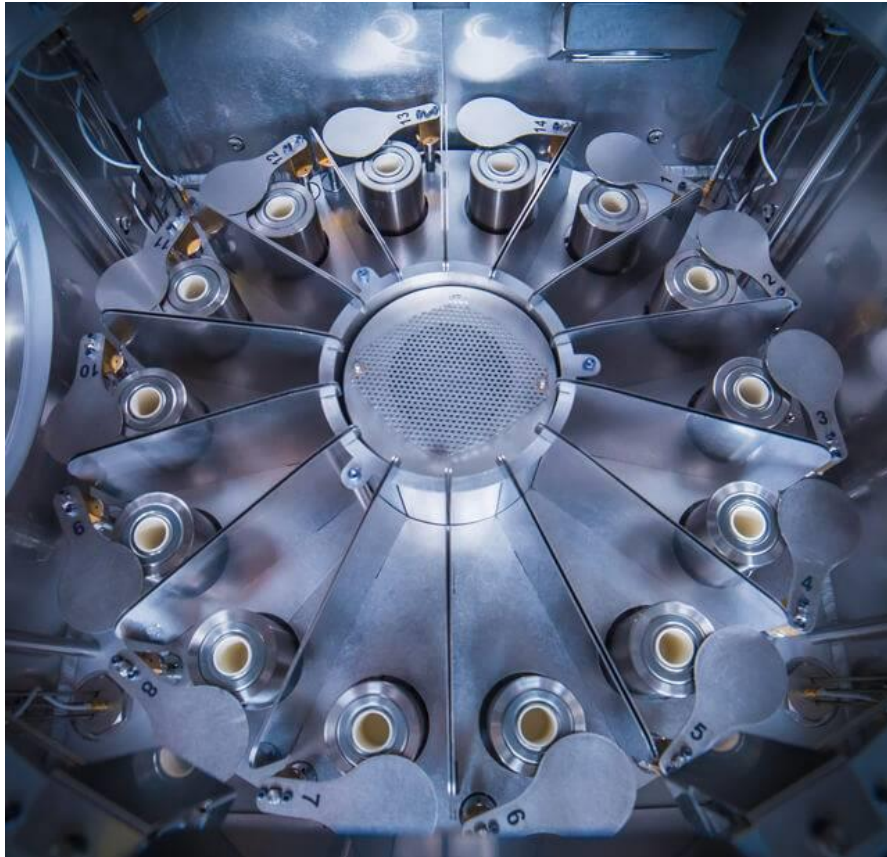
$$E_c = \frac{3}{2} kT$$

Example: $T = 1200\text{ °C} = 1473\text{ K} \Rightarrow E_c = 0,16\text{ eV}$

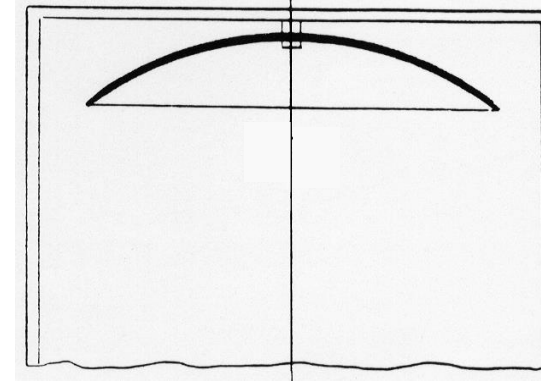
The kinetic energy of the evaporated species is of the order of **a few tenths of eV** (low compared to sputtering)

Thickness uniformity

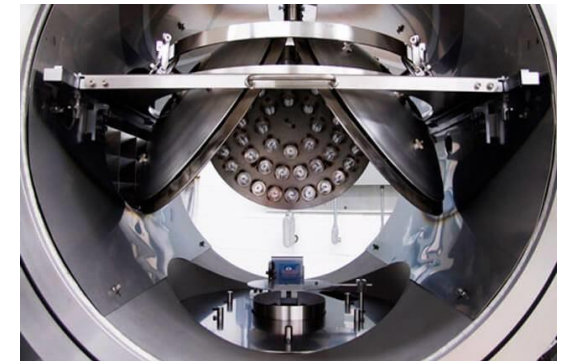
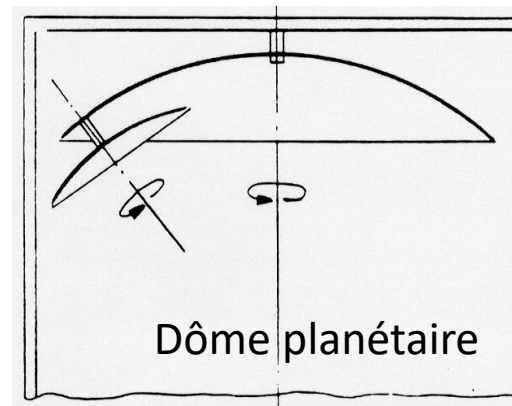
→ Increase the number of sources or increase the surface of sources



