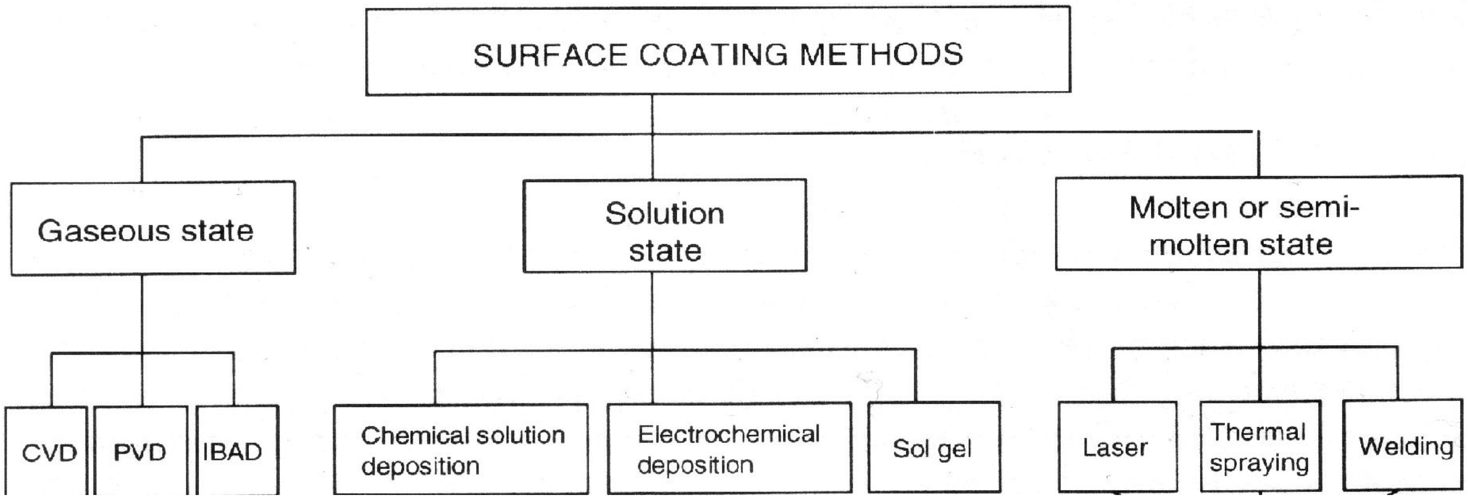
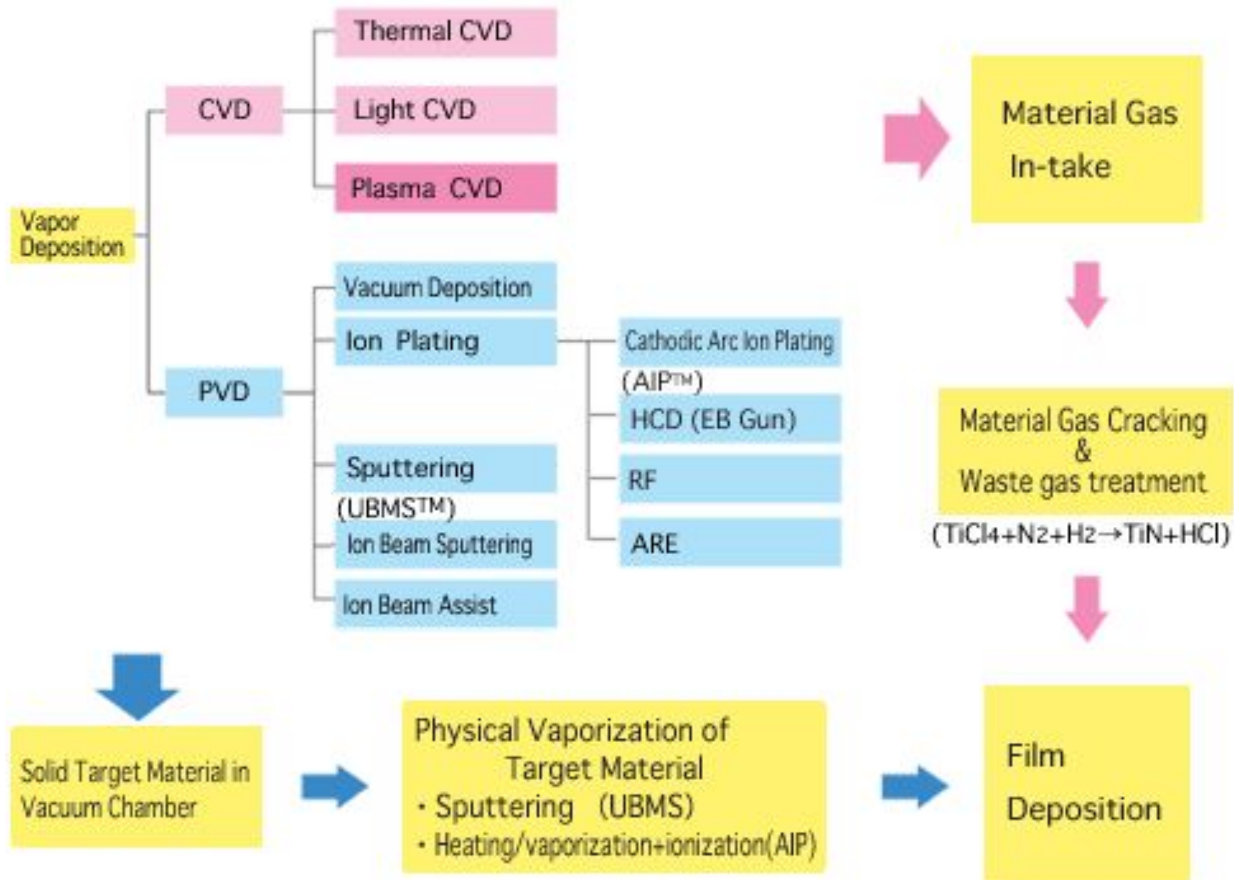
Deposition
(PVD and CVD)

Deposition methods classification[2]



Deposition methods
- PVD (Physical Vapour Deposition)
- CVD (Chemical Vapour Deposition)

PVD and CVD methods[3]



Factors that distinguish PVD from CVD:

1. Reliance on solid or molten sources, as opposed to generally gaseous precursors in CVD
2. The physical mechanisms (evaporation or collision impact) by which source atoms enter the gas phase
3. A reduced pressure environment through which the gaseous species are transported
4. The general absence of chemical reactions in the gas phase and at the substrate surface (reactive PVD processes are exceptions)

