Thin-Film Processing

PV-lab
IEM NEUCHATEL

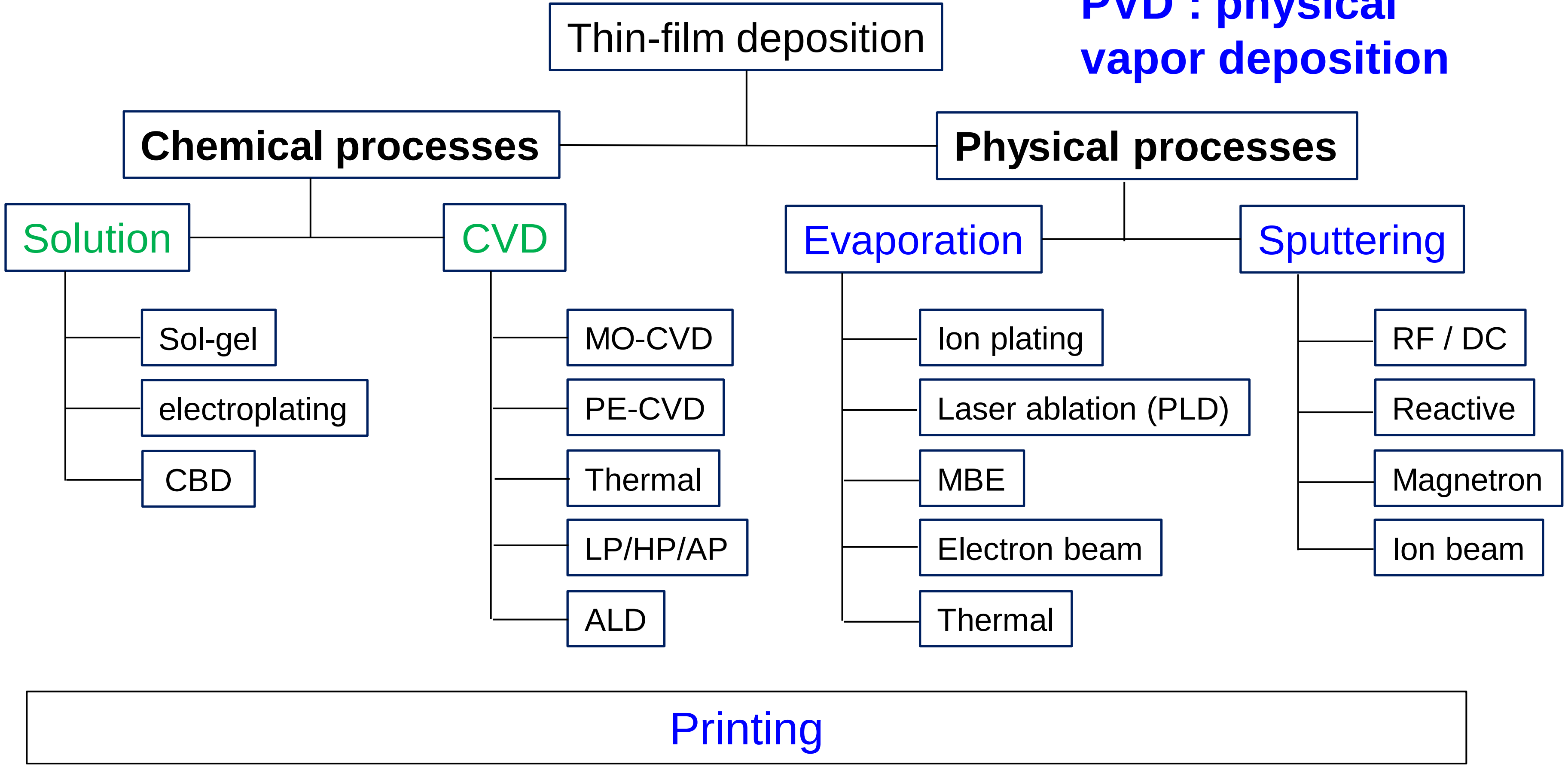
Thin-Films

- Thin films vs. bulk:
  - Thin films are deposited onto bulk materials (substrates) to achieve properties unattainable by the substrate alone.
- Multiple functionalities:
  - Electrical (insulation, conduction), optical (reflective/antireflective coatings, decorative), magnetic (memory discs), thermal (heat sinks), chemical (diffusion barriers, protection against oxidation), mechanical (hard coatings), sensing, energy harvesting, ….
  - Multilayer structures or anisotropic layers can behave as completely new engineered materials unknown in the bulk form.
- Cost effective:
  - Large areas possible
  - Large device or large number of devices

nDECO™ - Beneq ALD coatings for decorative coatings

Thin-Film Deposition Techniques

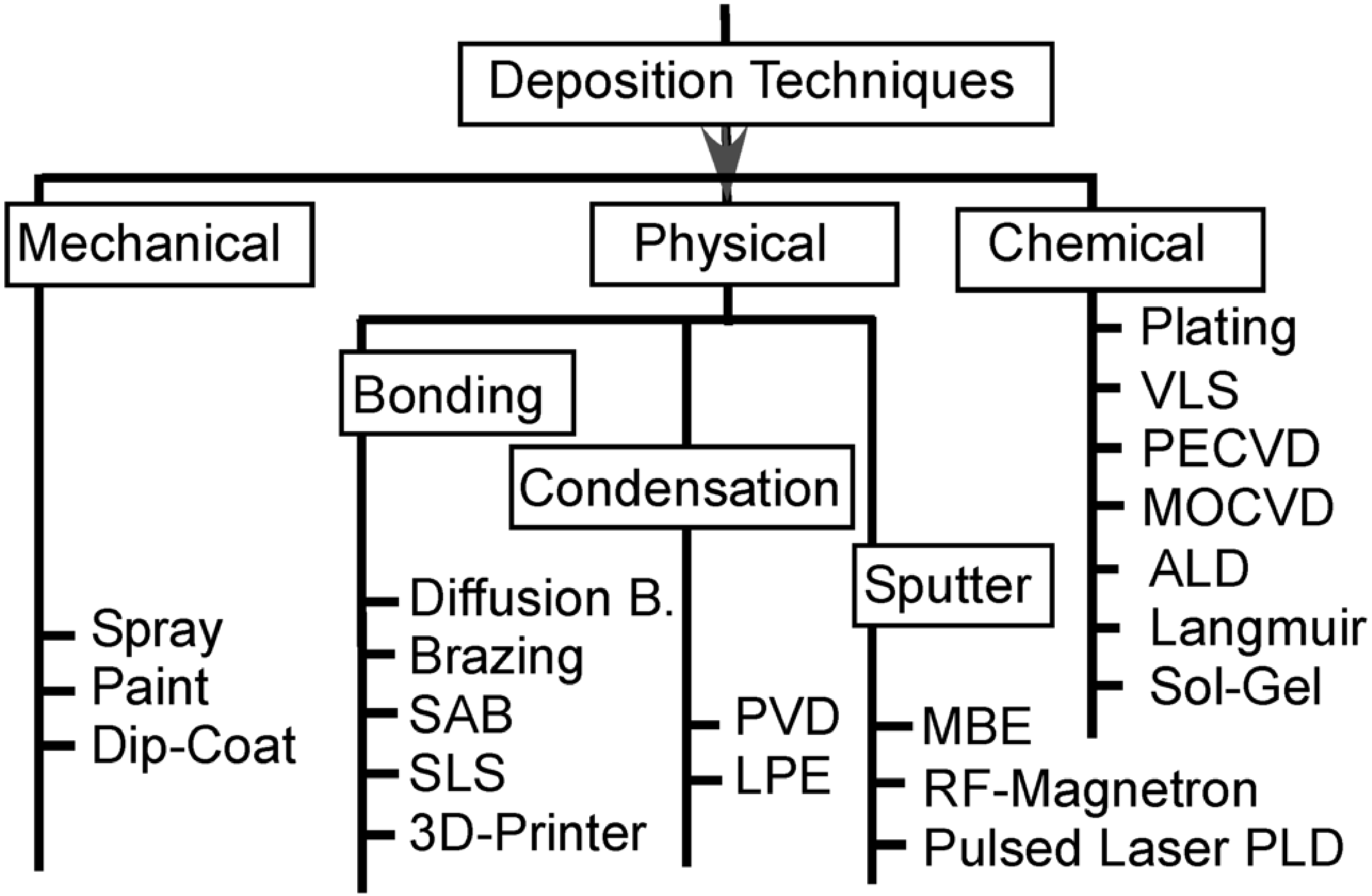
PVD : physical vapor deposition



- Thin-film deposition
  - **Chemical processes**
    - Solution
      - Sol-gel
      - electroplating
      - CBD
    - CVD
      - MO-CVD
      - PE-CVD
      - Thermal
      - LP/HP/AP
      - ALD
  - **Physical processes**
    - Evaporation
      - Ion plating
      - Laser ablation (PLD)
      - MBE
      - Electron beam
      - Thermal
    - Sputtering
      - RF / DC
      - Reactive
      - Magnetron
      - Ion beam
- Printing

CBD: chemical bath deposition/ **CVD**: chemical vapor deposition/ **MO**: metal organic/ **PE**: plasma enhanced/ **LP**: low pressure/ **HP**: high pressure/ **AP**: atmospheric pressure/ **ALD**: atomic layer deposition/ **PLD**: pulse laser deposition/ **MBE**: molecular beam epitaxy.

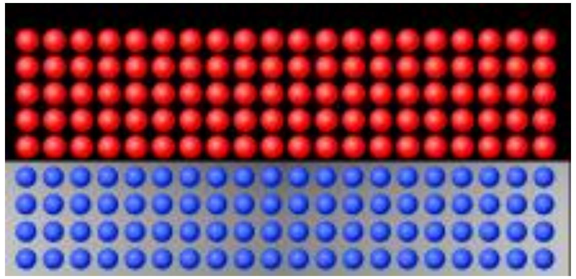
Other classification



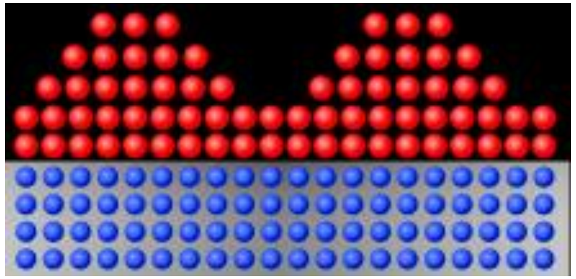
W. Wuderlich (2014), doi:10.3390/met4030410

Growth modes

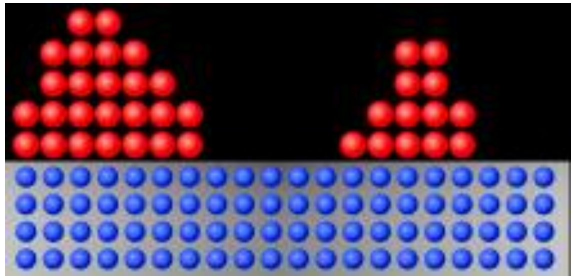
- **Frank-van-der-Merwe** ("layer-by-layer"):
  In this growth mode the adsorbate-surface and adsorbate-adsorbate interactions are balanced. This type of growth requires lattice matching, and hence considered an "ideal" growth mechanism.



- **Stranski–Krastanov** ("joint islands" or "layer-plus-island"):
  In this growth mode the adsorbate-surface interactions are stronger than adsorbate-adsorbate interactions.



- **Volmer-Weber** ("isolated islands"):
  In this growth mode the adsorbate-adsorbate interactions are stronger than adsorbate-surface interactions, hence "islands" are formed right away.



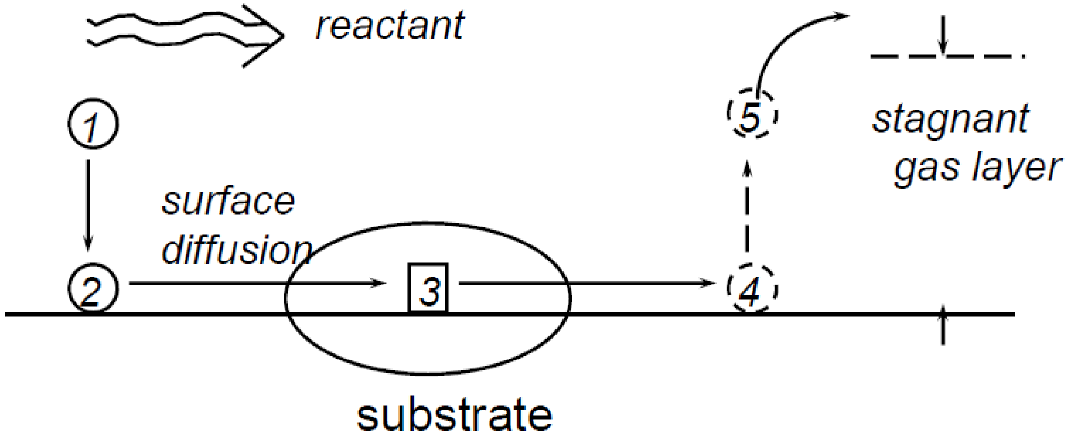
Wikipedia

- **It is here assumed that material transport parallel to the surface is faster than incoming material flux.**

Chemical Vapor Deposition (CVD)

- CVD (simplest form): involves flowing a precursor gas or gases into a chamber containing a heated substrate (or object) to coat it.
- Process sequence:

- Volatile compound of the material to be deposited with other gases (e.g. SiH_4 for Si, H_2O for O)
- Gas flow usually in the viscous regime



1 = Diffusion of reactant to surface
2 = Absorption of reactant to surface
3 = Chemical reaction
4 = Desorption of gas by-products
5 = Outdiffusion of by-product gas

Deposition activated by (high) substrate temperature

Professor N Cheung, U.C. Berkeley

Chemical Vapor Deposition (CVD)

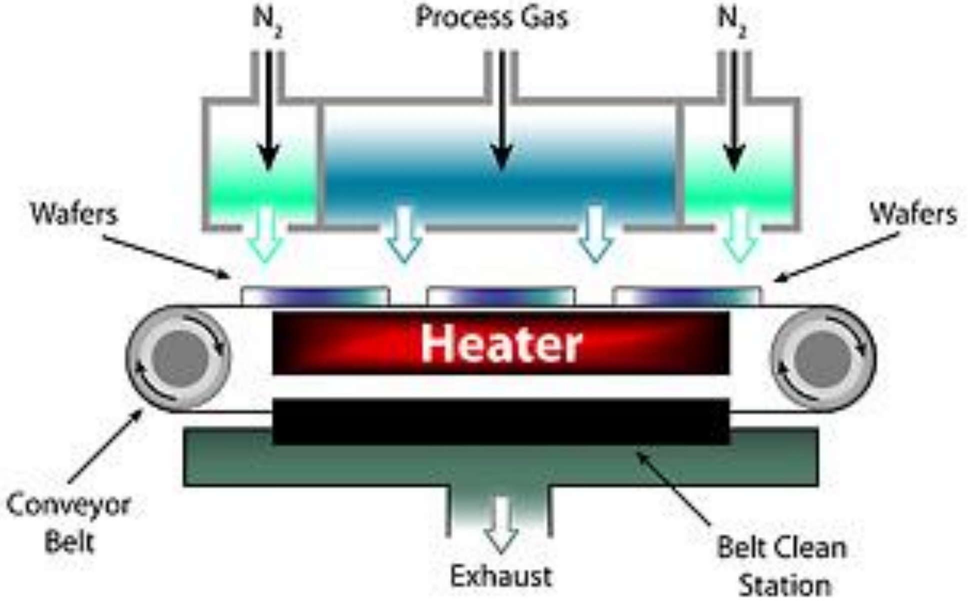
Advantages

- Higher deposition rates than physical vapor deposition (PVD).
- Most important: Conformal coverage: Usually sticking coefficient << 1 (Sticking coefficient for PVD ~ 1)
- Less expensive technology than PVD (less vacuum, no electrical needs)
- Large area deposition (upscaling possible)
- Wide range of pressure

e.g. for transparent electrodes:

- SnO_2 is prepared by atmospheric pressure CVD (AP-CVD)
- ZnO prepared by low pressure CVD (LP-CVD)

APCVD Reactor



Examples of chemical reactions used in CVD

- Silicon oxide (SiO_2)
  - **$SiH_4(g) + 2O_2(g) \rightarrow SiO_2\,(c) + 2\,H_2\,(g)\uparrow$** *350 – 500 °C*

    SiH_4: silane

- Zinc oxide (ZnO)
  - **$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO\,(c) + 2\,C_2H_6\,(g)\uparrow$** *180 – 300 °C*

    $Zn(C_2H_5)_2$: diethylzinc (DEZ) – metalorganic compound (MOCVD)

- Graphene
  - **$CH_4(g) + H_2(g) \rightarrow C\,(c) + 3\,H_2\,(g)\uparrow$** *1000 °C*