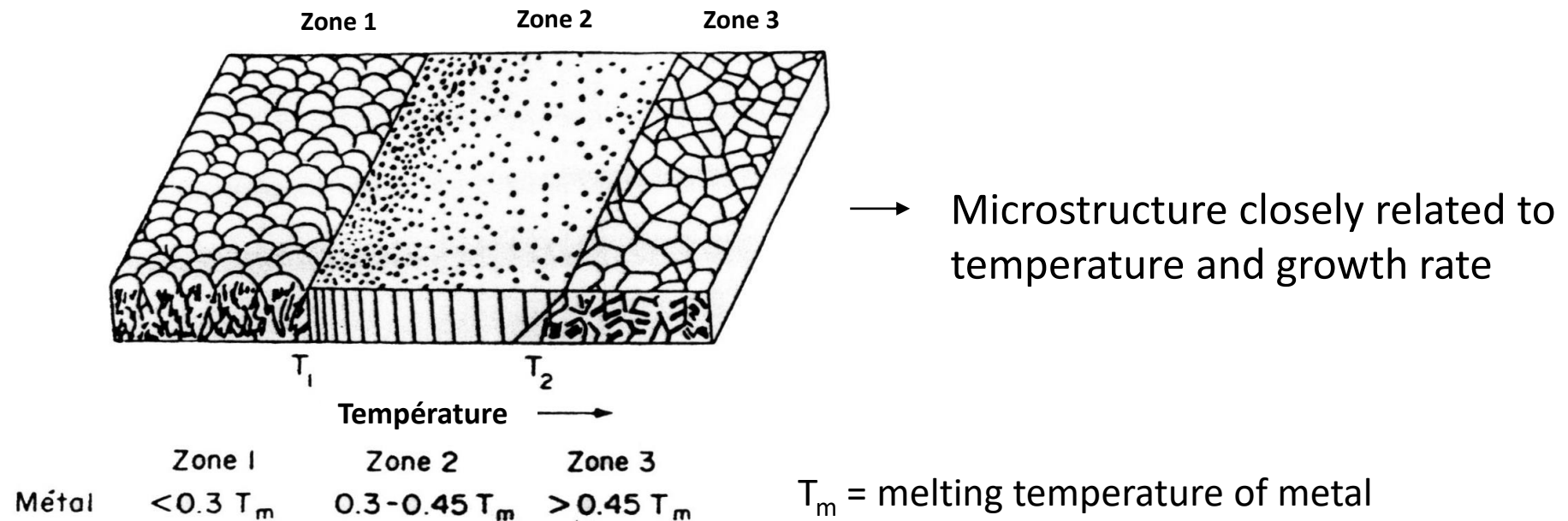
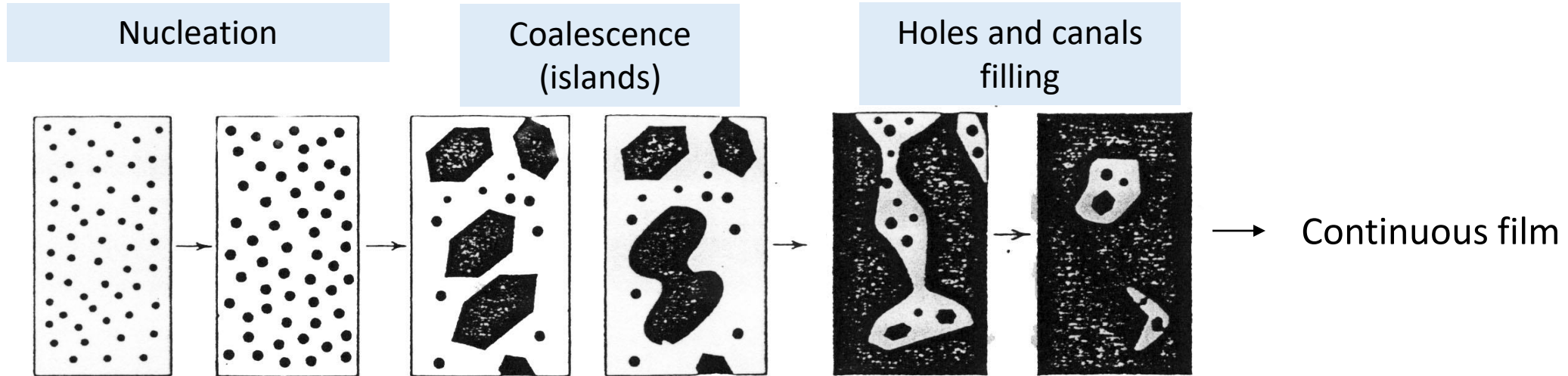
→ Substrate holder shape



→ Substrate holder mouvement



Thin film microstructure



A bright, circular light source, possibly a lamp or a spotlight, casting a strong glow against a dark background. The light is a warm, yellowish-white color, and the surrounding area is dark, creating a high-contrast effect. The light source is centered in the frame, and the glow is most intense in the center, fading out towards the edges.

Merci de votre attention