CVD – Chemical Vapor Deposition

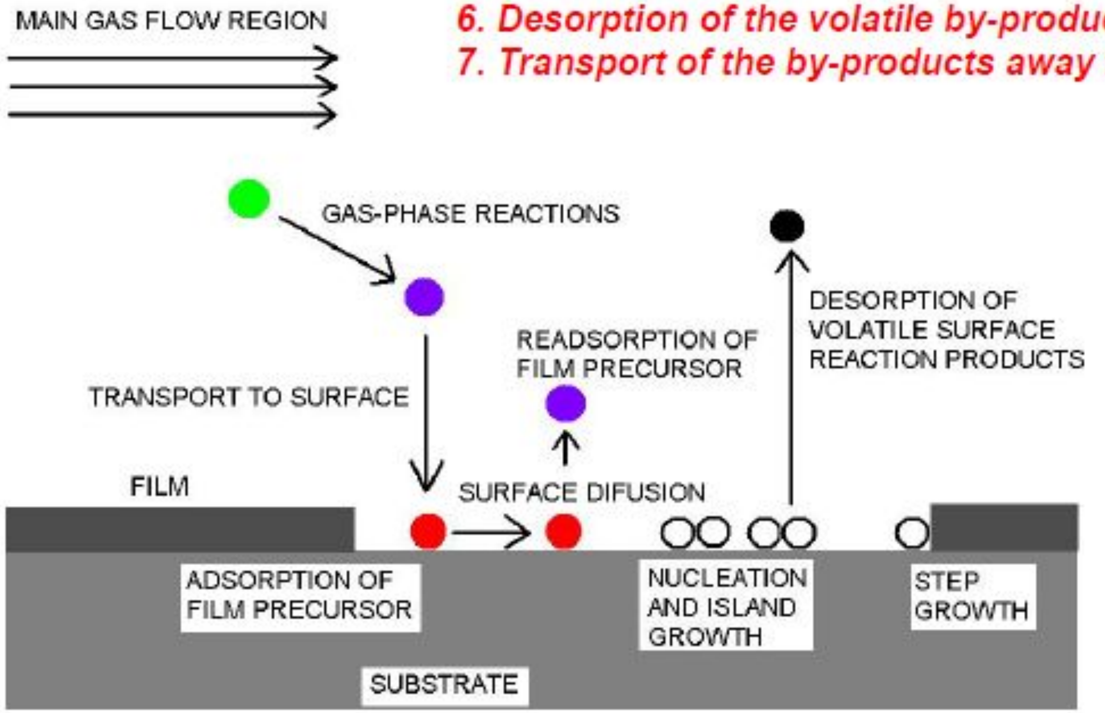
CVD is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomically on a suitable placed substrate.
Thermal CVD – heat energy for activation of the required gas and gas-solid phase reactions.
Plasma-enhanced CVD – plasma activation of the chemical species

1. APCVD – atmospheric pressure CVD
2. LPCVD – low pressure CVD
3. MOCVD – metalorganic CVD
4. LECVD – laser-enhanced CVD
5. PECVD (PACVD) – plasma-enhanced (assisted) CVD

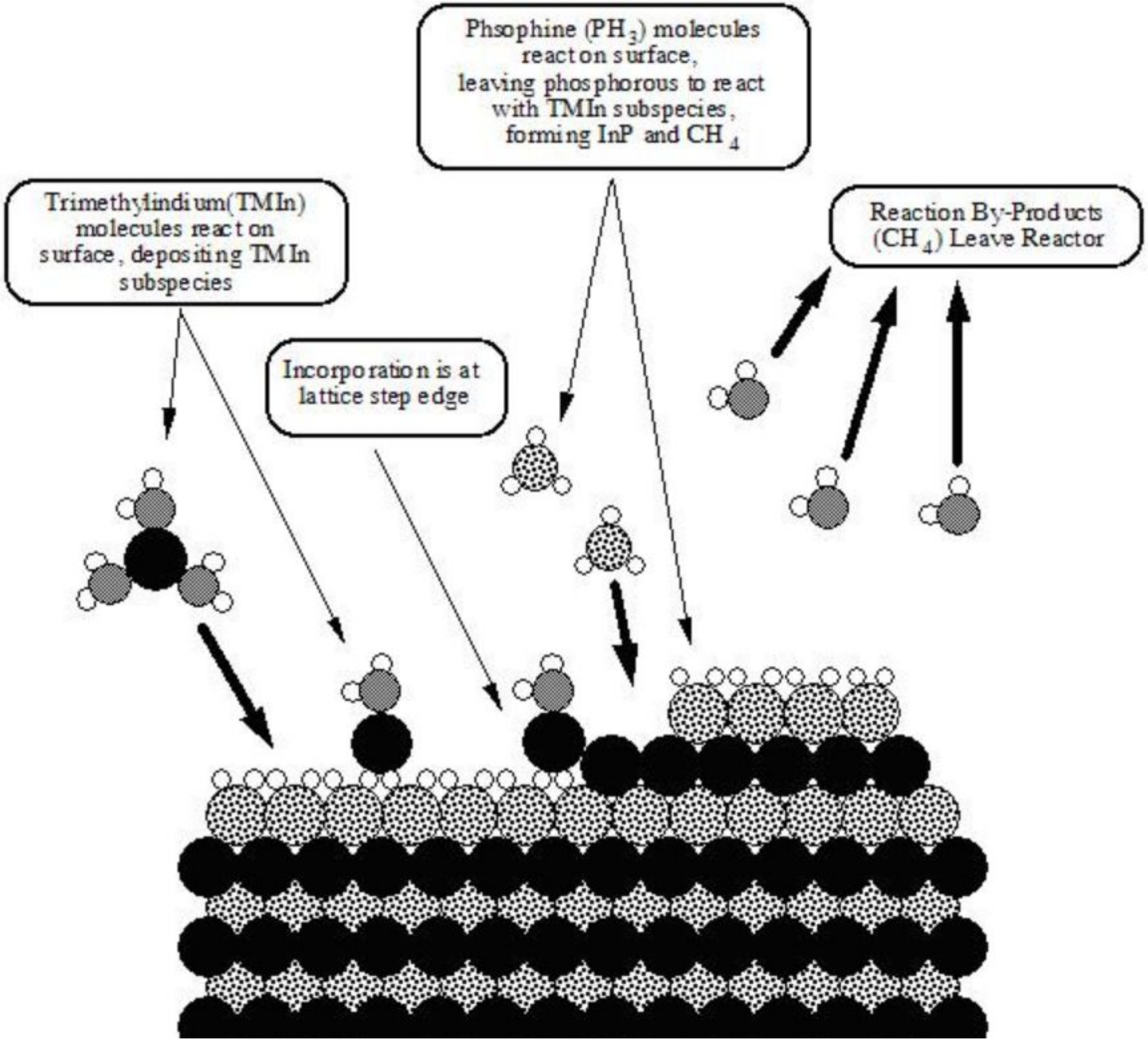
CVD – Chemical Vapor Deposition

The fundamental sequential steps of CVD process:

1. *Transport of reactants to the reaction zone.*
2. *Chemical reactions in the gas phase.*
3. *Transport of reactants and their products to the substrate.*
4. *Adsorption and diffusion on the substrate surface.*
5. *Heterogeneous reactions catalyzed by the surface leading to film formation.*
6. *Desorption of the volatile by-products of surface reactions.*
7. *Transport of the by-products away from the reaction zone.*



Metalorganic CVD



Plasma Enhanced CVD (PECVD)

PECVD – plasma-enhanced CVD:

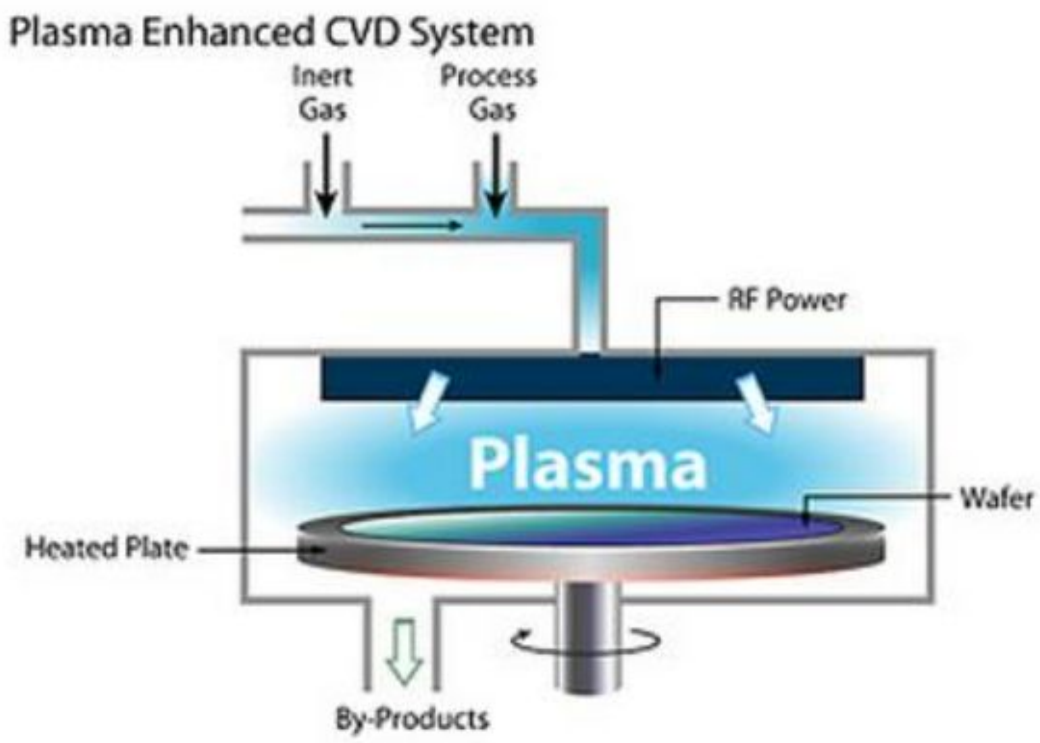
– glow-discharge plasmas (usually RF field: 100 kHz – 40 MHz), or MW – 2.54 GHz plazma at reduced gas pressure between 50 mtorr and 5 torr) are sustained within chambers where simultaneous vapor-phase chemical reactions and film depositions occur

– plasma activation of reactions (average electron energies range from 1 to 10 eV) ! chemical reactions occur at much lower temperatures than in thermal CVD

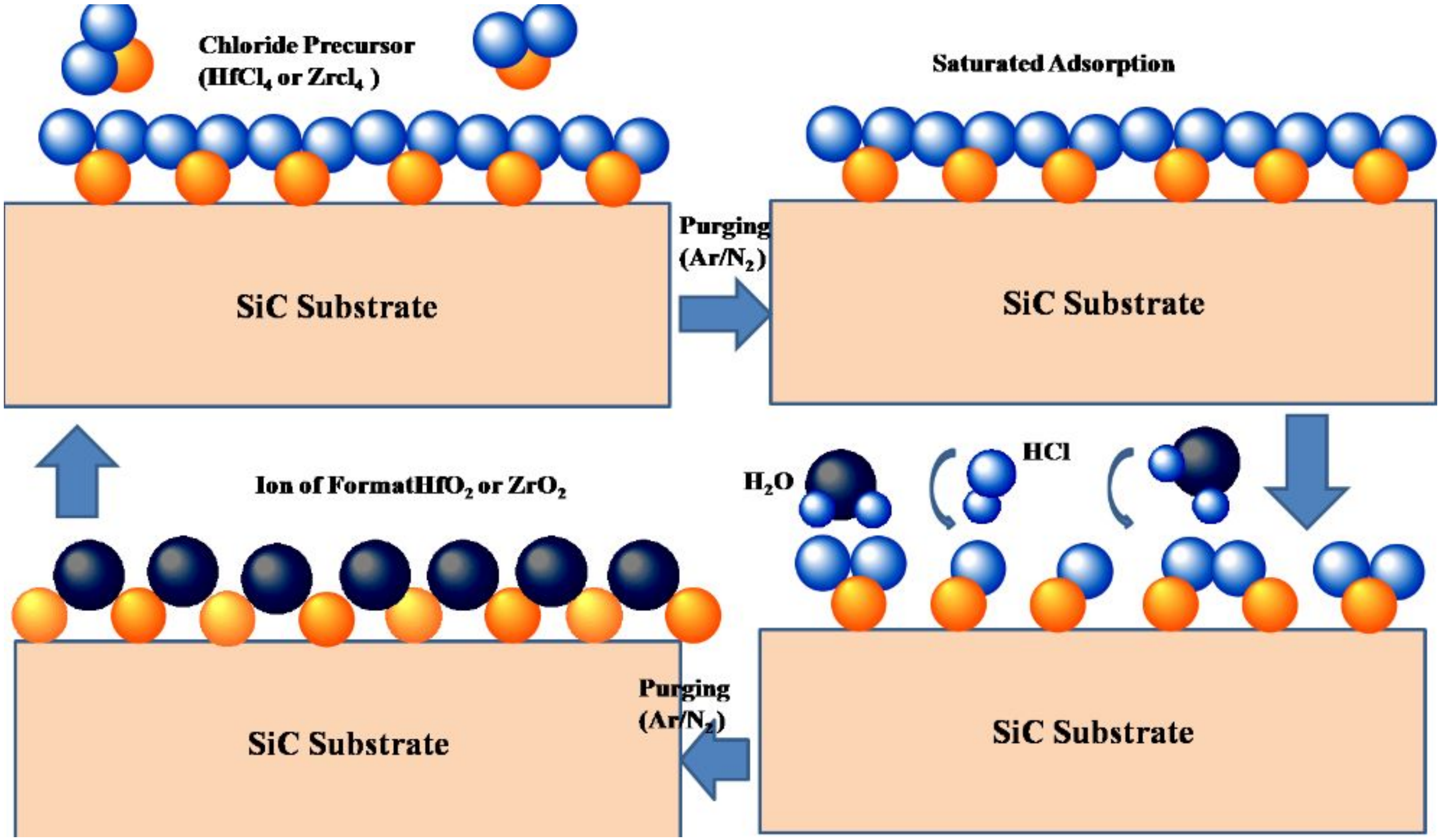
Main applications of PECVD:

- **microelectronics (DRAM cells)**
- **plasma modification of metal surfaces (nitriding, carburizing):**
  the atoms of nitrogen and carbon that deposit on metal surfaces modify them by diffusing into the underlying matrix
- **diamond films**

Plasma Enhanced CVD (PECVD)



Atomic Layer deposition (CVD like)



Atomic scale deposition. ALD is similar in chemistry to CVD, except that the ALD reaction breaks the CVD reaction into two half- reactions, keeping the precursor materials separate during the reaction.

CVD – Chemical Vapor Deposition

advantages	disadvantages	applications
• high wear resistance • do not require vacuum or unusual levels of electric power • do not need rotation of the substrates • widely varying stoichiometry of films • affordable cost of the equipment and operating expenses – economical production of thicker coatings • selective deposition of films • also suitable for bore holes, slots etc.	• safety: reactant or product gases are typically toxic, flammable, pyrophoric, or corrosive substances – ecologically problematic • edges become rounded (coating thickness) • high processing temperature • coatings with several metals (e.g. TiAlN) are not possible	• large array of film materials, for example: the fabrication of solid-state electronic devices, the manufacture of ball bearings, cutting tools, the production of rocket engine and nuclear reactor components

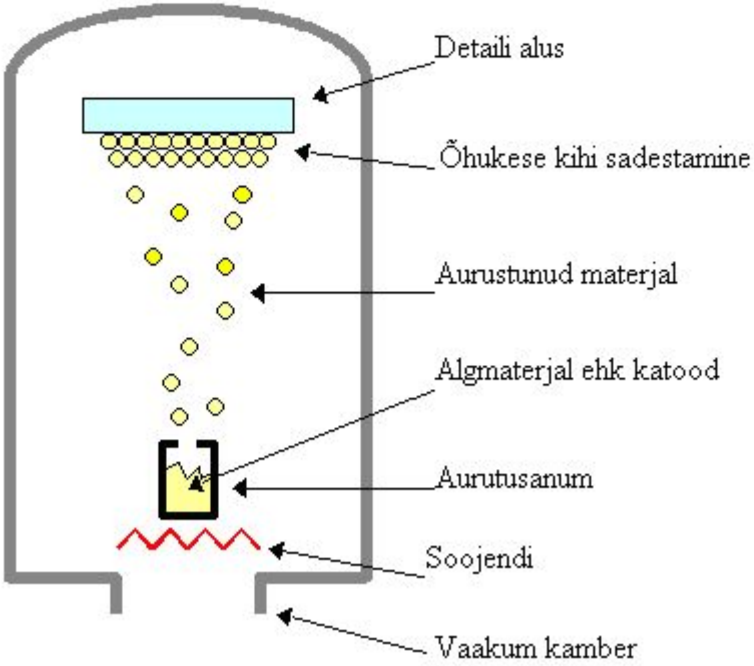
PVD – Physical Vapor Deposition
Evaporation

Evaporation: controllably transfer atoms from a heated source to a substrate located a distance away, where film formation and growth proceed atomistically.

Thermal energy is imparted to atoms in a liquid or solid source such that their temperature is raised to the point where they either efficiently evaporate or sublime.

- **Electrically heated evaporation sources (Thermal evaporation)**
- **Pulsed laser deposition**
- **Electron-beam evaporation**
- **Molecular beam epitaxy**
- **Ion beam assisted evaporation**
- **Discharge based deposition methods (sputtering, arc evaporation)**

Thermal evaporation (PVD)



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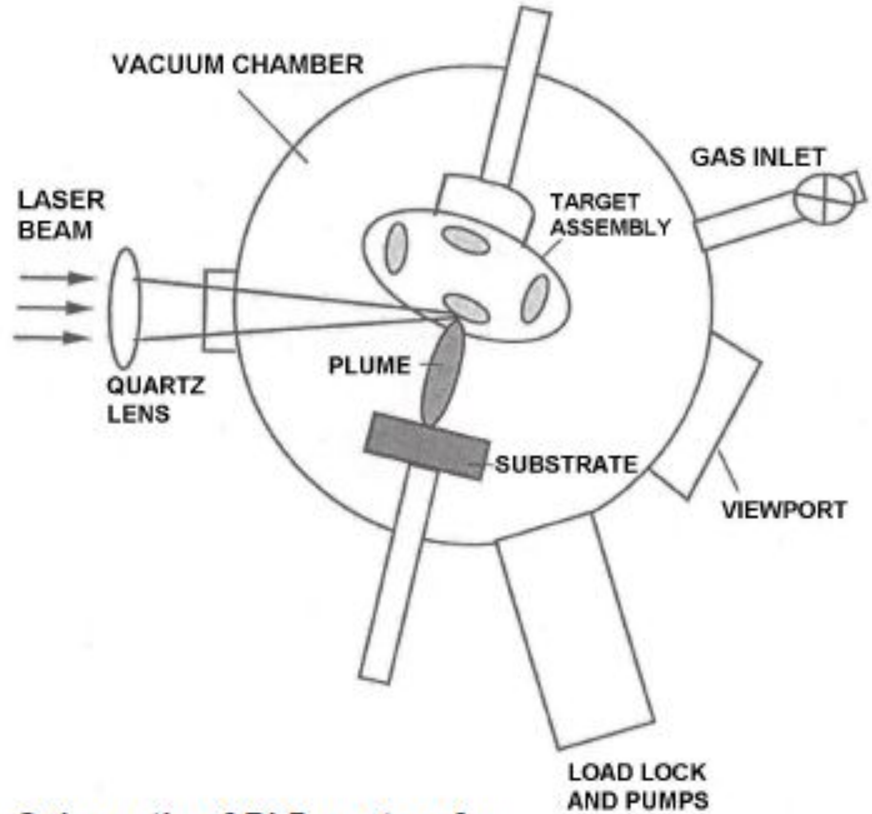
PVD – Physical Vapor Deposition
EVAPORATION