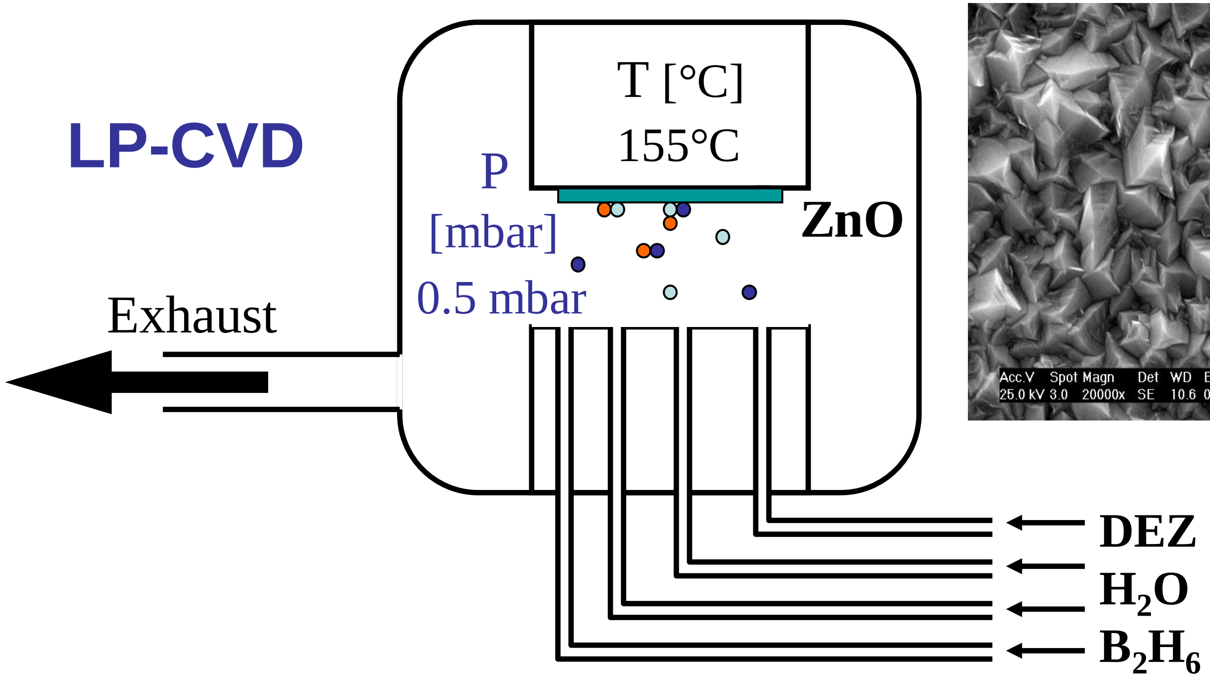
    CH_4: methane

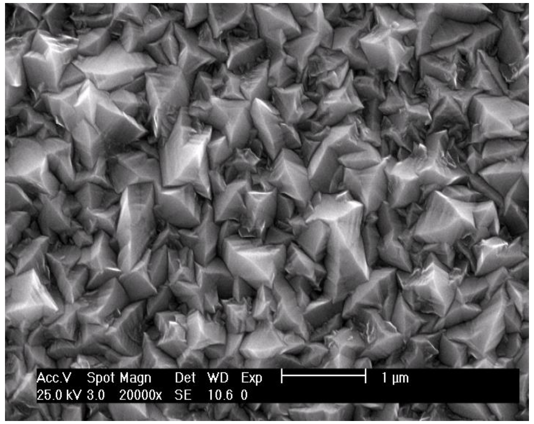
Example LP-CVD ZnO

Chemical reaction at the surface:

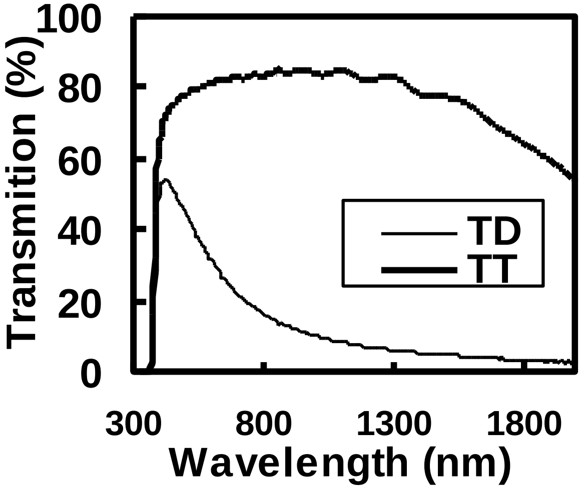
$$(C_2H_5)_2Zn + H_2O \rightarrow ZnO + 2C_2H_6$$

LP-CVD



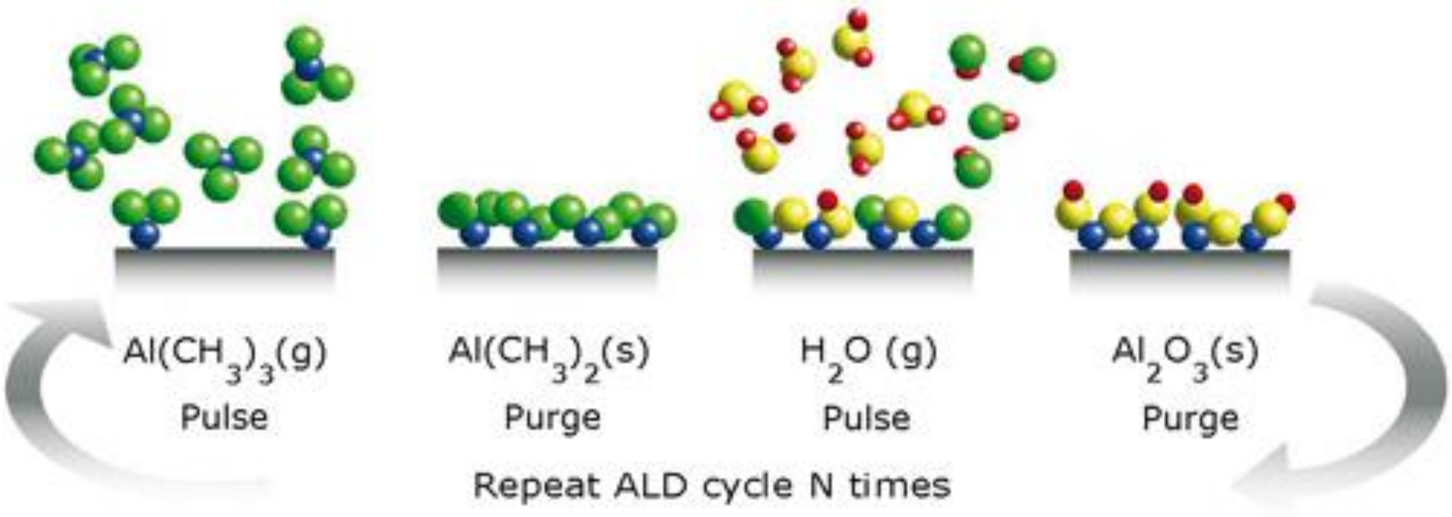


1.4 m^2 Oerlikon/TEL tool



Atomic Layer Deposition (ALD)

- ALD: subclass of CVD based on the **sequential** use of gas phases (precursors react one at a time with the substrate). Thin film formation by repeated cycles of precursor exposure.
- Advantages:
  - Conformal deposition in complex structures
  - Controlled method to produce a film to an atomically specified thickness.
  - Low temperature process.
  - BUT: lower deposition rates as compared to standard CVD.



https://www.youtube.com/watch?v=XMda8TXLIFk

www.beneq.com

CVD – The case of a-Si:H

The case of hydrogenated amorphous silicon (a-Si:H) and related alloys:

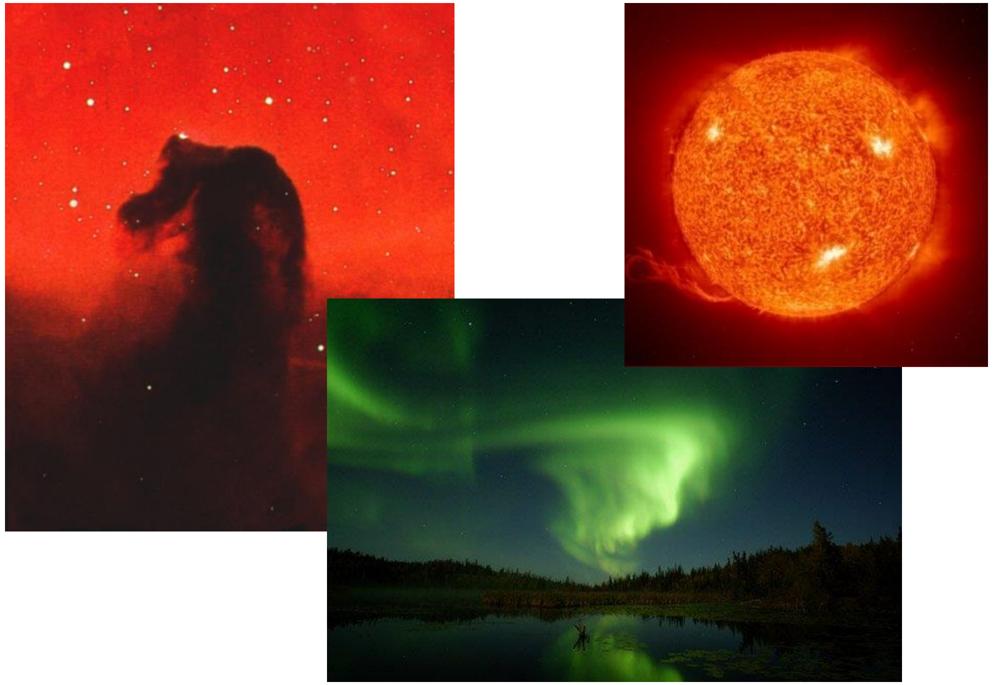
- 1969: Chittick *et al.* demonstrated that decomposition of SiH_4 in a glow discharges yielded a-Si:H with good conductivity.
- Decomposition of silane (SiH_4) can be provided by:

  – Thermal energy: heating a filament
    - **Hot Wire CVD (HW-CVD)**

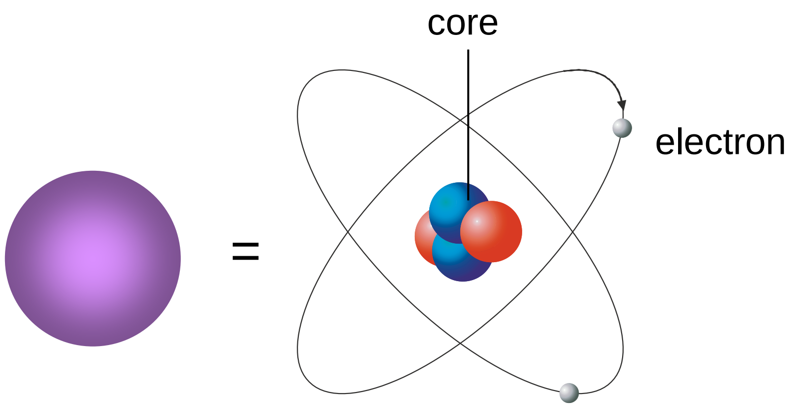
  – Optical energy: UV light absorption
    - **UV-CVD**

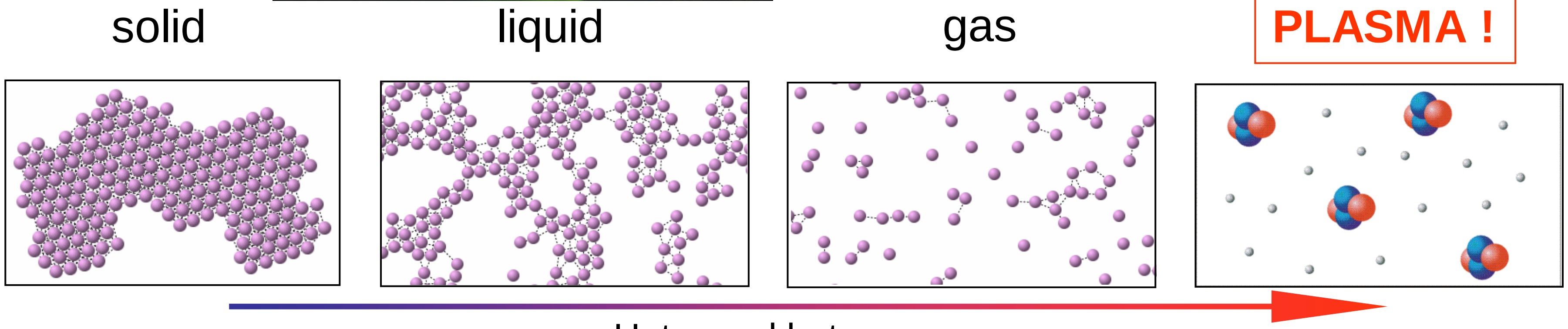
  – Electrical energy: glow discharge (plasma)
    - **Plasma Enhanced CVD (PE-CVD)**

Introduction to plasma



Plasma: the fourth state of matter

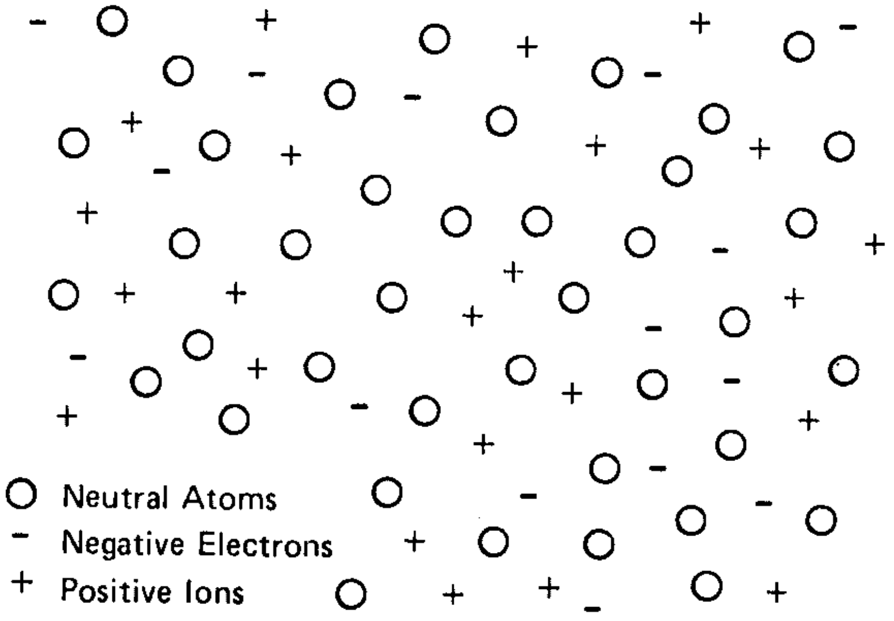




Hoter and hoter…

Plasma definition

Plasma = gas with significant fraction of ionized molecules and free electrons. A plasma is neutral on a macroscopic scale.



Particles present in plasmas:

- Neutral atoms/molecules
- Excited neutral atoms/radicals
- Ions (mostly positive, density n_i)
- electrons (density $n_e = n_i$)

Example: SiH_4, SiH_3, SiH_2^*, H^+, H_2, e^-

If n = density of neutrals :

We consider medium ionised plasma ⟷

$n_e/n \sim 10^{-7} - 10^{-4}$
$n_e \sim 10^8\text{-}10^{14}\ \text{cm}^{-3}$

Strongly ionised plasma $n_e/n > 10^{-4}$ in stars, nuclear fusions

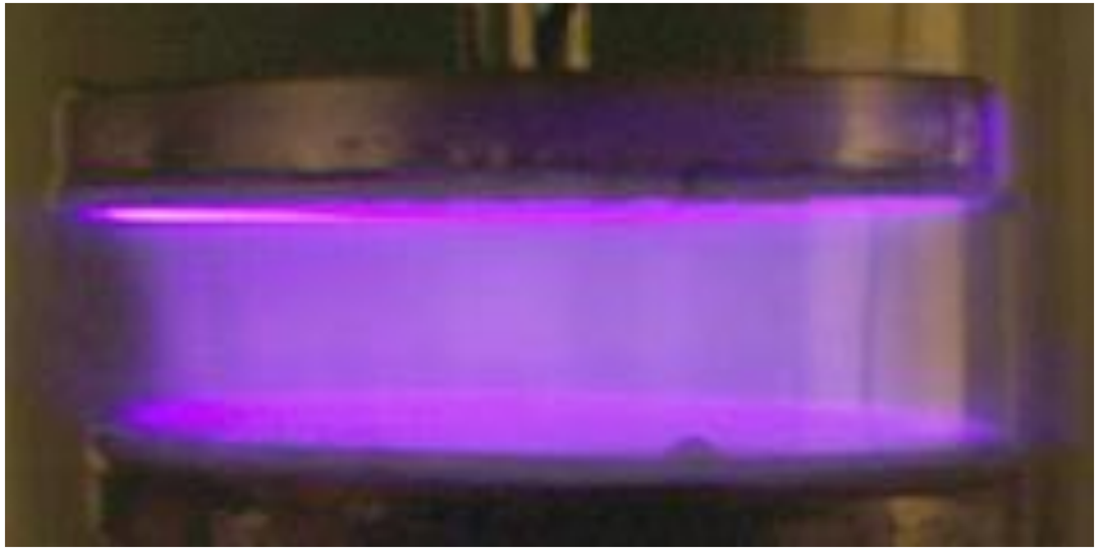
Role of plasma in the process

Plasma can promote deposition that occurs otherwise at higher substrate temperature.

PE-CVD is a good way to perform
high temperature chemistry at low substrate temperature.

