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PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes
2 February	Fabrication methods - Plasma-surfaces interactions and diagnostics
9*	Fabrication methods – Thermal/Plasma spray technologies
16***	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1* March	*Presentations – Emerging fabrication techniques (30%)*

March 4-8 - Winter/Spring break

15***	Tribomechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact
19***	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

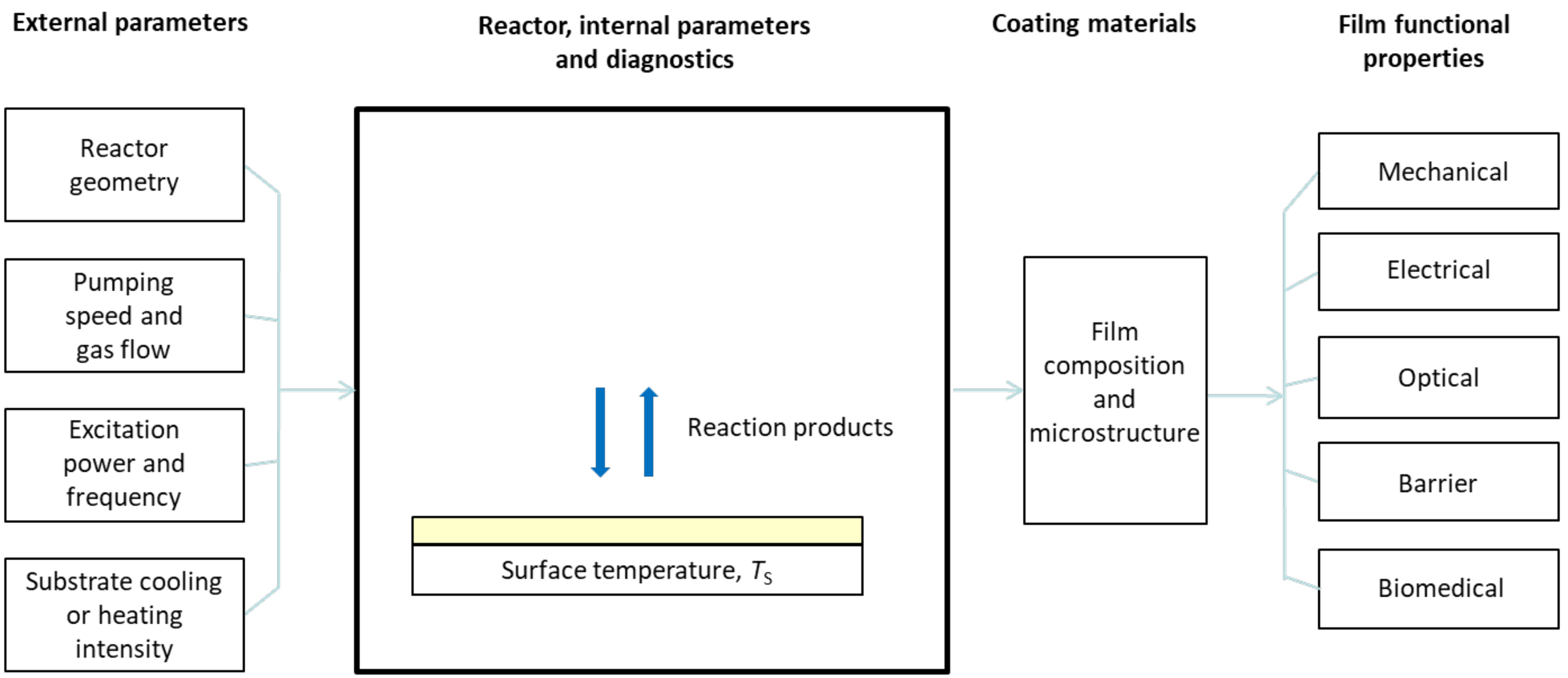
Projet #3 – Application of nanostructred thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Report and presentation: **19 April**

Thin film processes



Today:

Basics of vacuum physics and technology – Vacuum systems
Deposition processes
Physical vapor deposition (PVD)
Basics of plasma processes
Plasma-based processes
Chemical vapor deposition (CVD)