Pulsed laser deposition:

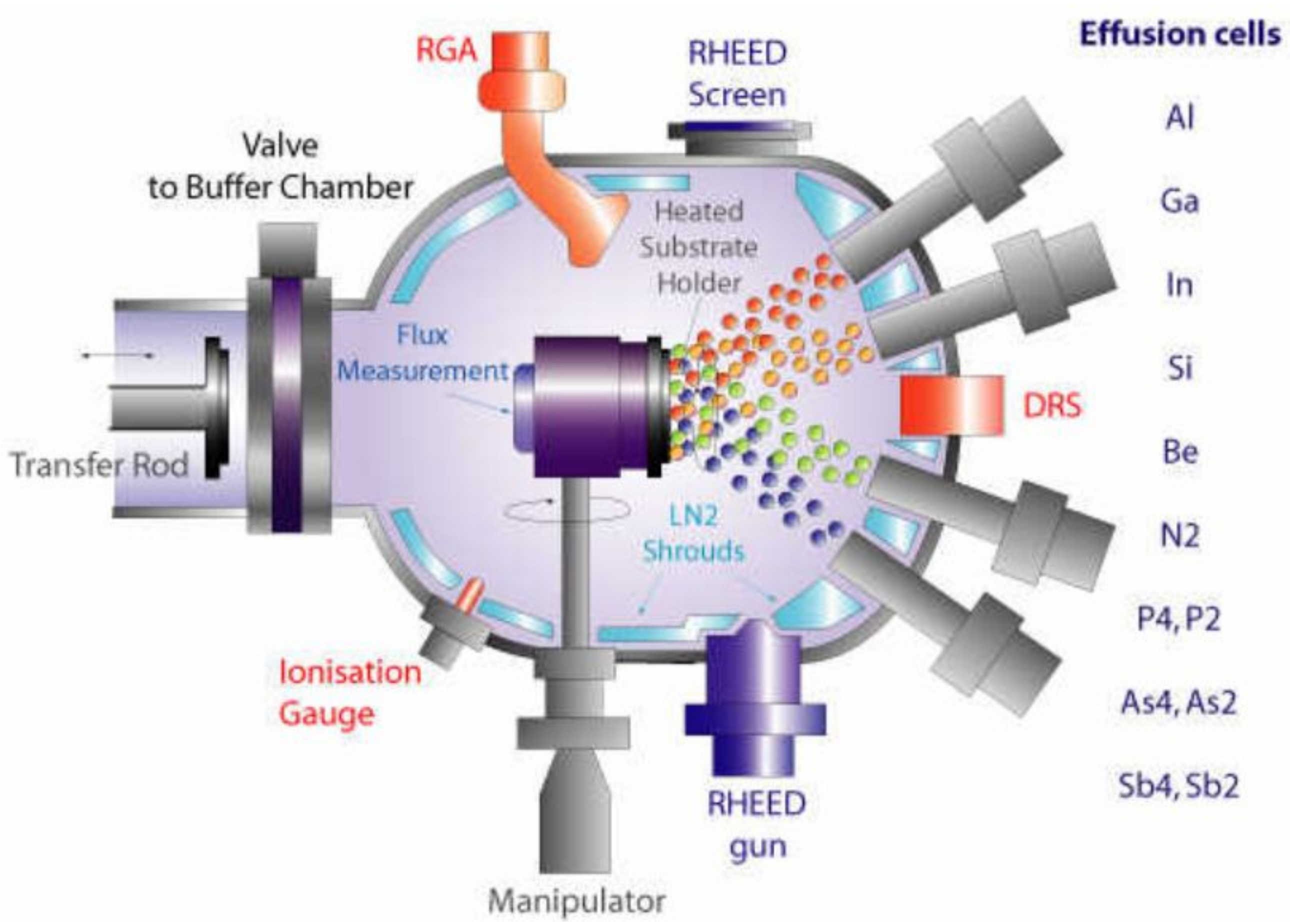
Problems:
- minimize the number of gross particulates ejected as a result of splashing from being incorporated into the depositing film
- highly directed plume – problem with uniform deposition of large substrate area

Unique feature of pulsed laser evaporation: deposition of stoichiometric ceramic films.



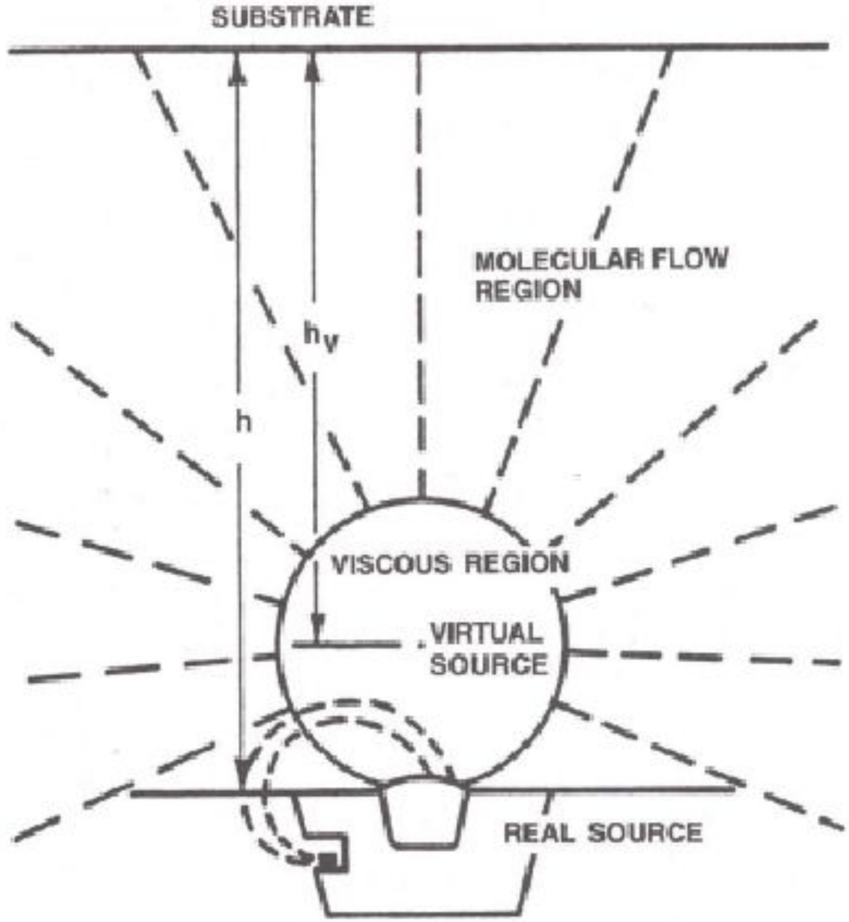
Schematic of PLD system for the deposition of metal oxide films.