Film properties are controlled by:

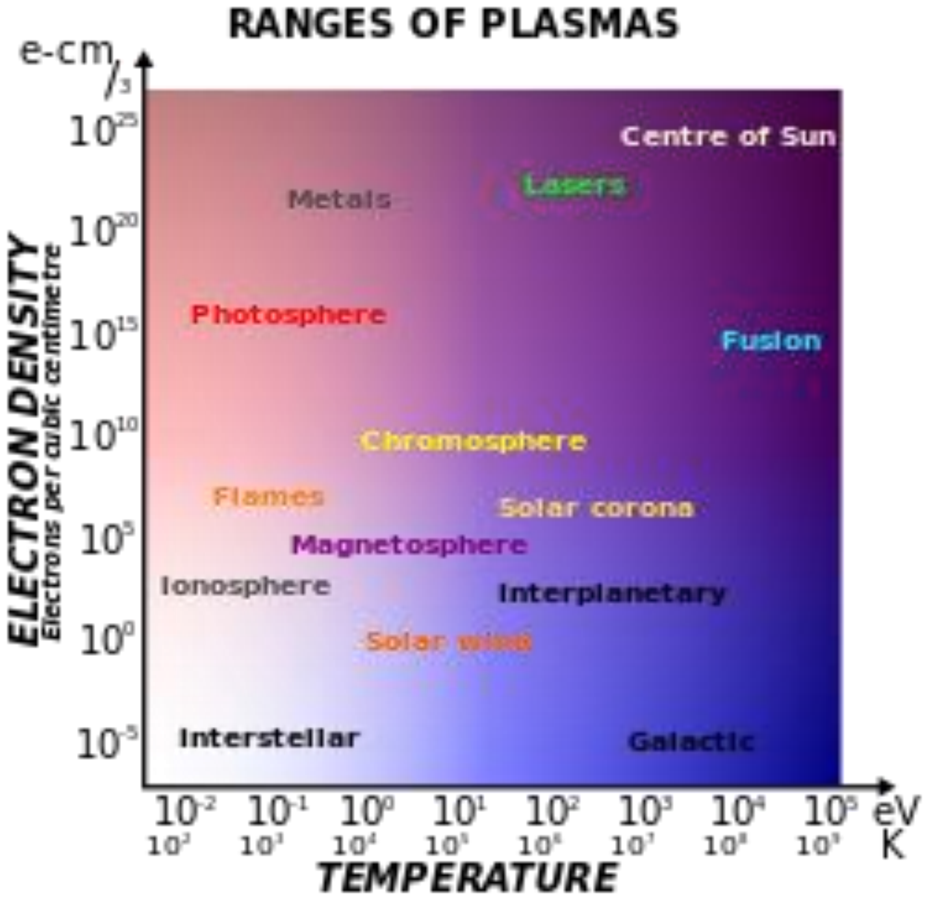
- The nature of the species reaching the substrate
- The ion energy (up to ~ 100 eV)
- Temperature of the substrate



Plasma properties: Electron and ion temperature

In plasma, particle energies given by their kinetic energies

- High electron temperature :
  E_e ~1-10 eV, $\langle E_e \rangle$ ~2 eV ↔ $T_e = E/k_B$ ~23’000 K
  (but no influence on heating of the chamber walls !)
- Low gas temperature T_{Neutral} ~300 K
- Low ion temperature T_i ~500 K
  (can be accelerated in the electric field close to the electrodes !)
- Excited species can acquire rotational and vibrational energy
  T_{ex} up to 1’000 - 3’000 K



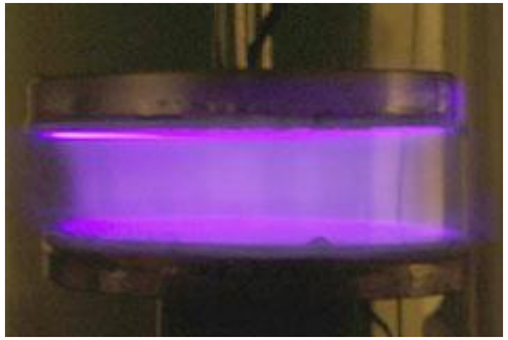
http://schools-wikipedia.org/wp/p/Plasma_%2528physics%2529.htm

In processing plasmas, electron much hotter than neutrals and ions !

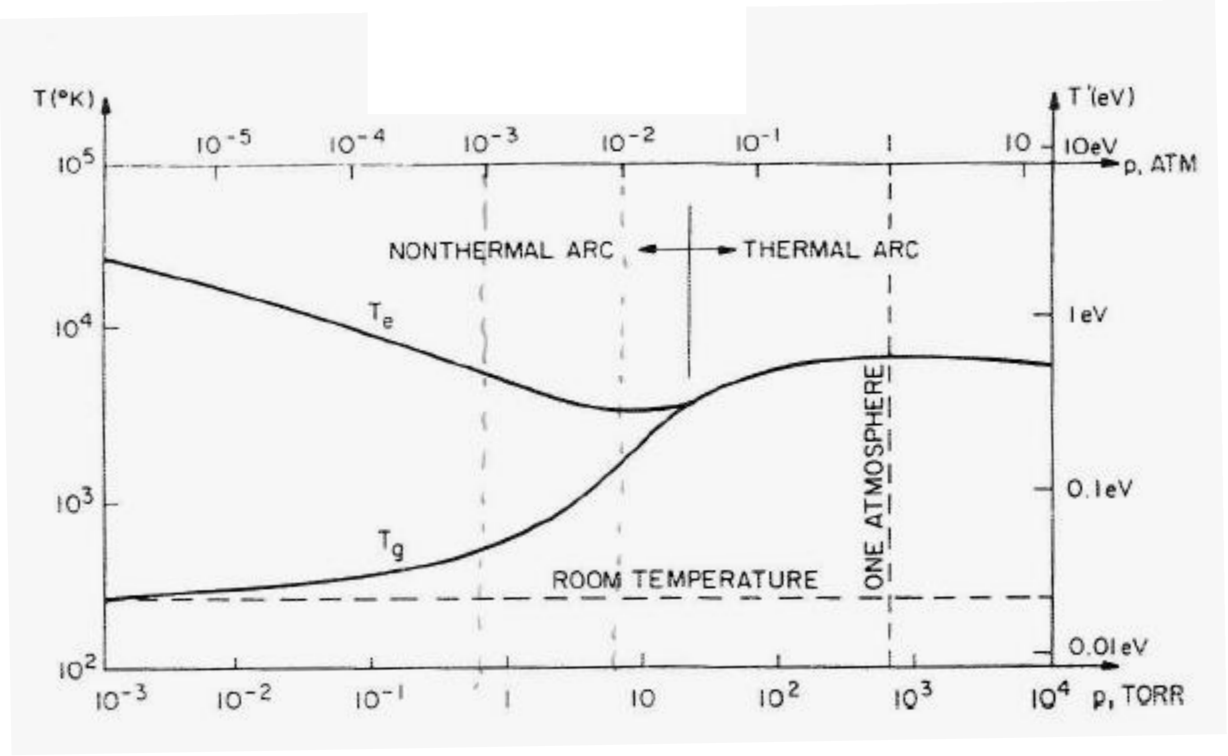
« cold high-temperature-chemistry ».

Thermal and non-thermal plasma

$T_e \gg T_{gas}$



Coating

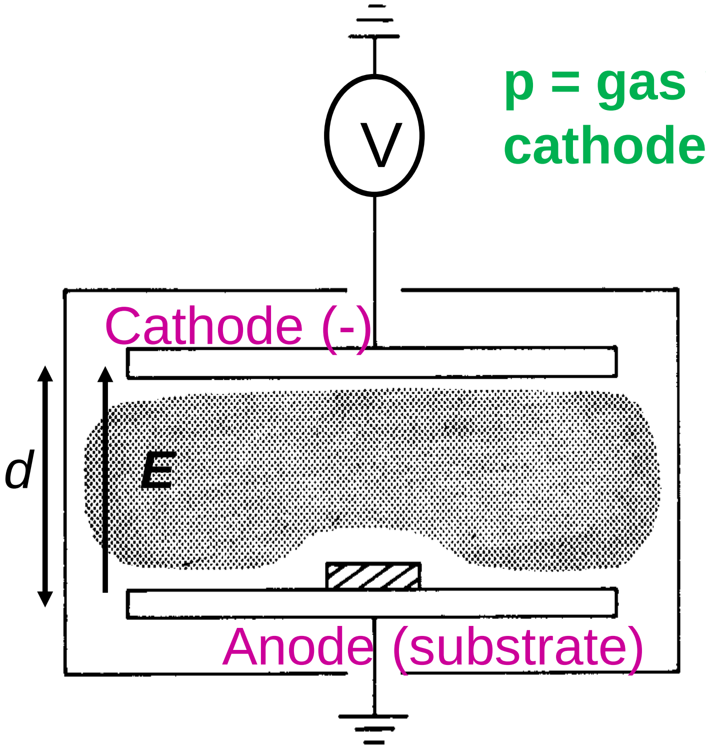


$T_e \approx T_{gas}$

Machining

- **Thermal plasma** are used for plasma cutting or deposition from powder with high fusion temperature (ceramic, super alloy, refractory materials…). Here $T_e \approx T_{gas}$.
- For sufficiently low pressures, the electron temperature and the gas temperature are no longer the same: $T_e \gg T_{gas} \approx T_{room}$

Initiation/ignition of a plasma discharge



p = gas pressure in chamber. Application of V between cathode (-) and anode (grounded) spaced by d

Free electrons are needed!

They can be produced by

a) UV light on cathode

b) Glowing filament (thermoemission)

c) Ion impact

- Electrons accelerated in ***E*** makes impact ionisation on neutrals

$$e^- + A \rightarrow 2e^- + A^+$$

- Also ions are accelerated to the cathode → secondary electron generation

For sufficiently high V → discharge !

Paschen law

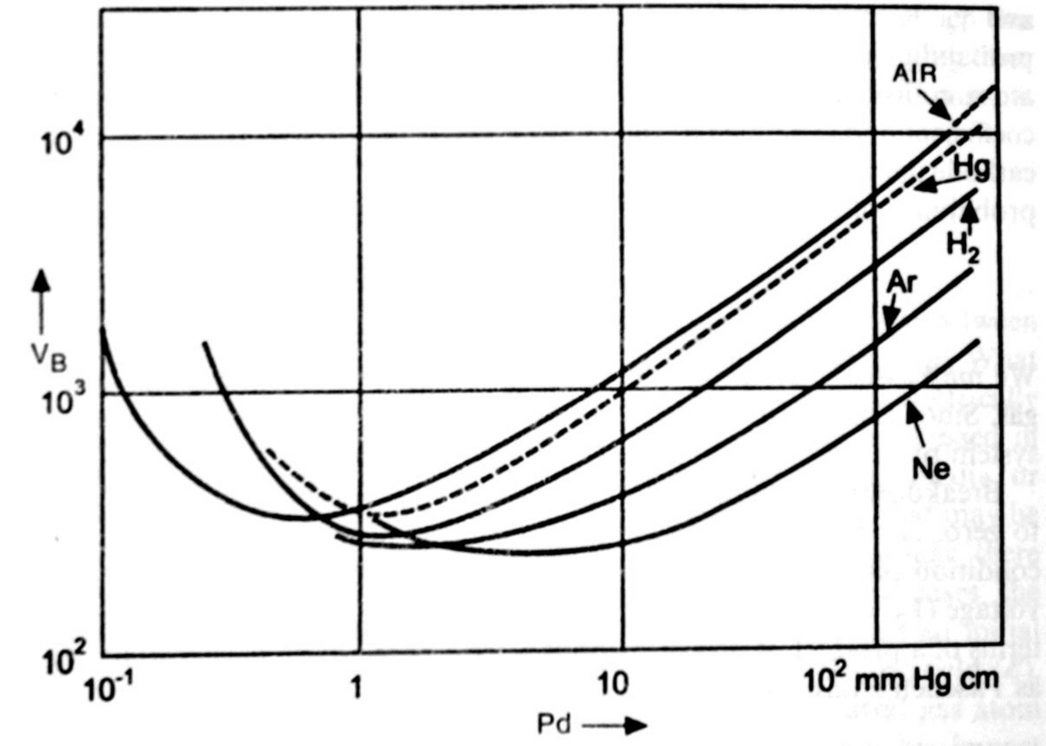


Figure 4-2 Paschen curves for a number of gases. (From A. von Engel, *Ionized Gases.* Oxford University Press, Oxford, 1965. Reprinted with permission.)

Ignition depends on cathode type and mostly on the product: *p·d* *(pressure x distance)*

Intuitive understanding:

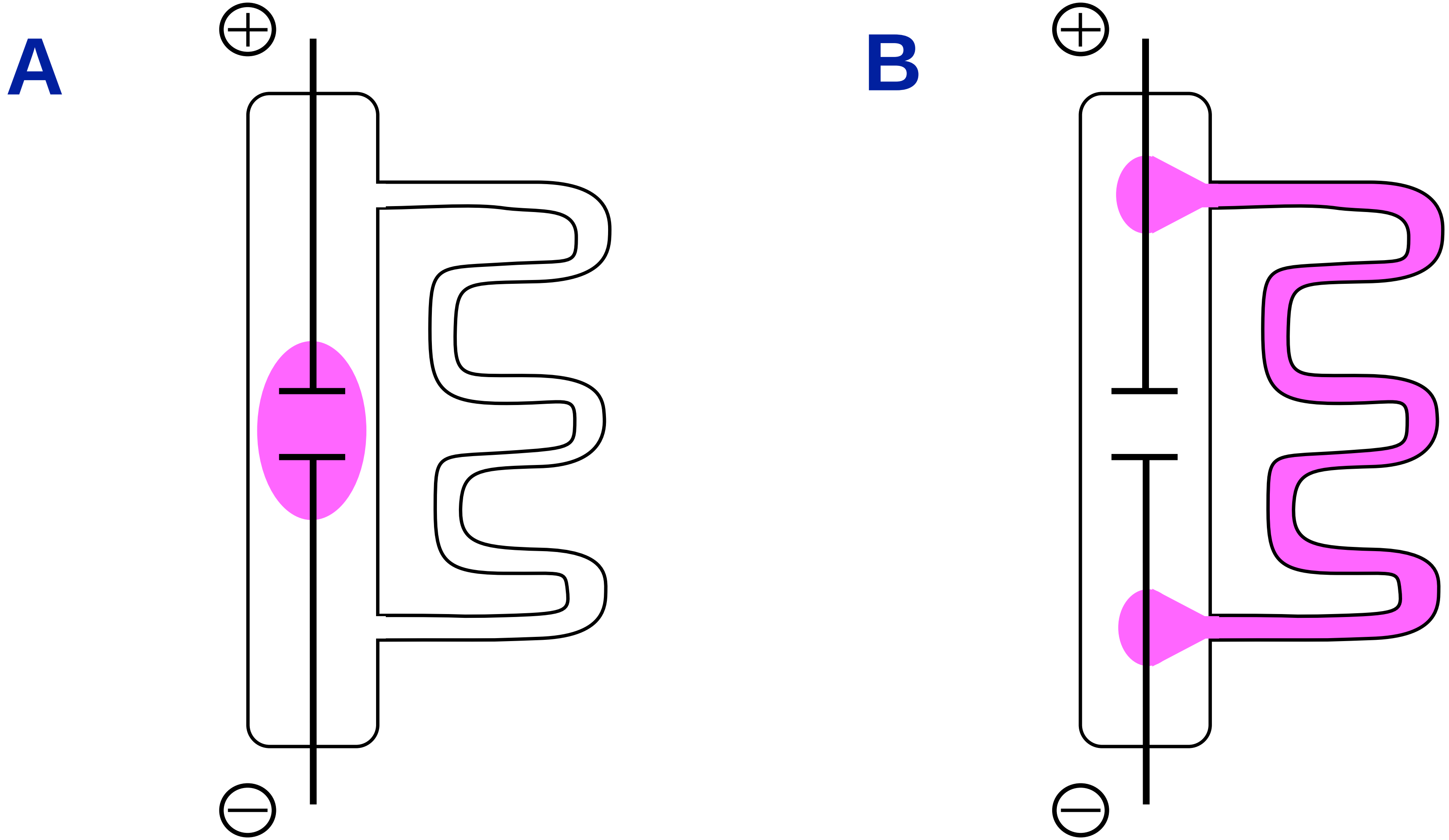
- *p* too low: not enough ionisation events
- *p* too high: not enough energy gained by the e^- to ionize the neutrals between two collisions

Rule of thumb p·d > 40 Pa·cm, p = 1-1’000 Pa V = 1...2 kV

1 Pa=1 N/m^2, 1 atm ≈ 760 mm Hg ≈ 10^5 Pa

Discharge tube

Where is the discharge going to take place in this discharge tube ?



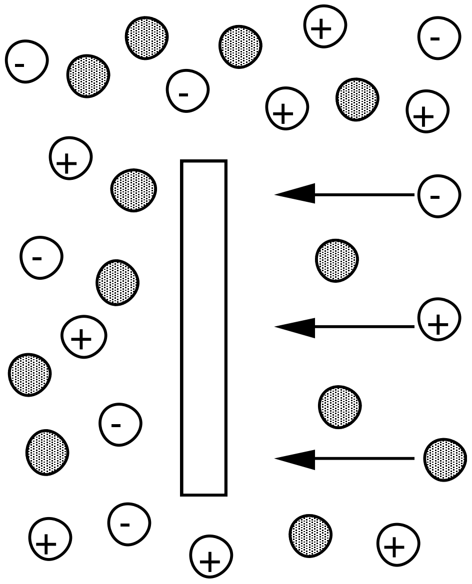
Reactions in the plasma

$e^- + AB \rightarrow e^- + A + B$	electron impact dissociation	**electrons**
$e^- + AB \rightarrow e^- + A^+ + B^-$	electron impact ionizing dissociation	
$e^- + A \rightarrow 2e^- + A^+$	electron impact ionization	
$e^- + A \rightarrow A^-$	electron attachment	
$e^- + A \rightarrow e^- + A^*$	electron impact excitation	
$h\nu + A \rightarrow e^- + A^+$	photon induced ionization	**photons**
$h\nu + A \rightarrow A^*$	photon induced excitation	
$A^* \rightarrow h\nu + A$	relaxation	
$A^+ + e^- + B \rightarrow A^* + B^*$	three body recombination	**ions**
$A^+ + e^- \rightarrow A + h\nu$	emissive recombination	
$A^+ + B^- \rightarrow A^* + B^*$	electron tranfer	
$A^+ + B \rightarrow A + B^+$	charge tranfer by ion-atom collision	
$A_{(\text{high speed})} + A \rightarrow A + A^+ + e^-$	ionization by atomic impact	

In addition, there are also all the reactions between the reactive species (ions and radicals) and stable atoms or molecules!