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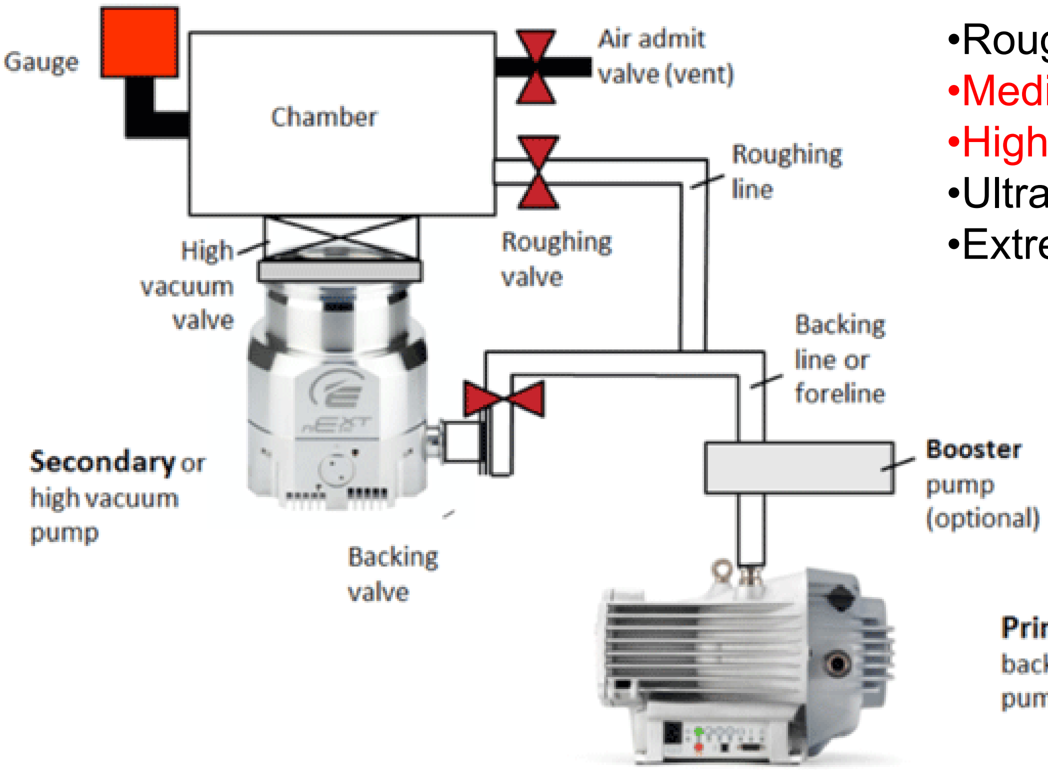
Deposition system



- Rough/Low Vacuum: > Atmosphere to 1 Torr
- Medium Vacuum: 1 Torr to 10^{-3} Torr
- High Vacuum: 10^{-3} Torr to 10^{-7} Torr
- Ultra-High Vacuum: 10^{-7} Torr to 10^{-11} Torr
- Extreme High Vacuum: < 10^{-11} Torr

https://vacaero.com/information-resources/vacuum-pump-technology-education-and-training/1039-an-introduction-to-vacuum-pumps.html