Molecular beam epitaxy



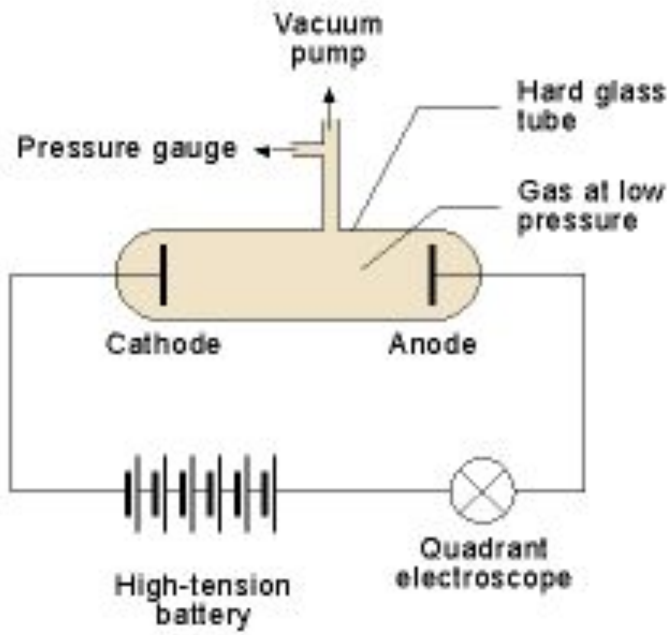
PVD – Physical Vapor Deposition
EVAPORATION

Electron-beam evaporation:



- *The evaporant charge is placed in either a water-cooled crucible or in the depression of a water-cooled copper hearth.*
- *Electrons are thermionically emitted from heated filaments and accelerated. A transverse magnetic field is applied to deflect the electron beam in a 270° circular arc and focus it on the evaporant.*
- *The vapor just above the hearth approximates a high-pressure viscous cloud of very hot evaporant.*
- *The effective (virtual) source plane is moved away from the melt surface toward the substrate.*

Discharge based deposition methods[5]

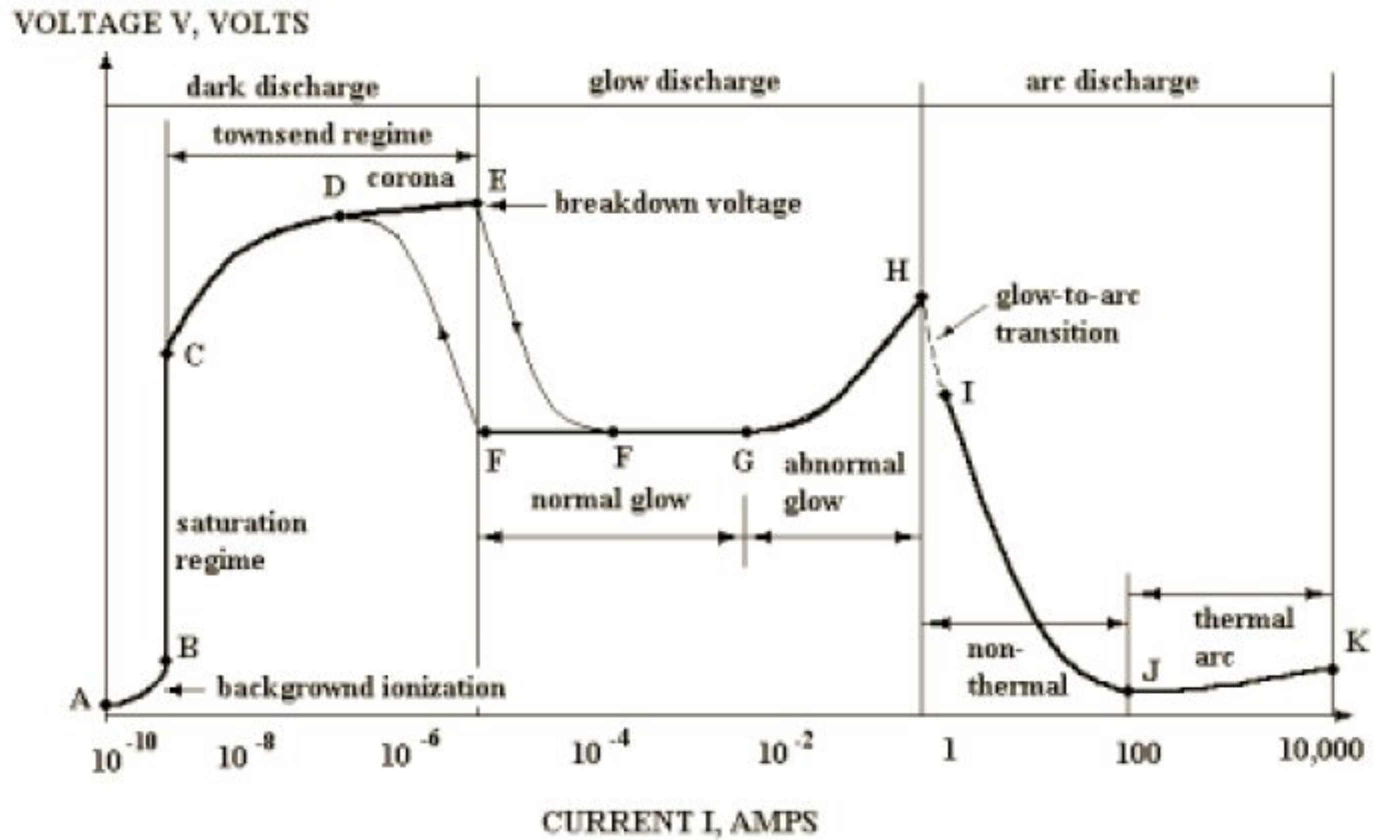


1. **SPUTTERING**
(katood-ioonpommitus)