Floating surface in a plasma

An electrically isolated surface inside a plasma will be exposed to different particle fluxes and will be charged.



initially electrons and ions will flow to the surface; their current densities are:

(Maxwell distribution assumed)

$$J_e = \frac{e \cdot n_e}{4} \overline{v_e} = e \cdot n_e \sqrt{\frac{kT_e}{2\pi m_e}}$$

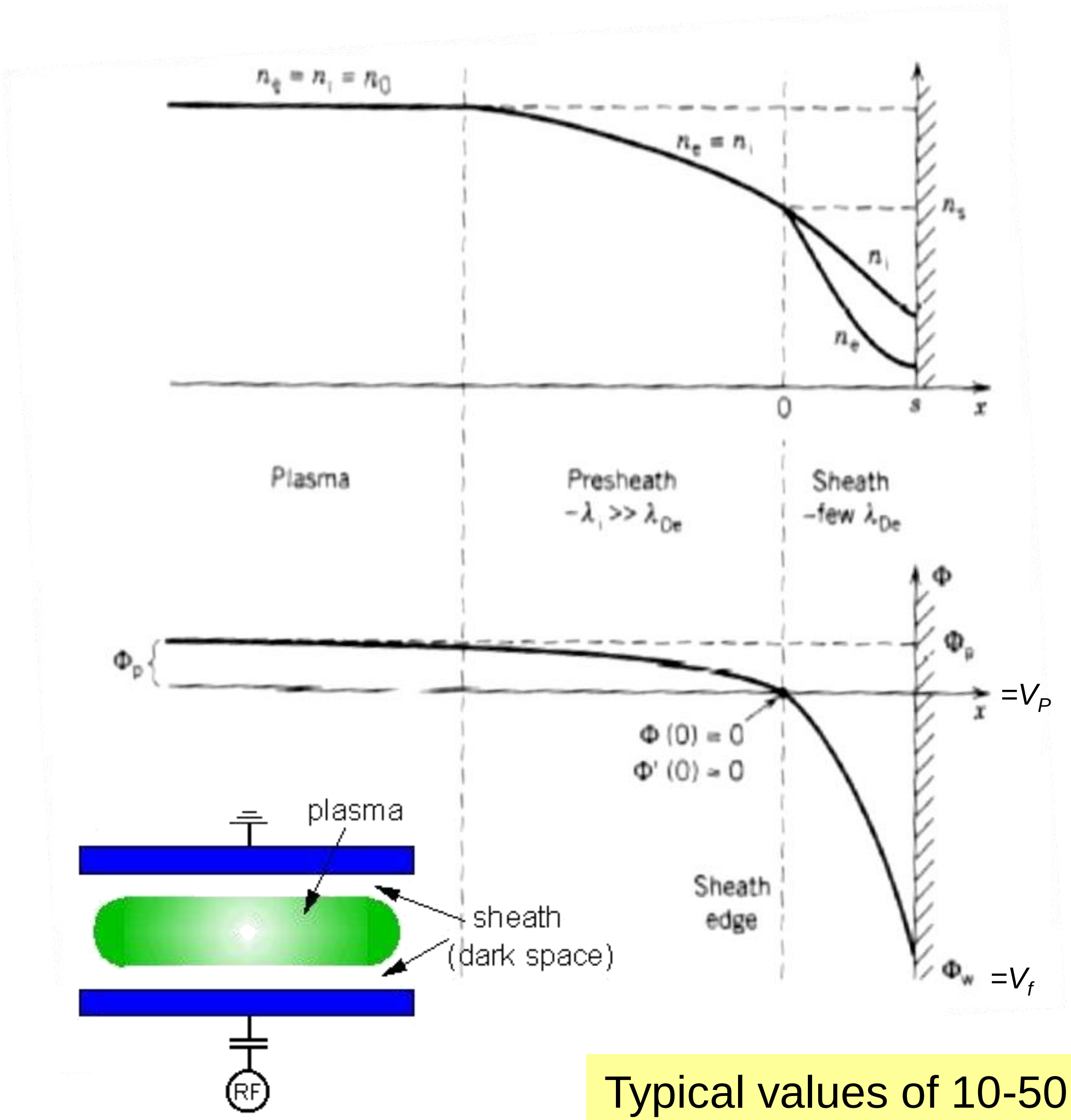
$$J_i = \frac{e \cdot n_i}{4} \overline{v_i} = e \cdot n_i \sqrt{\frac{kT_i}{2\pi m_i}}$$

(gas kinetics)

Initial electron current higher by a factor ~ 10^3-10^5 !

surface always charges itself negatively in a plasma and acquires a negative potential. The potential is such that ion and electron currents are then equal !

Sheath formation



Near an object or the substrate → apparition of a <u>sheath (dark space)</u>

This forms a potential barrier for the electrons of $e(V_p\text{-}V_f)$ only a fraction of the the electrons (at T_e) will reach the object/substrate:

$$\frac{n'_e}{n_e} = \exp\left(-\frac{e(V_p - V_f)}{kT_e}\right)$$

- **V_p = plasma potential**
- **V_f = floating potential**

(=0 for a grounded electrode)

$$V_p - V_f = \frac{k_B T_e}{2q}\ln\frac{m_i}{2.3 m_e}$$

Typical values of 10-50 V ! Important ion bombardment!

Plasma enhanced chemical vapor deposition (PE-CVD)

glow discharge plasma + vapor-phase chemical reactions + film deposition

“rich process”, chemical reactions, substrate bombardment

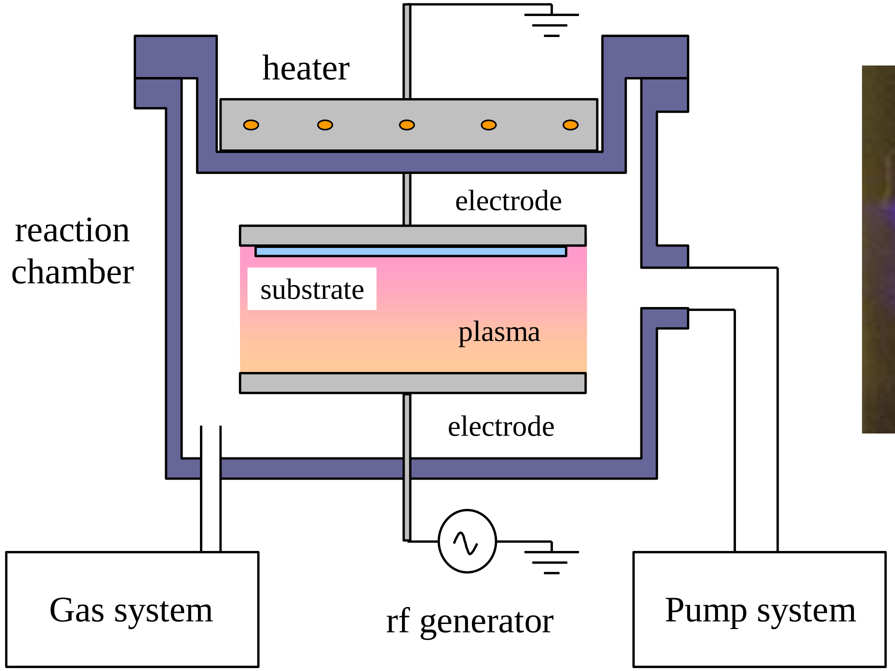
Lower reaction temperature achievable than CVD

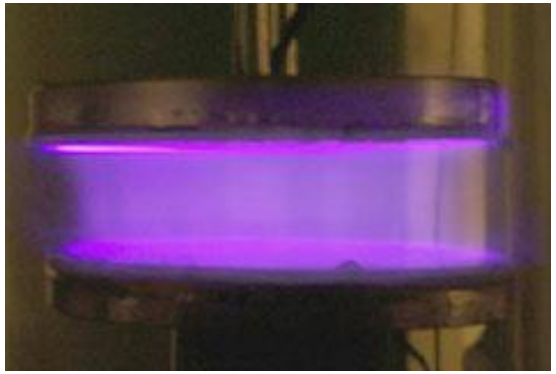
- a-Si:H, a-SiC, a-SiGe
- microcrystalline Si, Undoped SiO_2
- doped SiO_2 (BPSG)
- SiN
- SiO_yN_x
- Diamond like carbon

- Flat screen display
- Thin film Solar cells
- Dielectric layer in IC
- Dopant source
- Passivation layer
- Protective layer

Parallel plate reactor

- Parallel plates reactors are normally **coupled capacitively** (i.e. through a capacitor) to the plasma and activated with a radio-frequency (RF at 13.56 MHz, industrial frequency) or Very High Frequency (VHF) excitations
- Plasma in direct contact with the electrodes and substrates
- DC operated parallel plate reactors - non capacitively coupled - possible for conductive substrate and deposited materials!





- Gas arrival from the side of the system or through the cathode (<u>showerhead</u>)
- Gas convection to the plasma area
- Activation and reaction in the plasma
- Surface reactions and film growth
- Educts pumped away

Parallel plate PE-CVD: effect of electrode asymmetry

As ion/electron current densities to surfaces are identical

→ different sheath voltage develops at the electrodes

$$\frac{\overline{V}_1-\overline{V}_p}{\overline{V}_2-\overline{V}_p}=\frac{\overline{V}_{rf}}{\overline{V}_G}=\left(\frac{A_2}{A_1}\right)^a$$

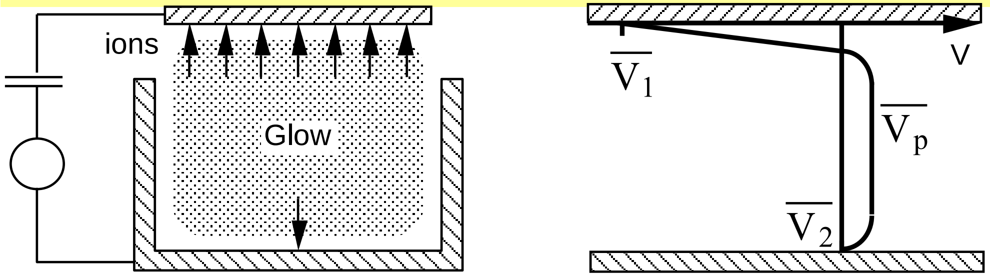
A_1 = cathode surface

A_2 = substrate/wall surface

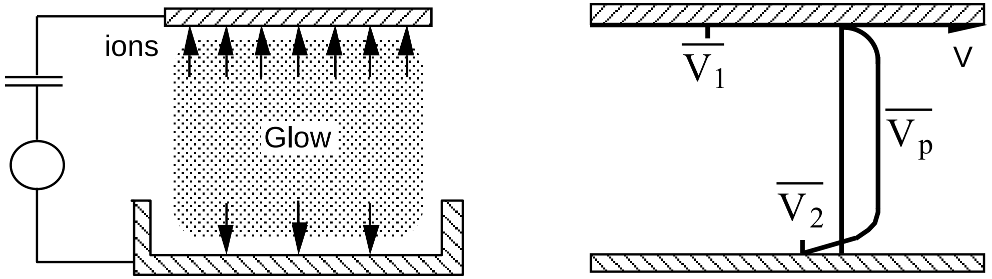
a = 1-3 (experimentally)

(a-) symmetry of reactor very important ! Smaller electrodes gets much higher ion energy bombardement !

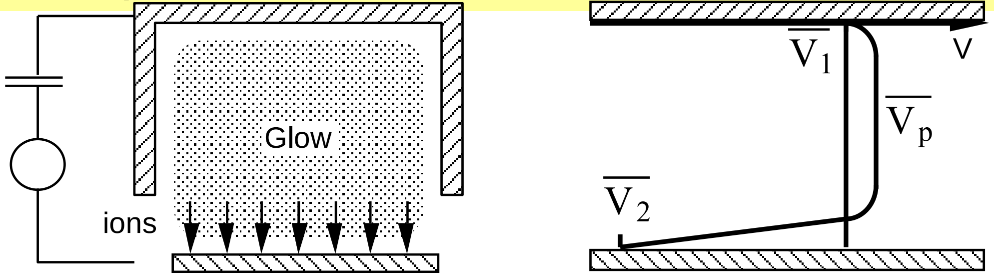
i. Sputtering of target



ii. PECVD (no efficient sputtering)

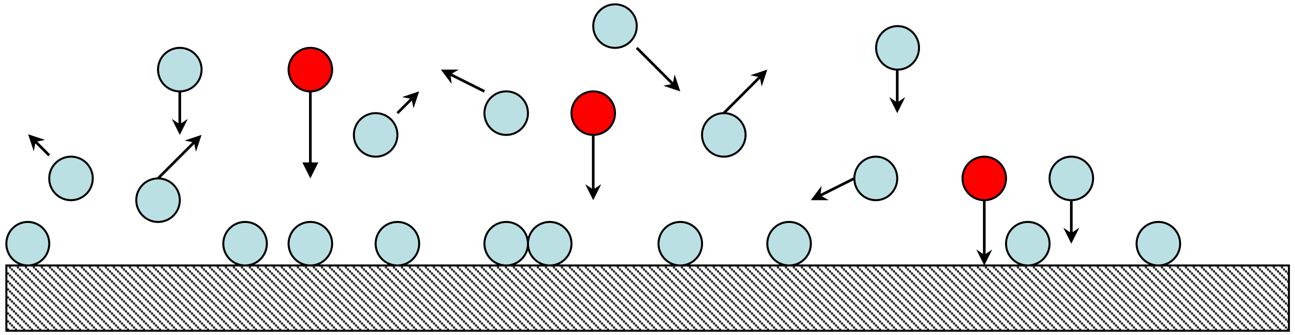


iii. Sputtering of substrate / Reactive ion etching



Example of plasma deposition (a-Si:H)

- The molecular source gas (e.g. Silane SiH_4) is decomposed into numerous neutral (but extremely reactive) (SiH, SiH_2, SiH_3, H….) or ionic species
- Some of these species leave the plasma and impinge on the substrate.
- Electrical fields near the substrate can lead to acceleration of ions and **bombardment** of the surface.



Growth of a thin film: nature of molecular species ● (reactivity), angular distribution, bombardement (direction + energy of ions 🔴) are critical parameters.

Chemistry and flow to the surface

Example of SiH_4-H_2 discharge :

Electron dissociation

$$\begin{aligned} e + SiH_4 &\rightarrow SiH_3 + H\,, \\ &\rightarrow SiH_2 + 2\,H\,, \\ &\rightarrow SiH + H + H_2\,, \\ &\rightarrow Si + 2\,H + H_2\,, \end{aligned}$$

Radical-molecule reaction

$$H + SiH_4 \rightarrow H_2 + SiH_3$$

$$\begin{aligned} Si + SiH_4 &\rightarrow Si_2H_2 + H_2 \\ &\rightarrow Si(H_2)Si + H_2 \\ Si^* + SiH_4 &\rightarrow Si_2H_2 + H_2 \\ &\rightarrow Si(H_2)Si + H_2 \\ SiH + SiH_4 &\leftrightarrow Si_2H_5^* \end{aligned}$$

Electron impact ionization

$$\begin{aligned} e + SiH_4 &\rightarrow SiH_3^- + H\,, \\ &\rightarrow SiH_2^- + 2\,H\,, \\ &\rightarrow SiH^- + 3\,H\,, \end{aligned}$$

ion-molecule reaction

H^+	$SiH_3^+ + H_2$
H_2^+	$SiH_3^+ + H_2 + H$
H_3^+	$SiH_3^+ + 2\,H_2$
Si^+	$Si_2H_2^+ + H_2$
SiH^+	$Si_2H_3^+ + H_2$
	$Si_2H^+ + 2\,H_2$
SiH_2^+	$SiH_3^+ + SiH_3$
	$Si_2H_4^+ + H_2$
	$Si_2H_2^+ + 2\,H_2$
	$Si_2H_6^+$
SiH_3^+	$SiH_4 + SiH_3^+$
	$Si_2H_5^+ + H_2$
	$Si_2H_3^+ + 2\,H_2$

Electron generation

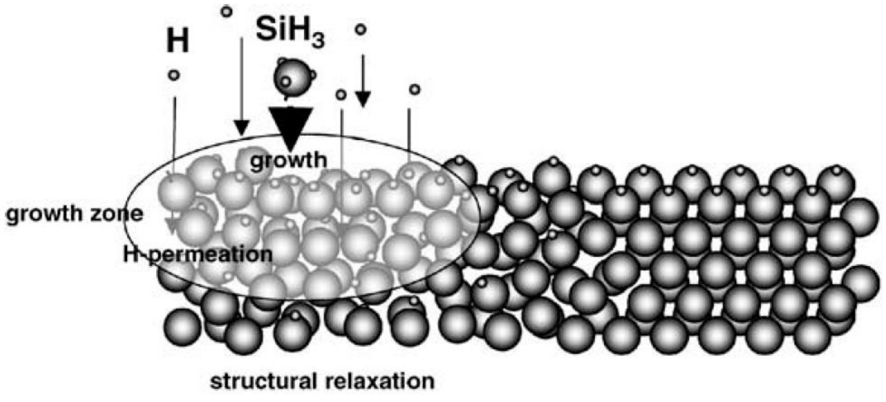
$$e(>EA) + X^- \rightarrow 2e + X$$

$$h\nu(>EA) + X^- \rightarrow e + X$$

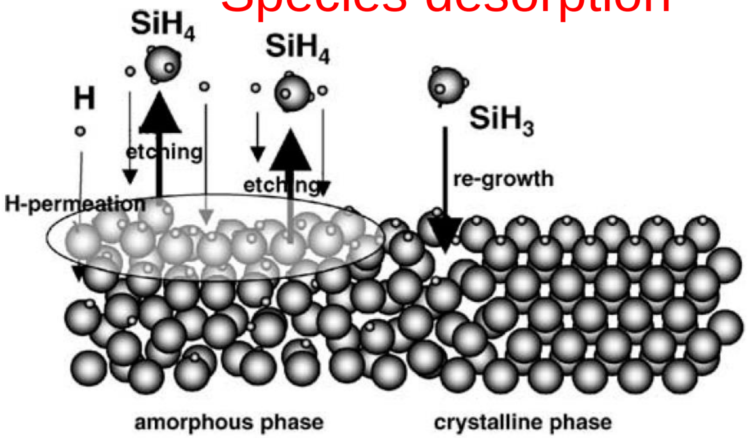
- important radicals for the growth (H, SiH_2, SiH_3)
- higher order silanes → powder formation

Surface reactions

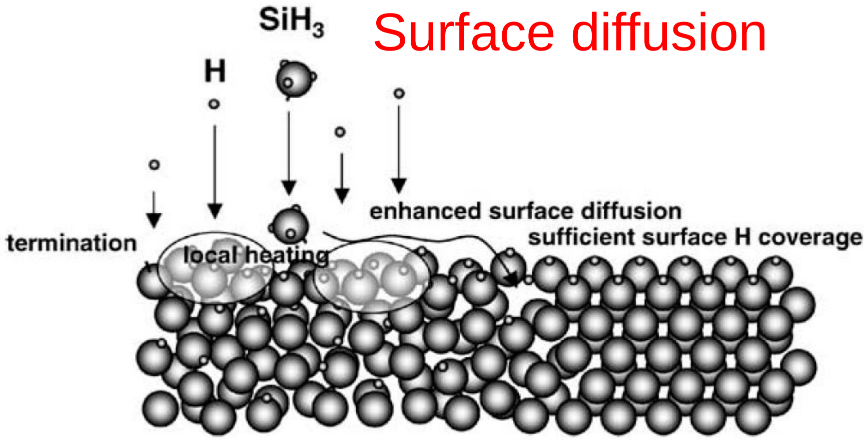
Species absorption

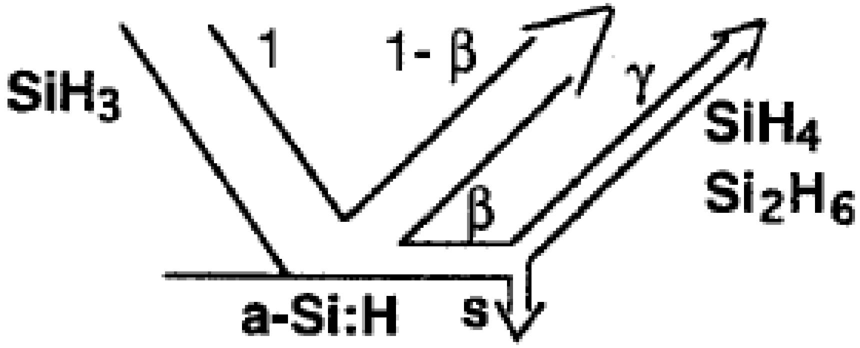


Species desorption



Surface diffusion





Surface reactions also affects the plasma composition and behavior!

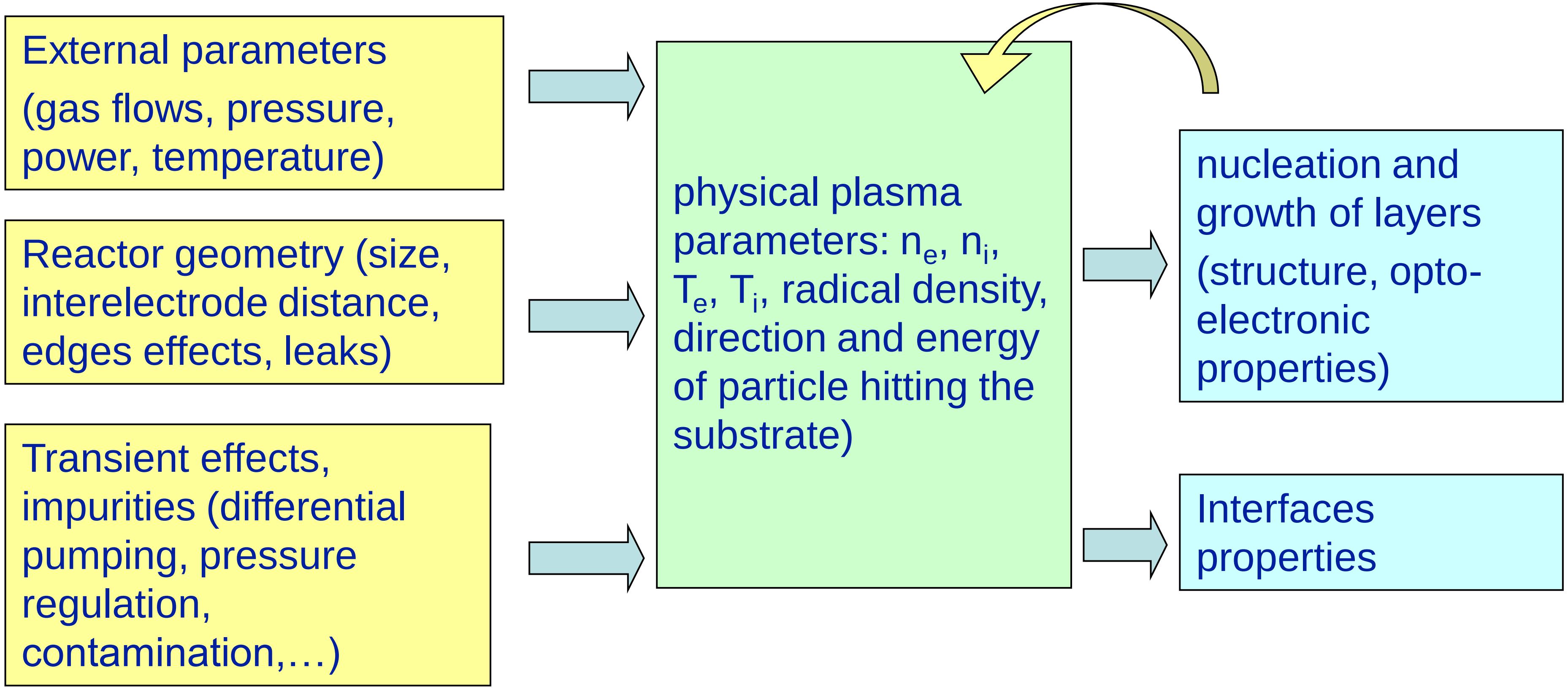
Plasma – growing film interactions

Most important things for the interactions between the plasma and the growing film:

1. The **flow and the energy** of reactive species towards the growing film which govern all the properties of the film
   (n.b. the substrate chemistry plays a role in governing the nucleation).
2. The flow of species towards the film is determined by the **plasma composition** (i.e. density of each species)
   and the **transport** from the plasma to all reactor walls.

Device grade material by PE-CVD

Goal : high carrier lifetime for solar cells or high mobility for TFT



External parameters (gas flows, pressure, power, temperature)

Reactor geometry (size, interelectrode distance, edges effects, leaks)

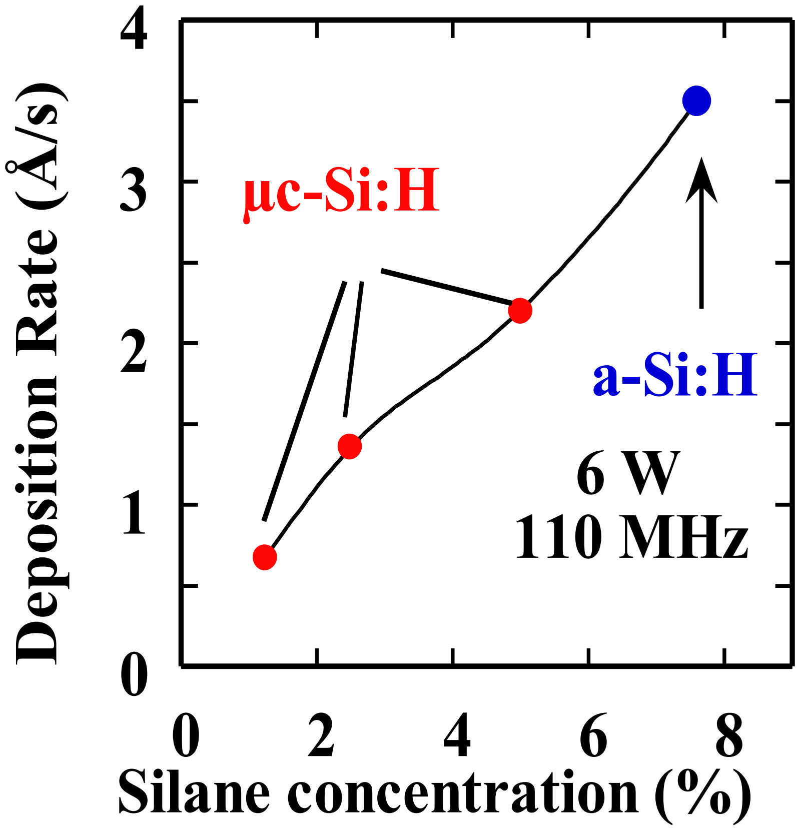
Transient effects, impurities (differential pumping, pressure regulation, contamination,…)

physical plasma parameters: n_e, n_i, T_e, T_i, radical density, direction and energy of particle hitting the substrate)

nucleation and growth of layers (structure, opto-electronic properties)

Interfaces properties

Film structure controlled by silane concentration



- Variable parameter

  Silane concentration (SC):

  $$\frac{SiH_4}{SiH_4 + H_2}$$

- Fixed parameters:

  Injected power 6W

  Frequency 110 MHz

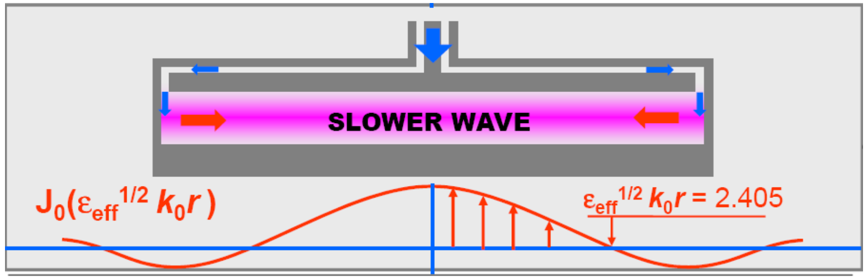
Transition a-si / μc-Si can be governed by Silane concentration

Increasing H/SiH_2 ratio → more crystalline films

PE-CVD reactor design and issues

- Edge effects: intense plasma can burn on edges of reactors or at reactor leaks creating gradient of species throughout the reactor !
- Species can retro-diffuse from open volumes where no plasma burns (e.g. silane from large chamber)
- In large reactors « standing wave appear » : no more homogeneous EM field (when reactor size > $\lambda/10$, non-uniformity starts to be observable)
- Globally all asymmetries (e.g. end of reactors) can lead to inhomogeneities
- Reactor cleaning/cross-contamination can be an issue
- At VHF: thinner sheaths (1-2 mm against 5-10 in RF) leads to easier parasitic plasma. VHF power coupling (skin effect) more delicate

RF frequency (MHz)	Wavelength λ (m)
13.56	22.11
27.12	11.05
40.7	7.37
60	5
81.38	3.68



Standing wave

In PE-CVD reactor

Parallel plate industrial systems

Oerlikon Solar

TFT 13 MHz, d=25 mm, 1.4 m2)

Solar: 40 MHz, d=25 mm, 1.4 m^2

Lens to compensate standing wave

d = interelectrode gap

AMAT (13MHz, d= ~13-20 mm)
5.6 $m^{2,}$ hollow cathodes to compensate
standing wave and incrase n_e

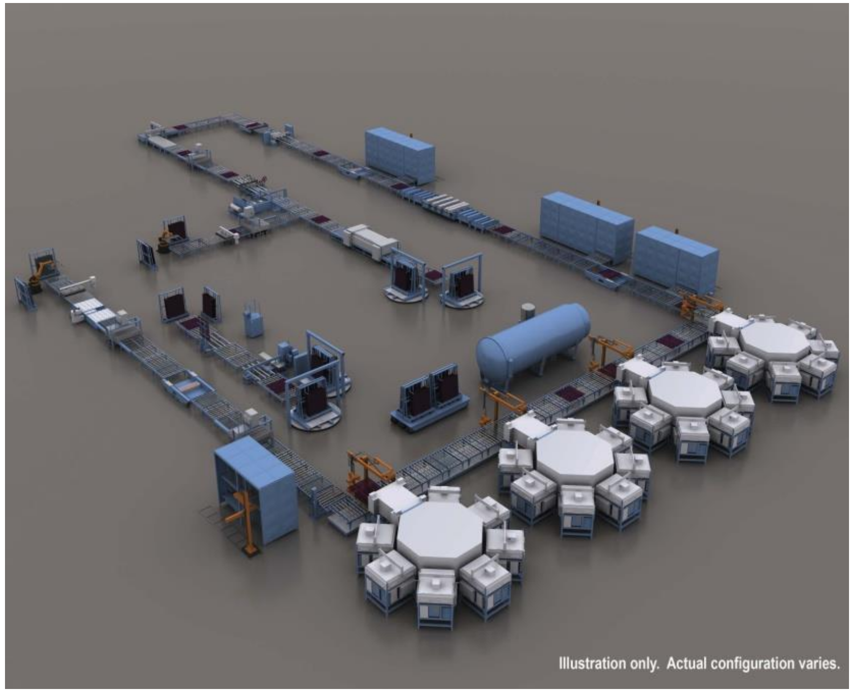


Illustration only. Actual configuration varies.

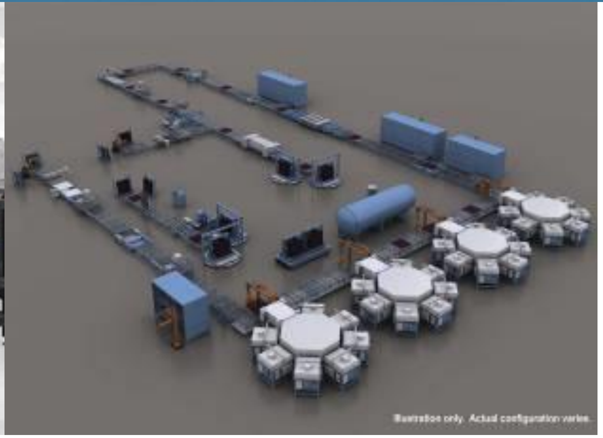
Applied films
(13 MHz, 1.8 m^2,
d= 13-15 mm)

Parallel plate industrial systems

Gen5 (1.4 m^2)
PECVD (e.g.
Oerlikon ThinFab)

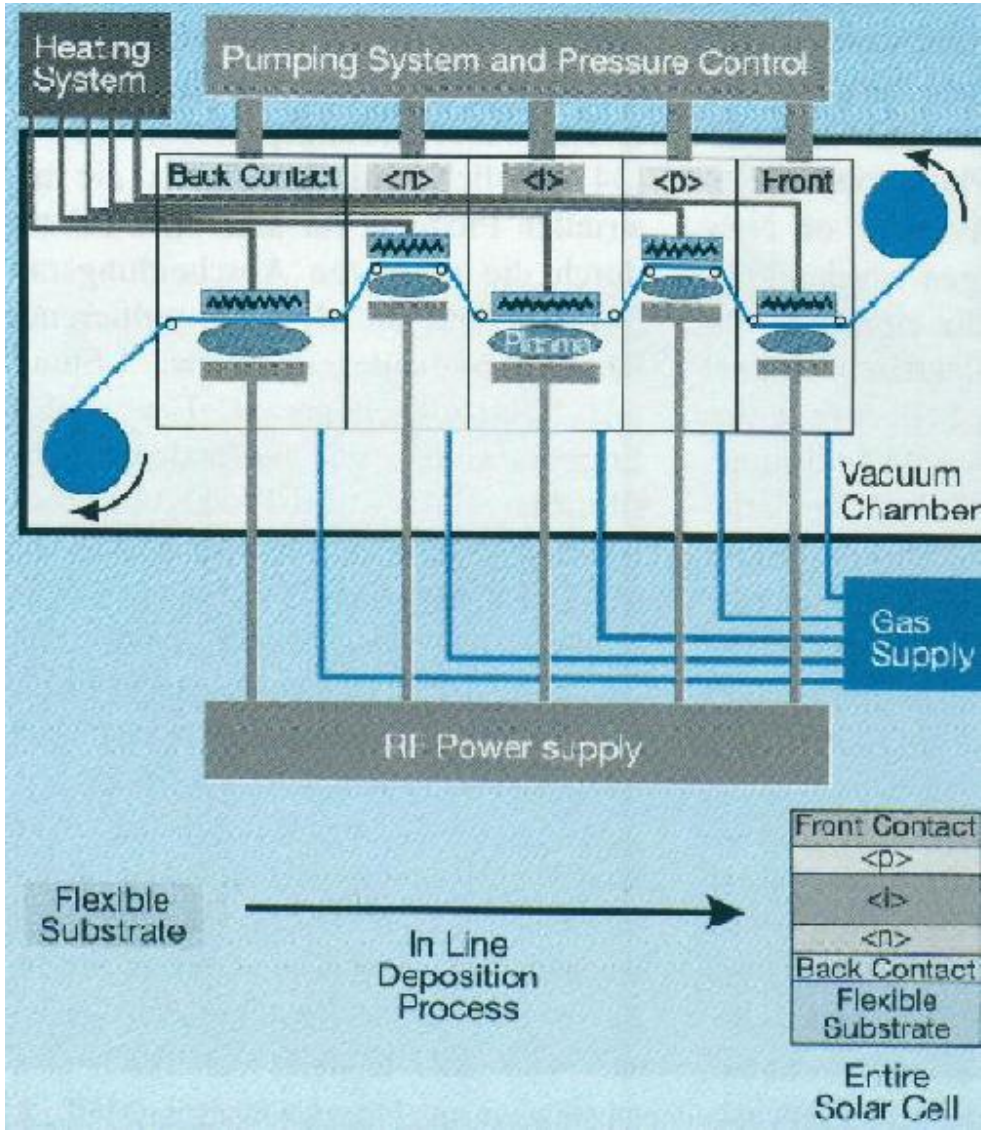
Octopus II. Indeotec

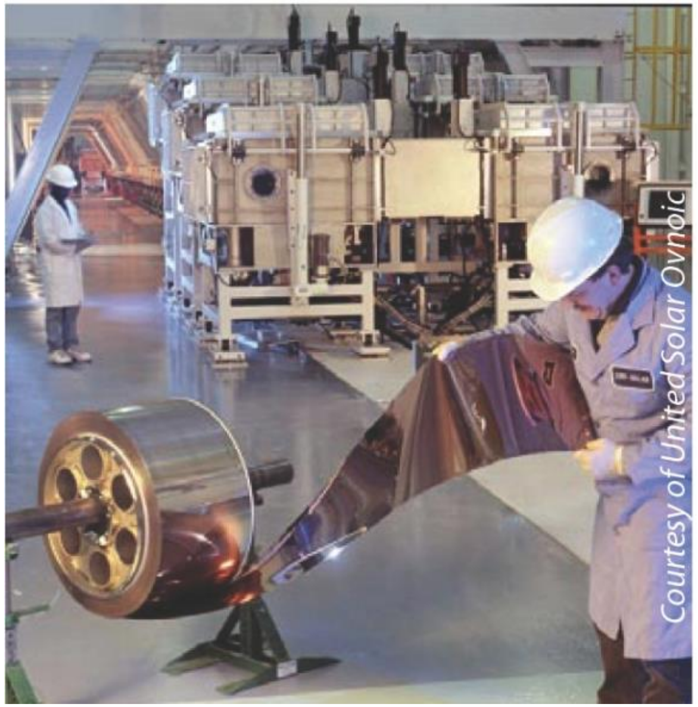
Gen7 (5.3 m^2)
PECVD cluster
(Applied Materials)



Other suppliers: Leybold, Ulvac,….