Magnetron Sputtering
DC
RF

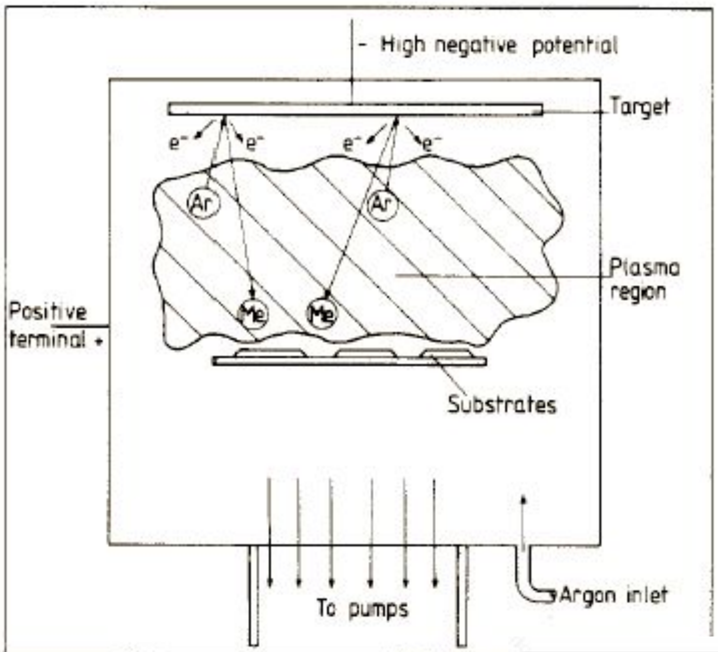
2. Cathode ARC ion Plating
(kaarleek sadestamist)

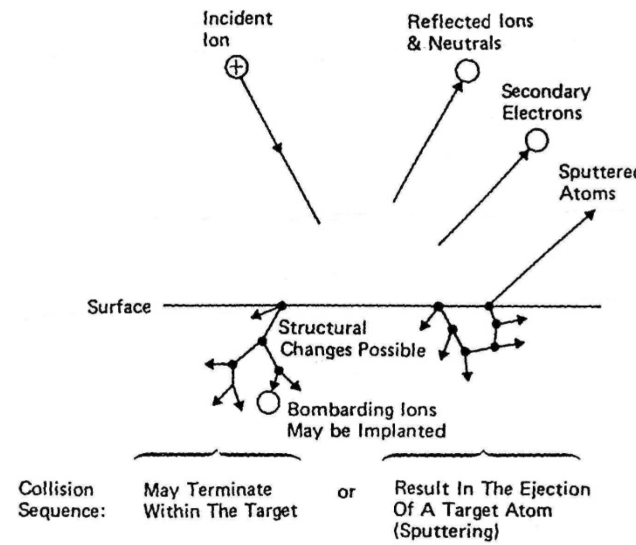
Voltage-current characteristics[6]

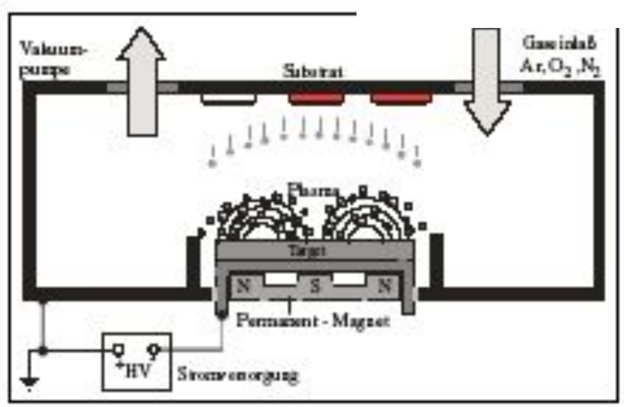


Sputtering (DC and RF)[7]

Katood-ioonpommitussadestus







Magnetron sputtering

PVD – Physical Vapor Deposition
ARC PLASMA DEPOSITION

Arc evaporation:

• high-current (tens to hundreds of A), low DC voltage (tens of V) gas discharges
• initiation of the arc requires two metal electrodes that first touch and then separate a small distance
• a very luminous small cathode spot (10^{-8} to 10^{-4} m diameter) forms that passes extremely high current densities ($\sim 10^{8}$ to 10^{12} A/m^2) $\Rightarrow$ erosion of the cathode by melting and vaporization as well as ejection of solid and molten particles
• current density at the anode $\sim 10^{5}$ A/m^2
• the vapor in the form of multivalent ions sustains the vacuum arc
• the spot rapidly jumps around the surface of the cathode (the spot velocity typically ~100 m/s)

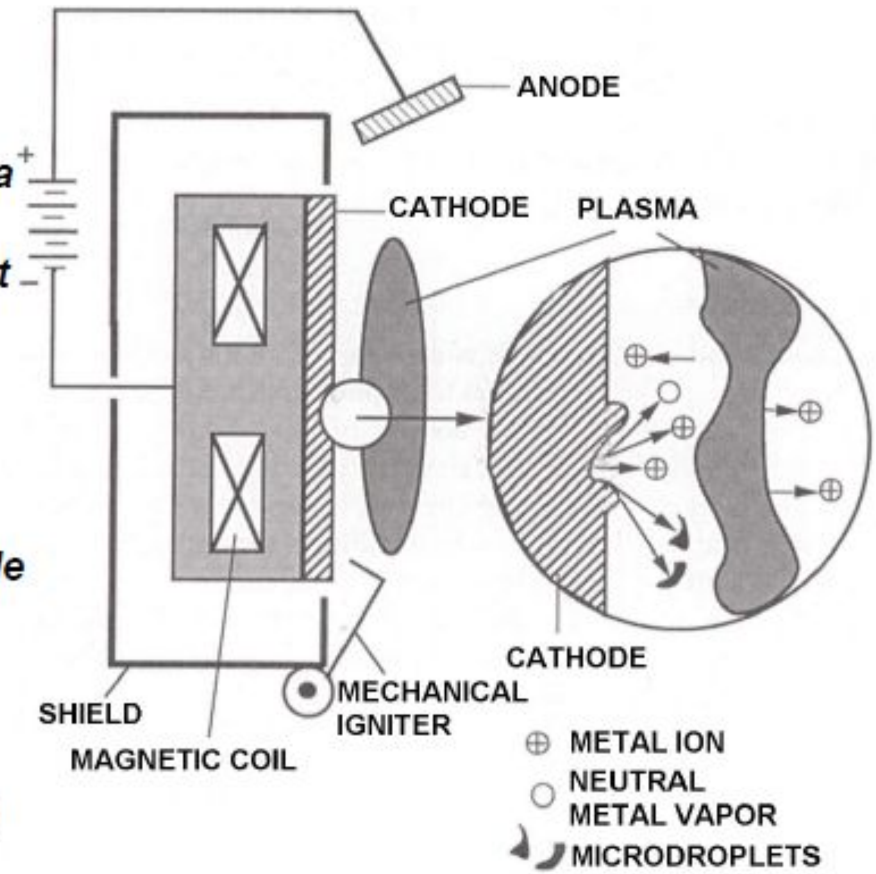
PVD – Physical Vapor Deposition

ARC PLASMA DEPOSITION

Cathodic arc:

Important:
- *arc ignition mechanism (usually a mechanical striker)*
- *the means to confine the arc spot to the cathode surface (boundary shields, magnetic fields, passive borders)*

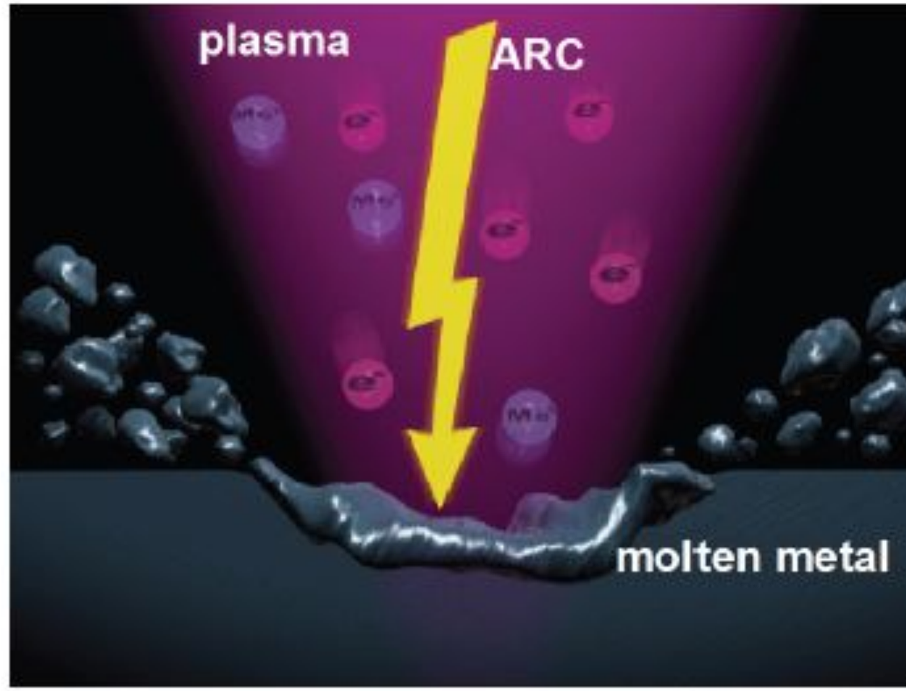
- arc is steered magnetically → material is eroded from the cathode in a series of flash evaporation events
-disadvantage: macroparticles
- deposition rates: greater than those for sputtering, but less than for e-gun evaporation
- cathodic arc plasmas are fully ionised



Cross section of cathodic-arc deposition system with a model of activity at a cathode spot.

PVD – Physical Vapor Deposition
ARC PLASMA DEPOSITION

Cathodic arc:



macroparticles - ablation of molten or solid cathode particles due to thermal shock and hydrodynamic effects, the majority of molten globules are emitted at low angles (0^o to 30^o) with respect to the cathode surface

Minimizing the number of macroparticles that reach the substrate:
low-angle shielding, reduction of arc current, adjustment of gas pressure in reactive processes, increasing the velocity of cathode-spot motion by magnetic methods, employing curved-sector electromagnetic mass filters

PVD – Physical Vapor Deposition
ARC PLASMA DEPOSITION

advantages	disadvantages	applications
• low voltage power supplies • mounting cathodes in any orientation • deposition rates are greater than those for sputtering	macroparticles	wear- and abrasion-resistant coatings in forming and cutting tools

PVD – Physical Vapor Deposition
Summary

advantages	disadvantages
• no environmentally damaging materials and emissions, no toxic reaction products • great variety of coatings can be produced • coating temperature below the final heat treatment temperature of most steels • small, precisely reproducible coating thickness (accurate surface replication, true to size) • high wear resistance • low frictional coefficient	• bore holes, slots etc. can only be coated down to a depth equal to the diameter or width of the opening • corrosion resistant only under certain conditions • in order to achieve a uniform coating thickness, the parts to be coated must be rotated during processing

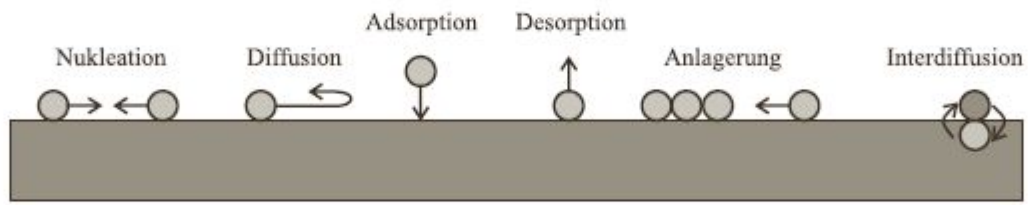
What you need to remember

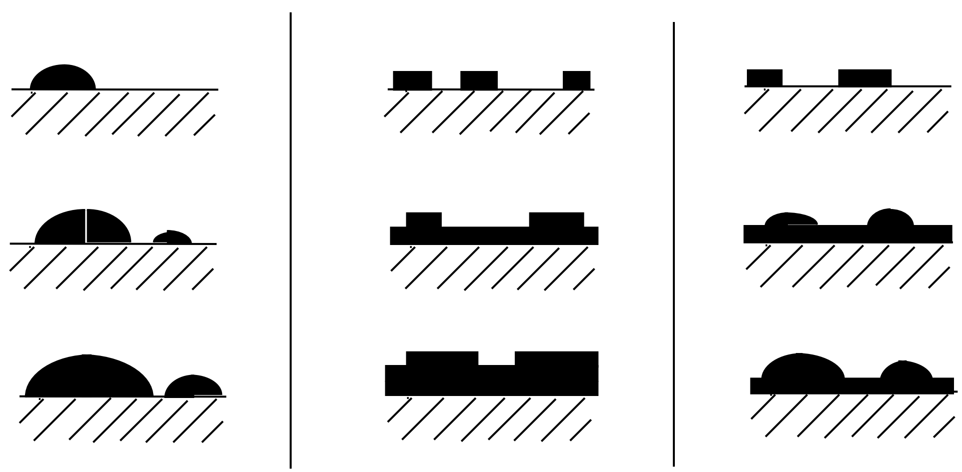
1. Difference between PVD and CVD.
   - PVD – evaporation or collision impact of the solid target
   - CVD – chemical processes in gaseous phase and the surface

2. The versatility of deposition methods is due to particular purposes including quality of the films (coating), size of sample, deposition price, ……

3. The quality of the film is a leading factor in the development of new deposition methods. Nowadays, those are:
   a. Layer by layer deposition :examples – MBE (PVD), ALD (CVD)
   b. PECVD

Mechanism of Growth[10]





Island growth

Layer-by-layer

Layer-by-layer+i
sland