Roll-to-Roll reactors





Challenges for PE-CVD

Scientific:

- Understand what governs the growth of a good material (role of precursors, energy,…)
- Understand fully why material quality degrades when deposition rate is increased

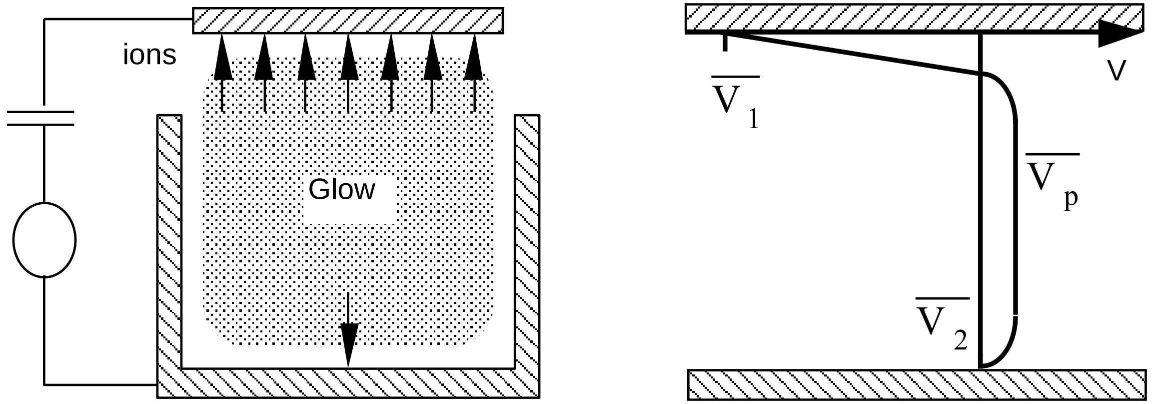
Technical:

- Achieve high deposition rate (currently ~ 0.5 nm/s)
- Achieve homogeneous layer deposition (especially critical for µc-Si, a material close to the transition when good)
- Realize cost effective systems if dep. rate not high enough
- Reduce cleaning costs and environmental impact (less or no NF_3 or SF_6 gases or mechanical cleaning) or use F_2 (no greenhouse equivalent)

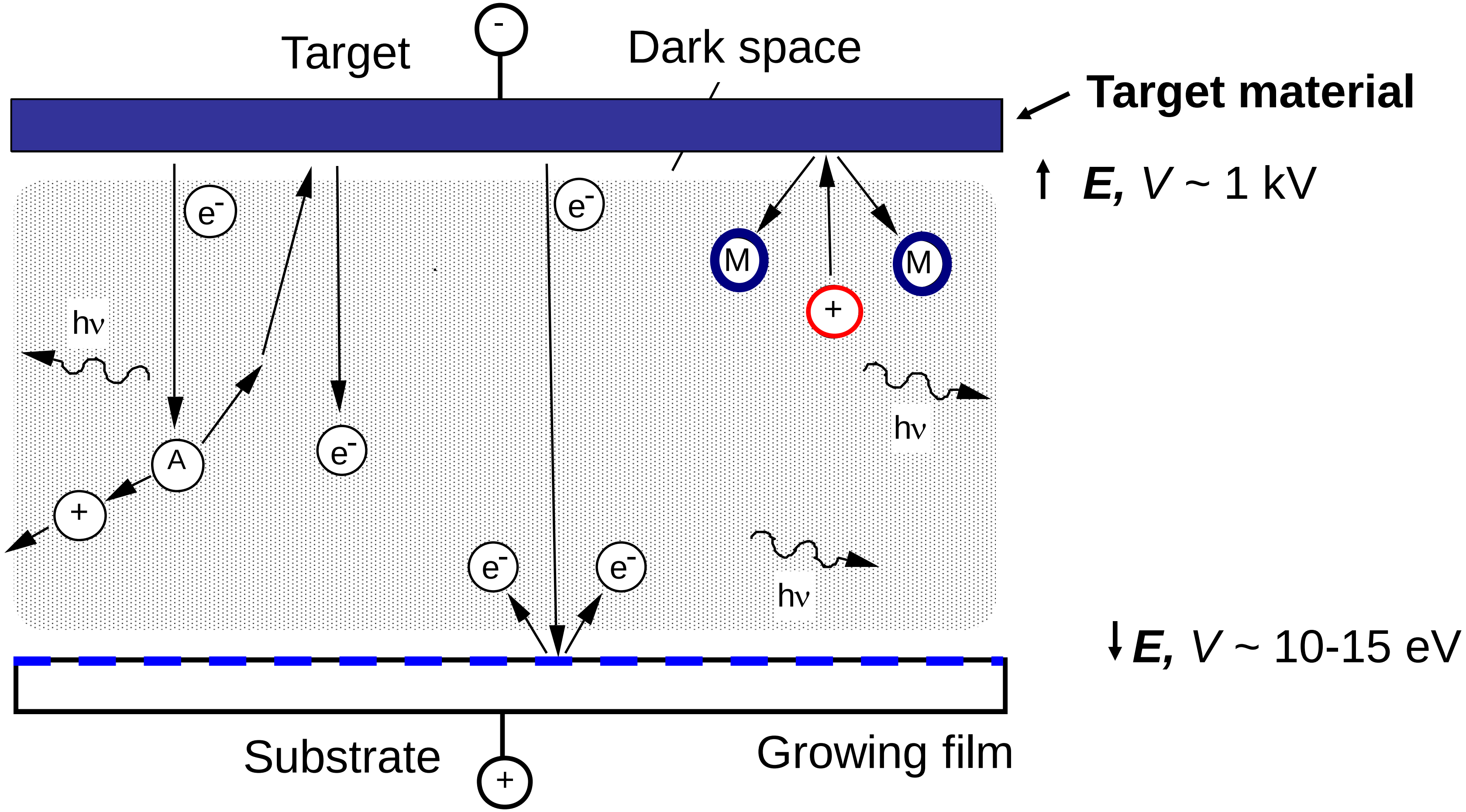
Physical Vapor deposition (PVD): Sputtering

In **sputtering processes**, asymmetry of electrodes area (RF case using large chamber walls area) or DC voltage applied to electrode: ions accelerated in the strong potential at the cathode sheath (e.g.) Ar^+ ions +) and hit a *target* (material to be deposited).

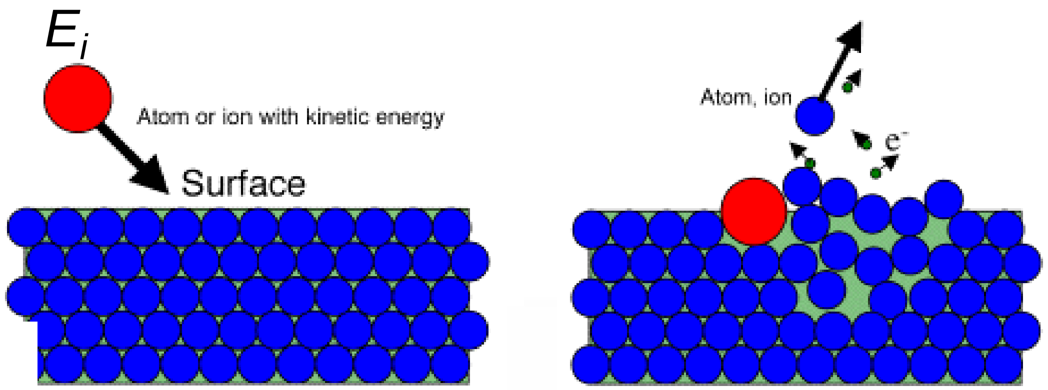
ii. Sputtering of target



Physical Vapor deposition (PVD): Sputtering



Sputtering

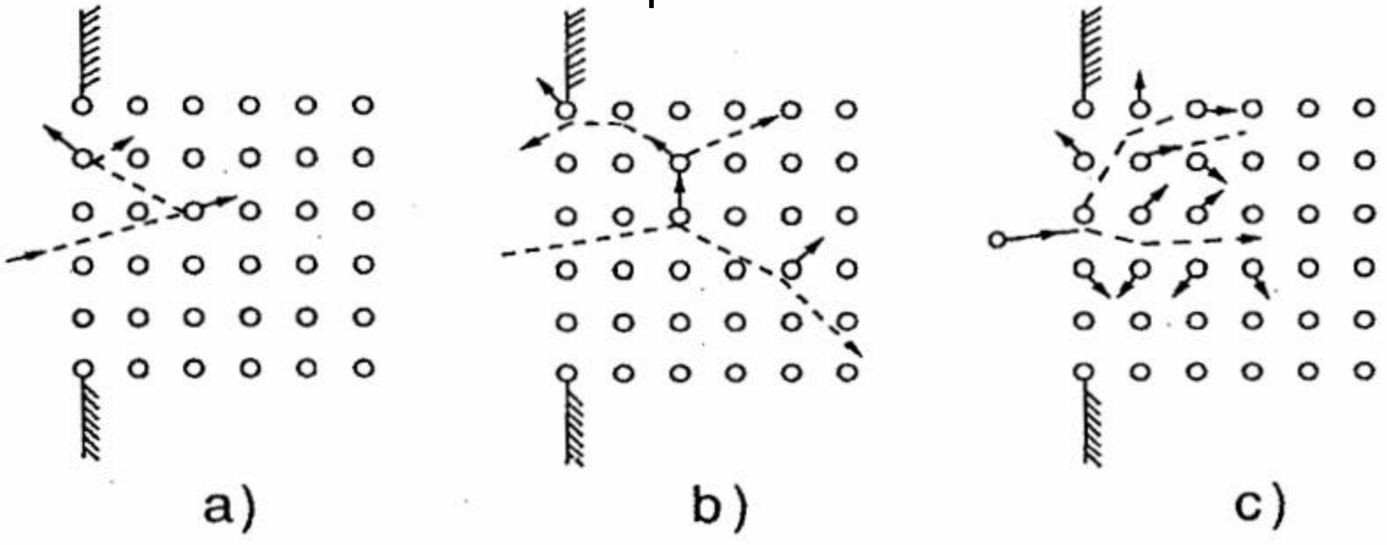


Atomic pool !

Sputtering yield:

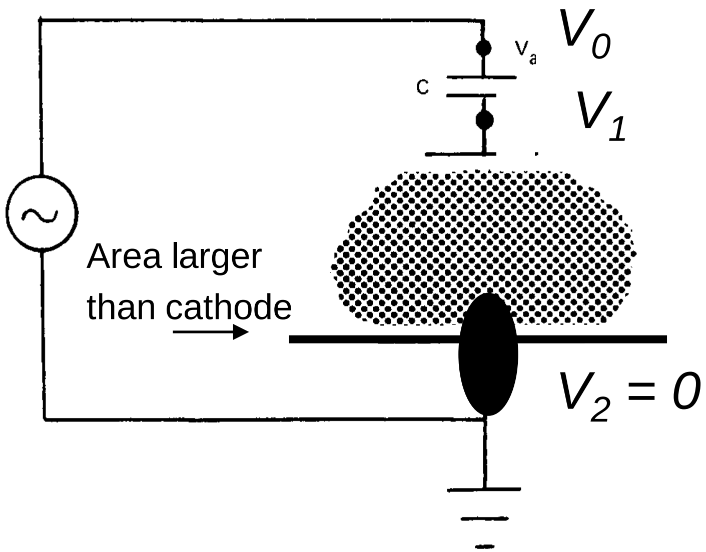
$$Y(E_i) = \frac{\text{Number of sputtered atoms}}{\text{incident particle}}$$

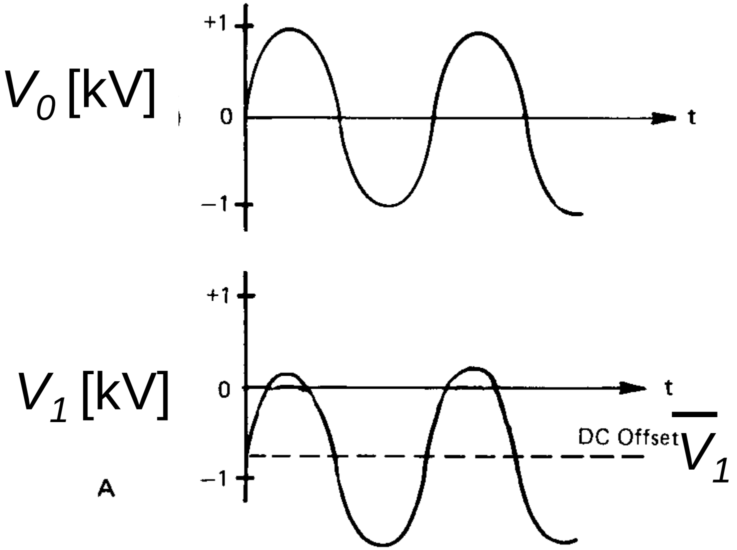
Typical Y value = 0.1-10

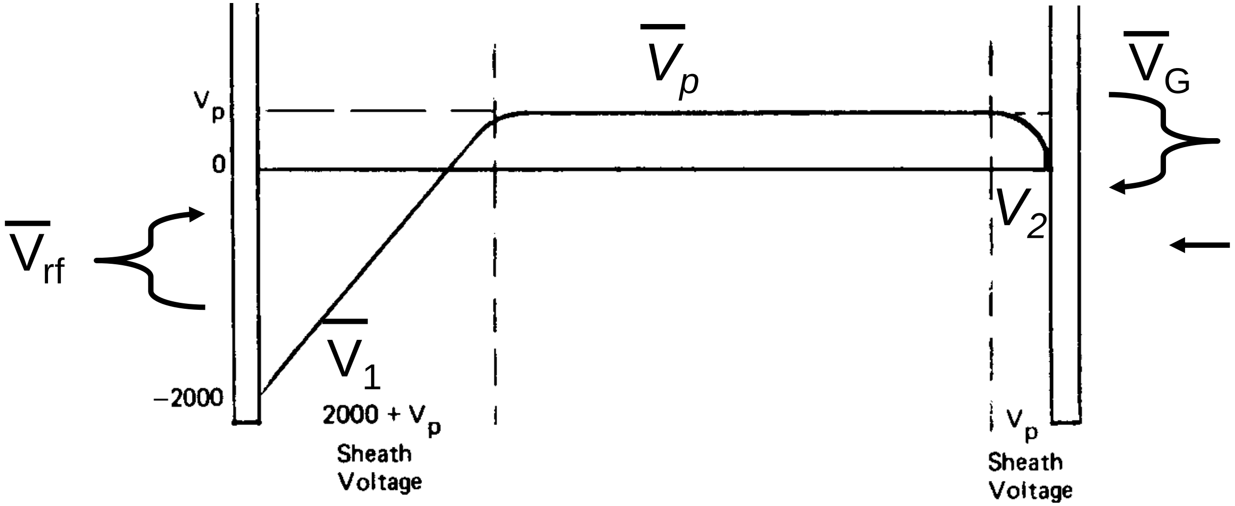


Sputtering a) single Knock-on (low E_i) b) linear cascade c) spike (high E_i)

Radio-frequency RF Sputtering

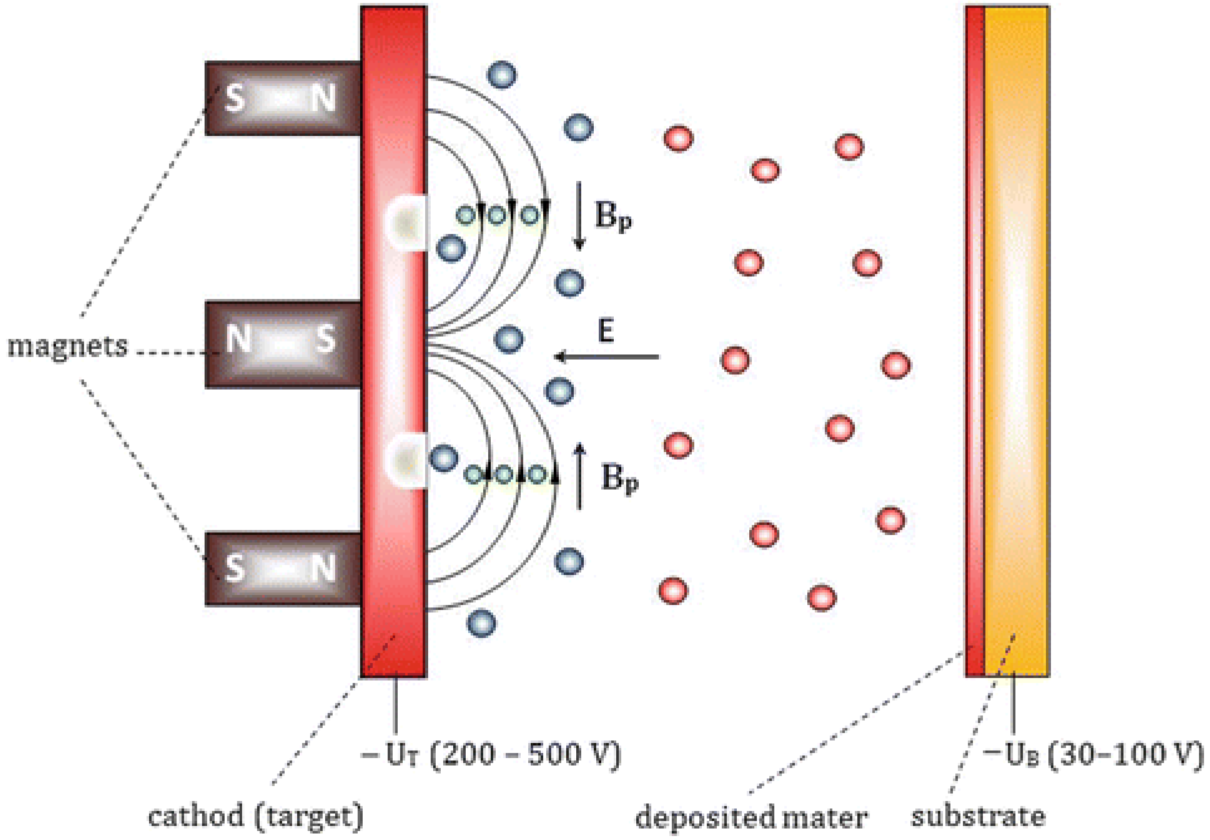






Time dependant and average potential in capacitive RF discharge

Magnetron Sputtering



● = argon gas atoms which are ionized by the **E** field

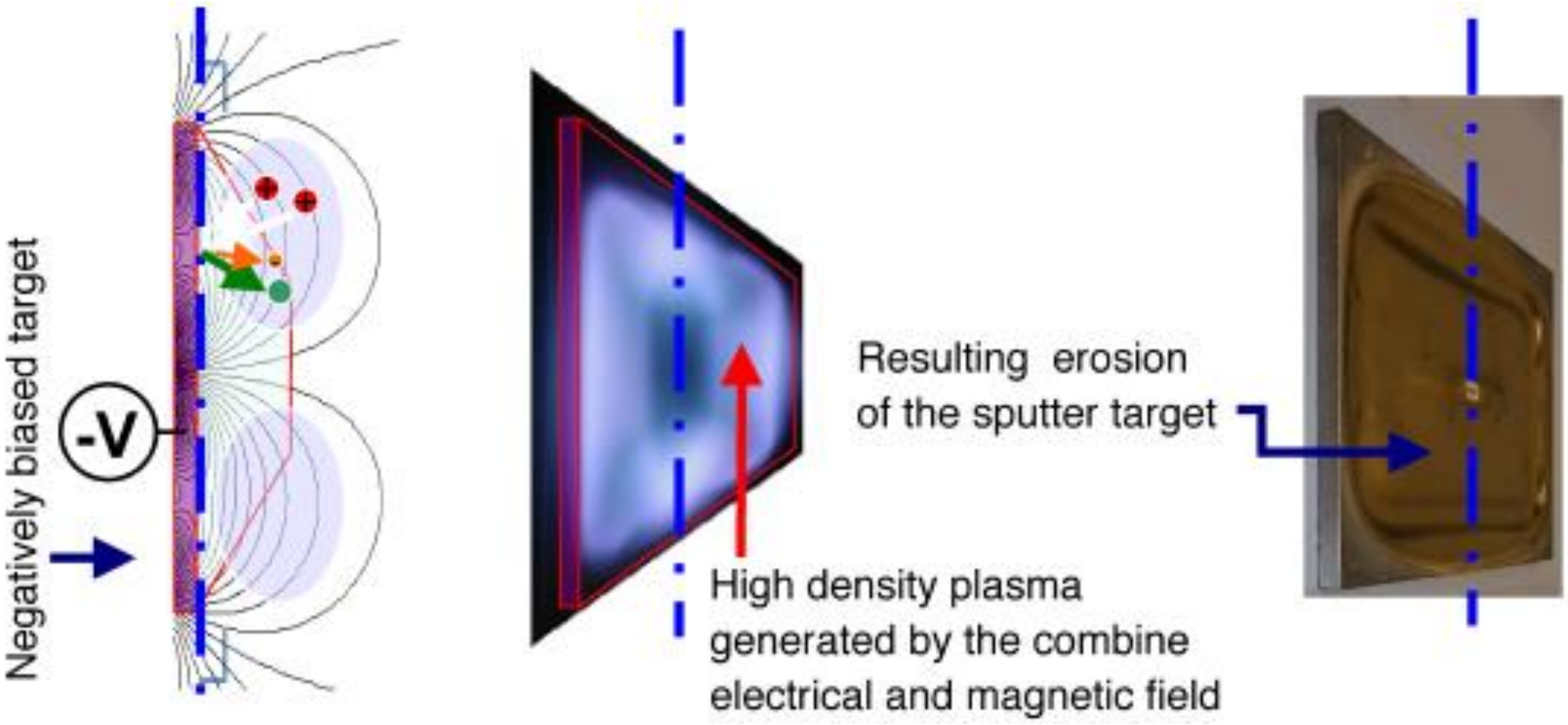
○ = trapped electrons

● = ejected (sputtered) target particles

Magnetron Sputtering

Increase density and localisation of plasma:

i.e. higher deposition rates



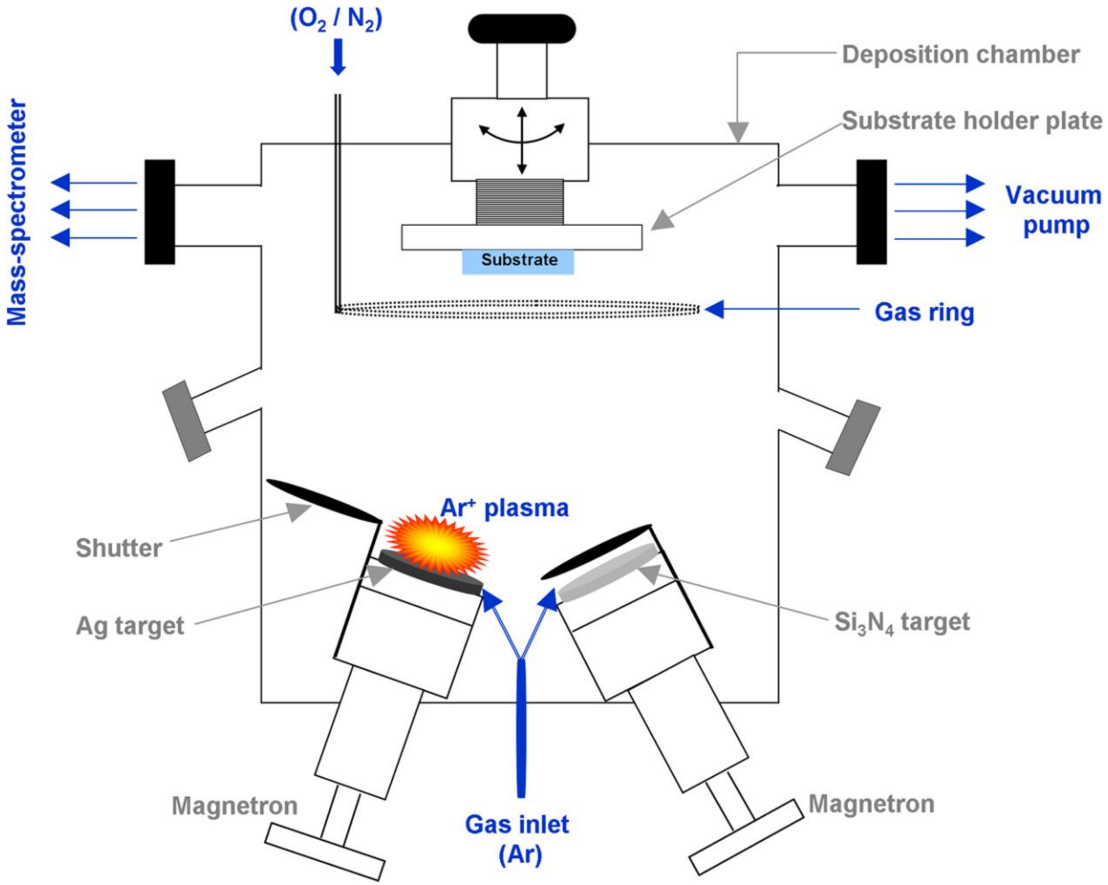
Problems with magnetron: inhomogeneous use of the target

In-line sputtering systems

Rotary Magnetron Sputtering

- Higher deposition rates than conventional planar magnetrons.
- Higher target utilization efficiency (particularly important for expensive materials).
- Cost of cylindrical targets higher than planar ones.

R&D sputtering systems



Reactive sputtering examples:

Zn (target) + O_2 (gas) → ZnO

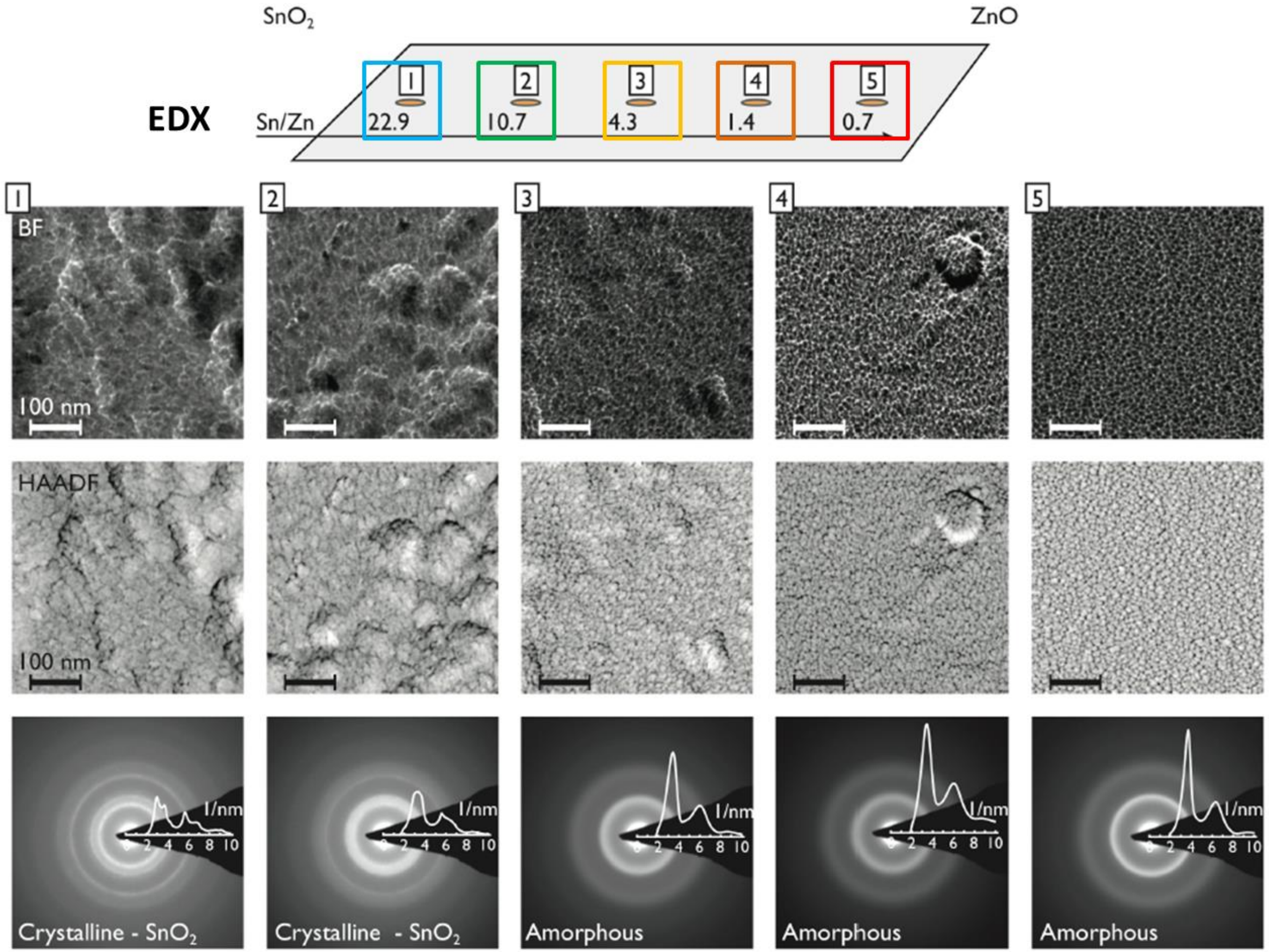
Cu (target) + H_2S (gas) → CuS_2

Co-sputtering deposition:

Use in small areas to develop new materials

Combinatorial study

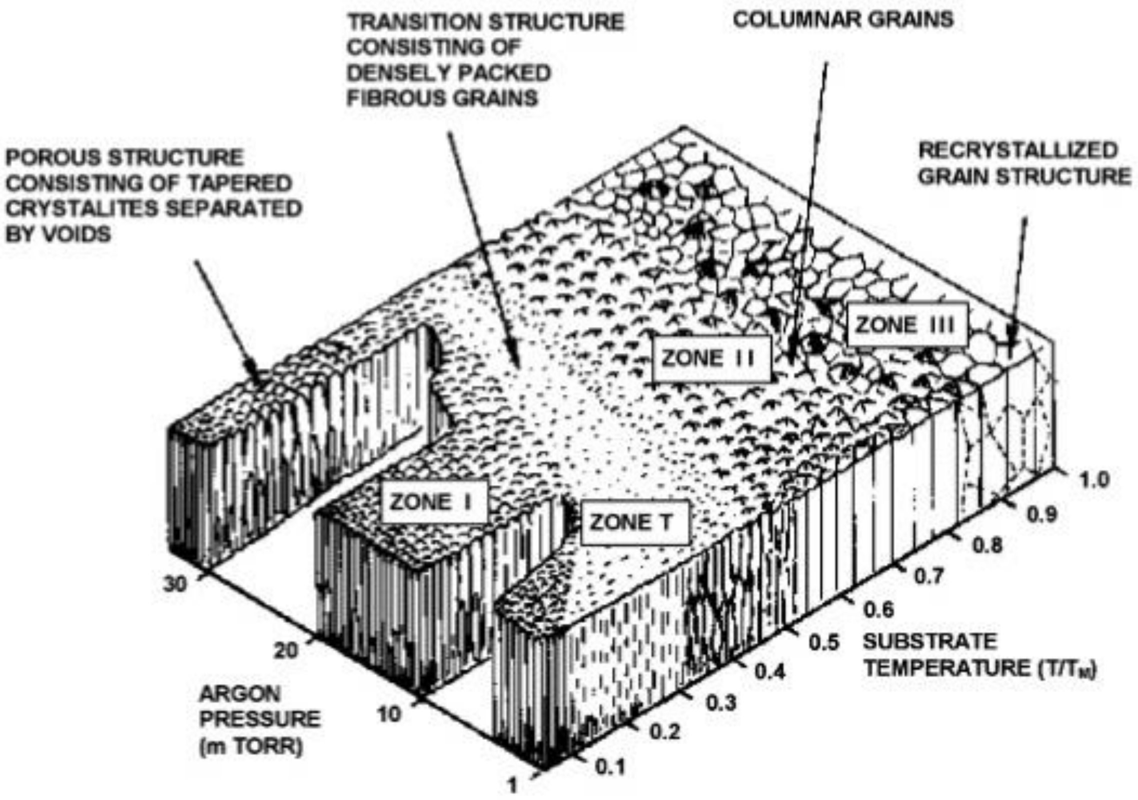
- For example, study of SnO_2-ZnO co-sputtering



Ref. *M. Morales-Masis, et al.* ***Adv. Funct. Mater****. 26, (2016) 384-392*

Sputtering parameters and film morphology

Structure zone indicating the relation between the deposition parameters (working pressure -Ar, O_2, reactive gasses- and temperature) on the final microstructure of thin films (dense amorphous, fibrous, porous, large-grain films).



Ref. Thornton, JVST 1982

In-line sputtering systems

The BigMag was the first cathode with separated targets on the market.

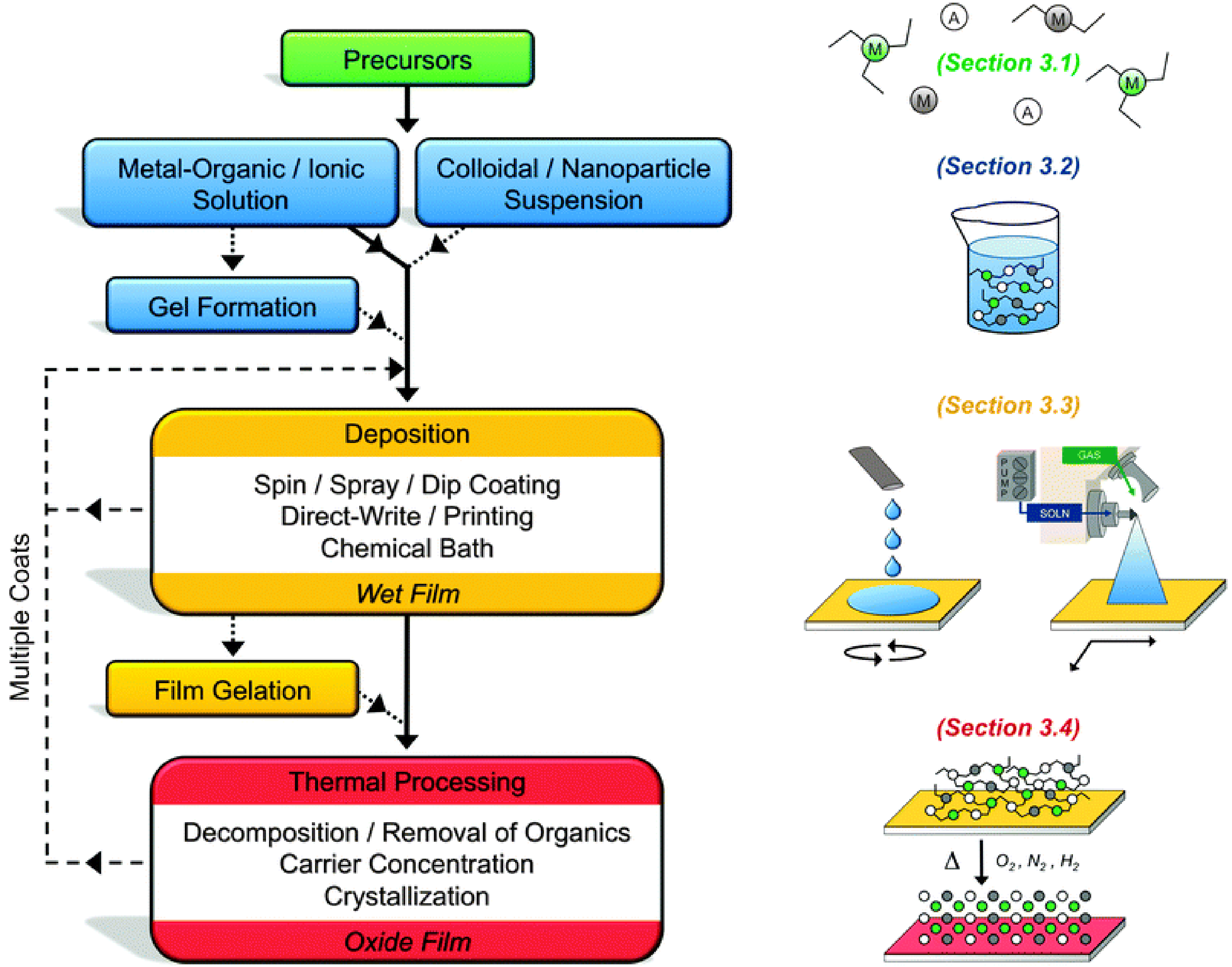
The unique magnet design uses rotating magnet systems.

Used mostly for transparent conductive oxides and metallic layer

- ITO (In_2O_3:Sn) →TCO for flat screen display
- ZnO: front TCO for PV, thin dielectric for backside
- Antireflection coating
- Optical stack for architectural glasses
- Metallic layer for packaging
- ….

Line for sputtering of architectural glass, 3.210 x 6.000 mm^2

Printing



Precursors

Metal-Organic / Ionic Solution

Colloidal / Nanoparticle Suspension

Gel Formation

Multiple Coats

Deposition

Spin / Spray / Dip Coating
Direct-Write / Printing
Chemical Bath

Wet Film

Film Gelation

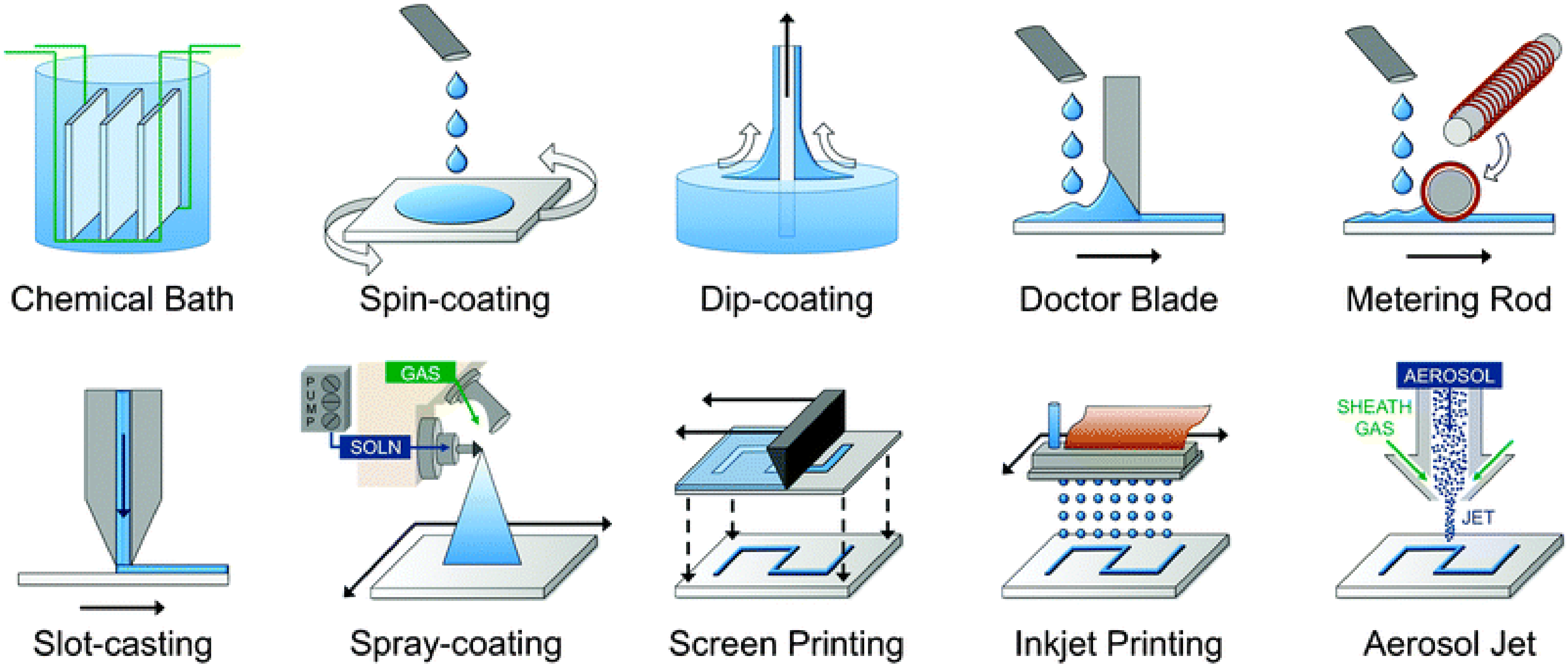
Thermal Processing

Decomposition / Removal of Organics
Carrier Concentration
Crystallization

Oxide Film

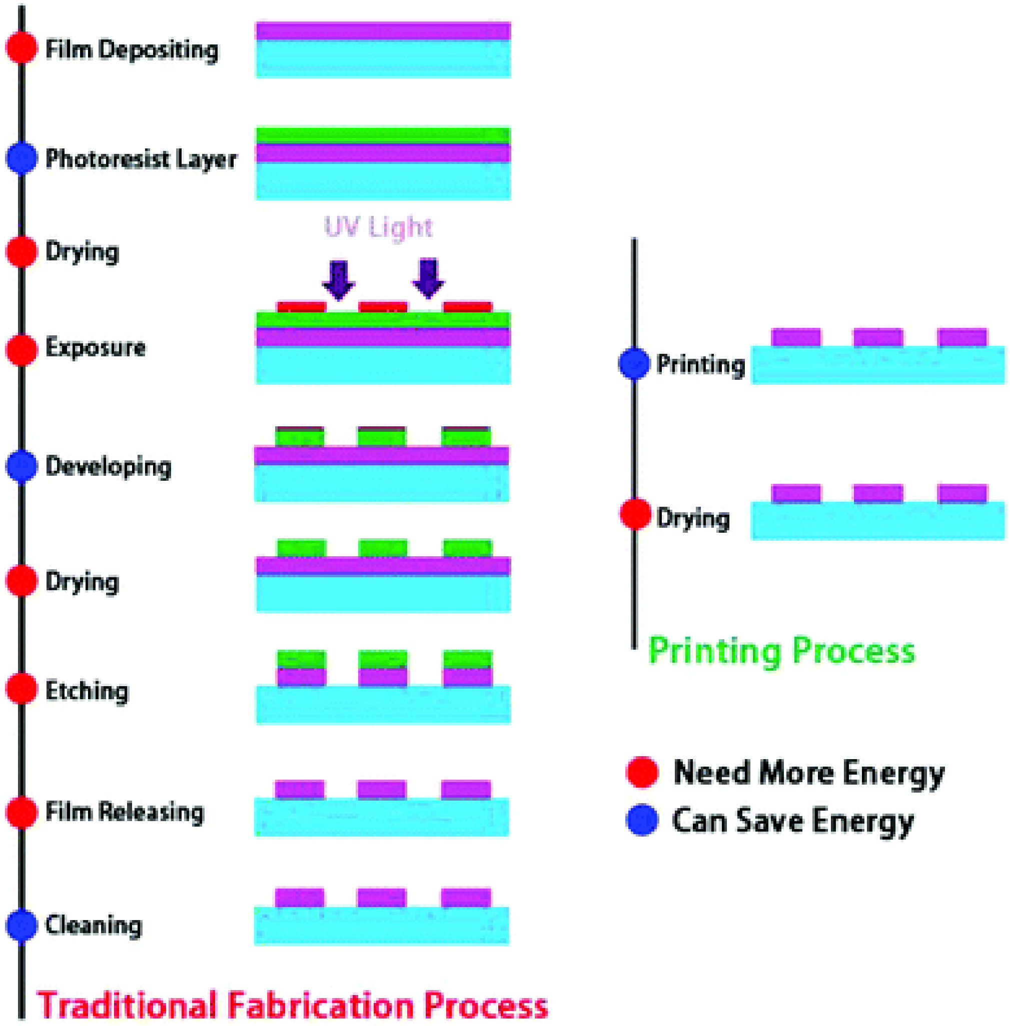
Robert M. Pasquarelli et al. (2011), DOI: 10.1039/C1CS15065K

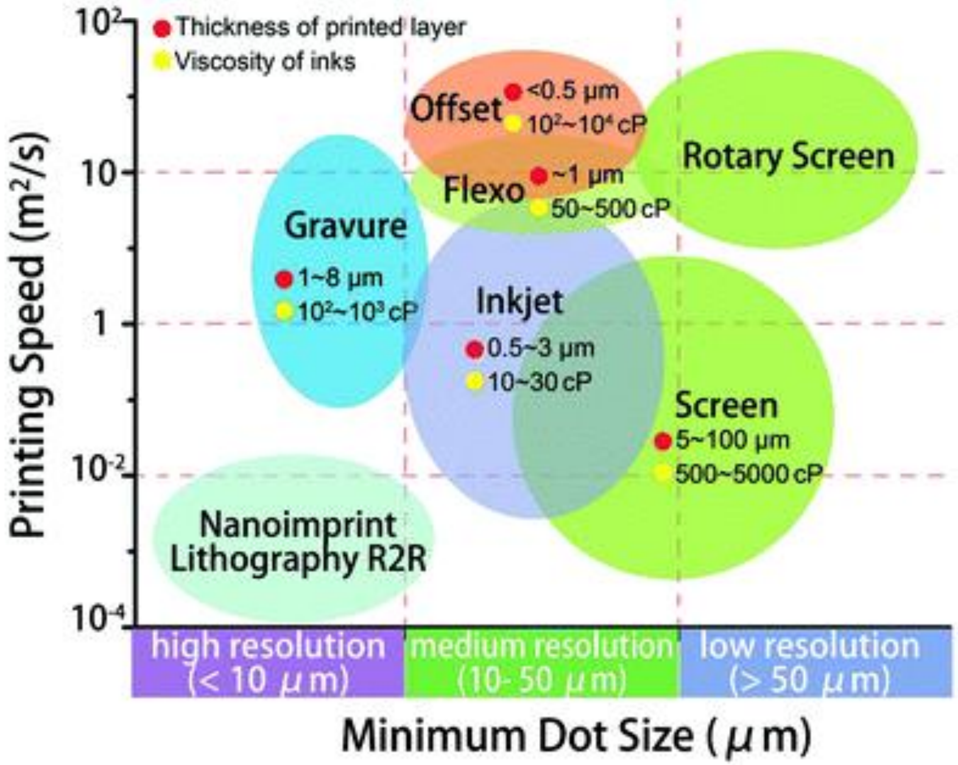
Printing technique



Robert M. Pasquarelli et al. (2011), DOI: 10.1039/C1CS15065K

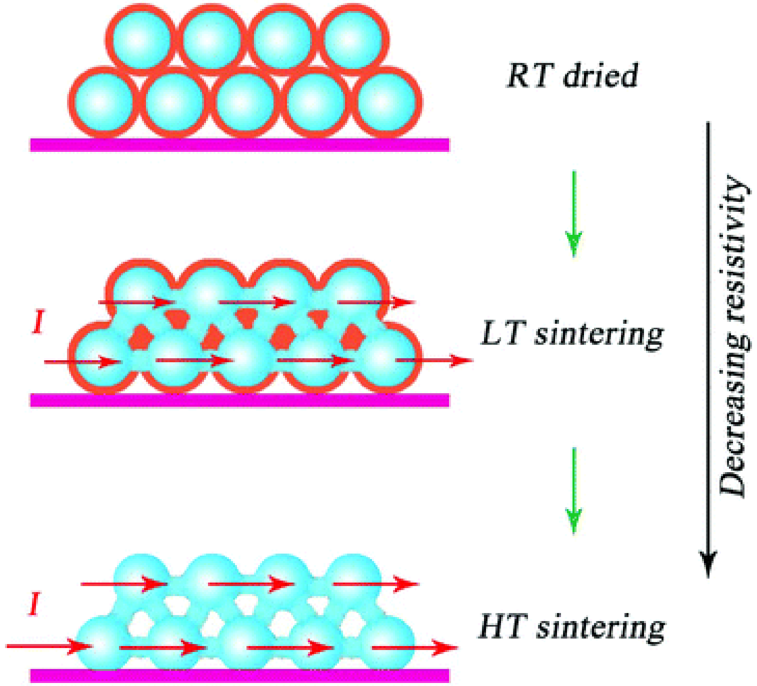
Printing vs. Film deposition

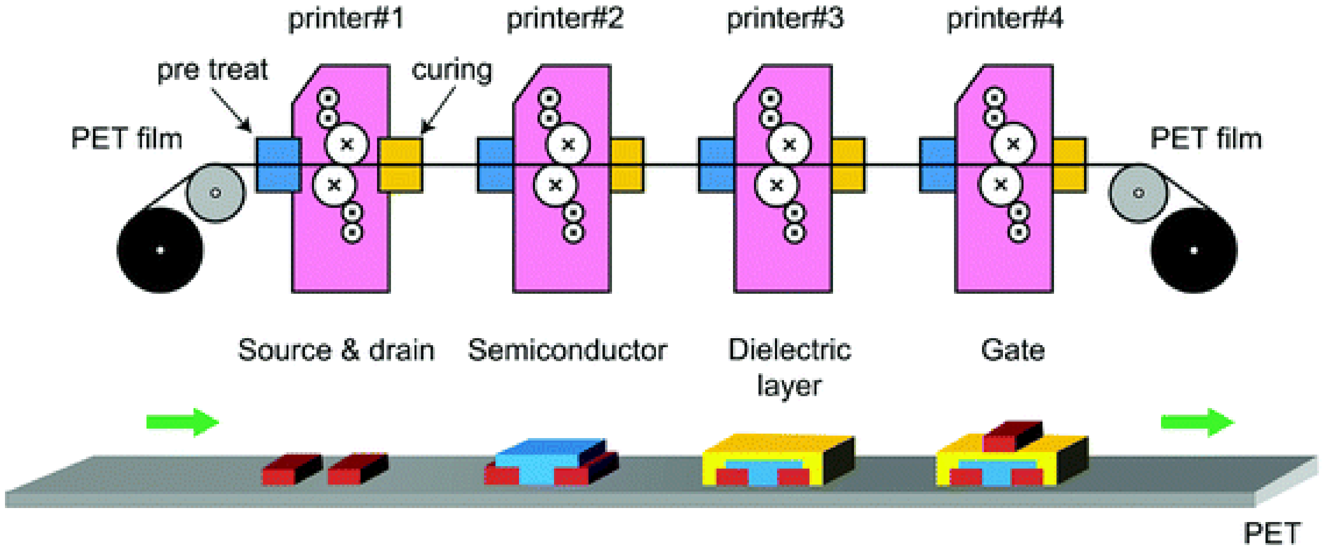




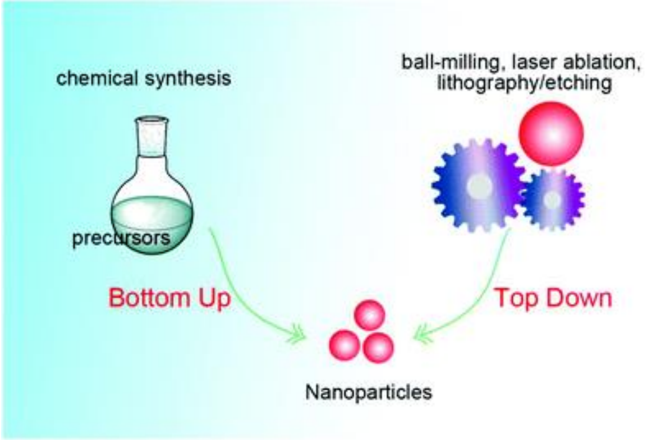
W. Wu (2017), DOI: 10.1039/C7NR01604B

Roll-to-roll transistor printing





- Printing needs formulation of precursors (ink formulation)
- Ink needs to have the right properties (viscosity, density, surface tension, etc.) adapted to the right printing technique → **printability!**



W. Wu (2017), DOI: 10.1039/C7NR01604B

Summary

You should

- Be able to describe a plasma (formation, nature, types,…)
- Know the working principle of PE-CVD and sputtering
- Understand the formations of sheaths
- Understand the voltage drop at sheath (V_p, V_f) and the origin/role of ion bombardment
- Know the difference between pure CVD, PE-CVD and sputtering
- Understand that PE-CVD or sputtering parameters may affect film properties
- Know the basics of printing