Gas-surface interactions at low pressure

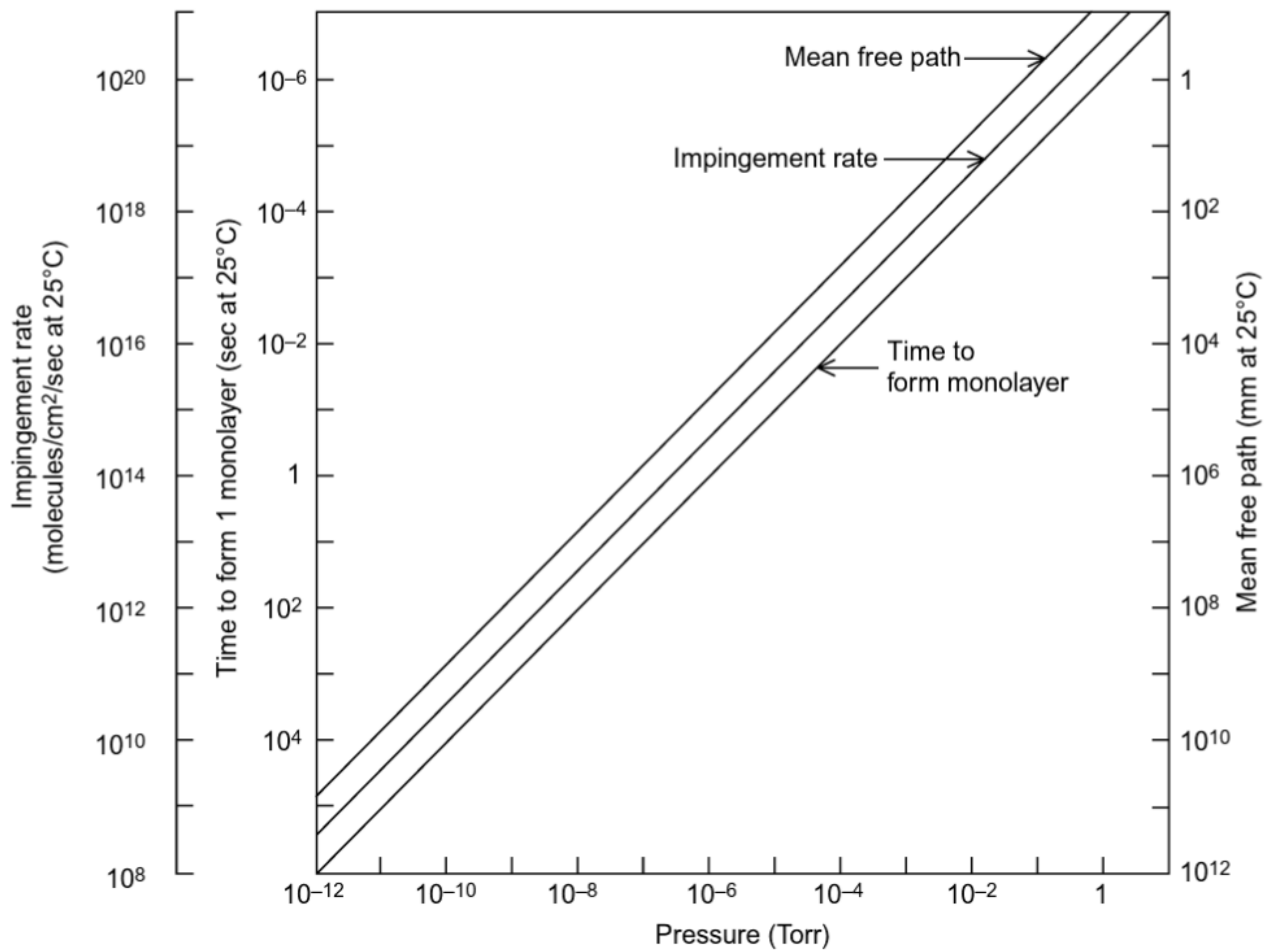
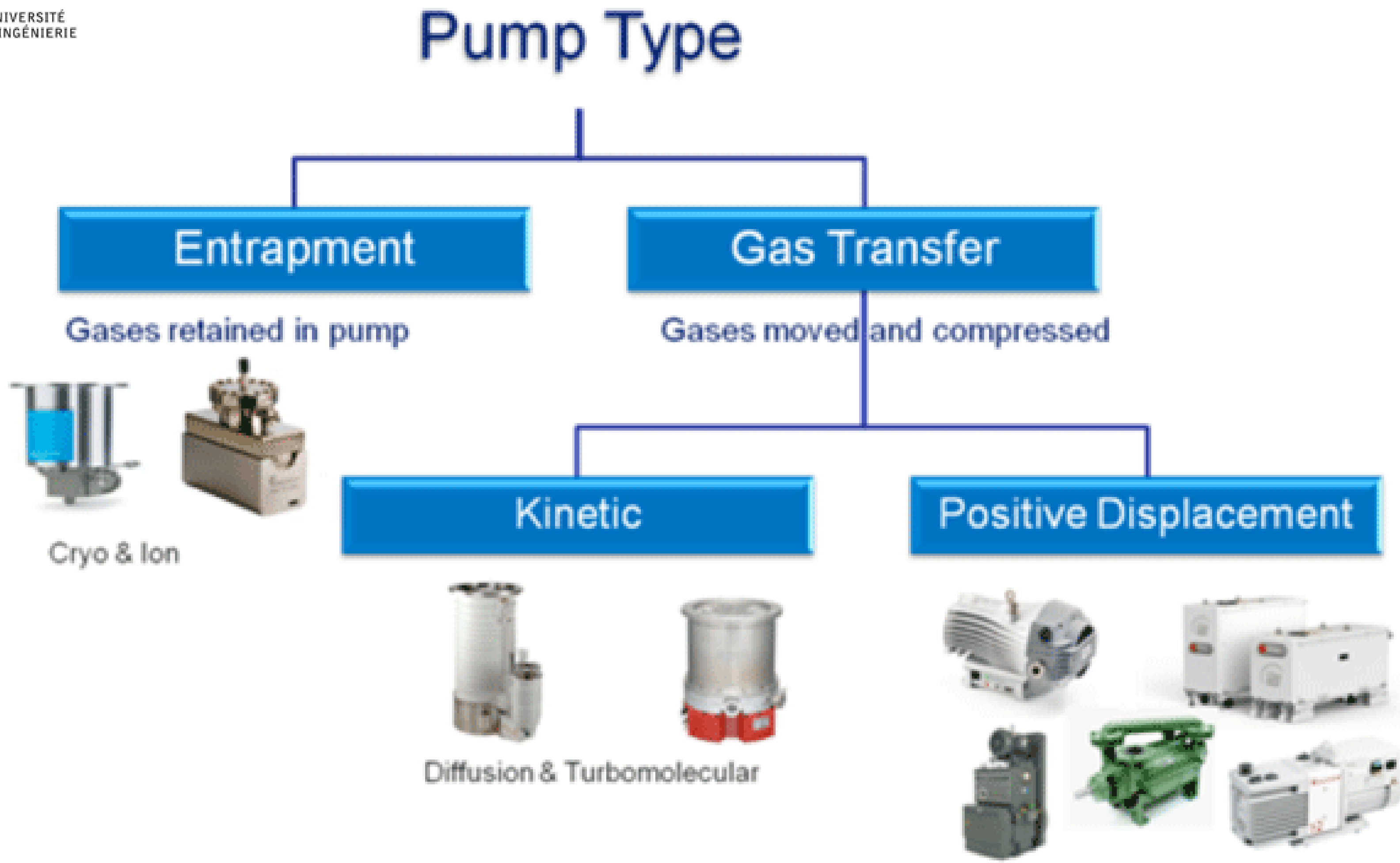


Figure 3.2: Mean Free Path, Impingement Rate, and Time to Form a ML as a Function of Gas Pressure at 25°C

Handbook of Physical Vapor Deposition (PVD) Processing

De Donald M. Mattox
ÉDITEUR
Elsevier Science & Technology Books
DATE
2010-04-29

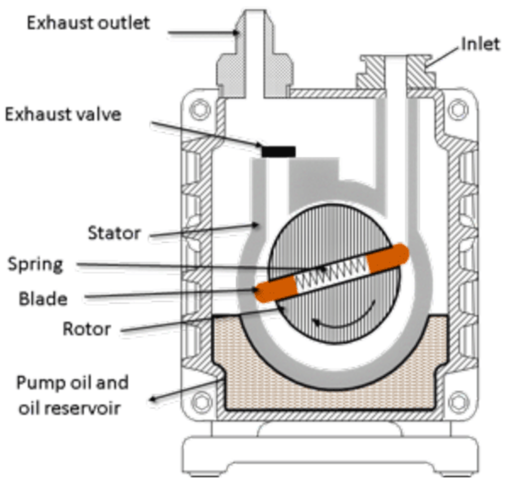


Secondary pumps: from medium to high/ultrahigh vacuum

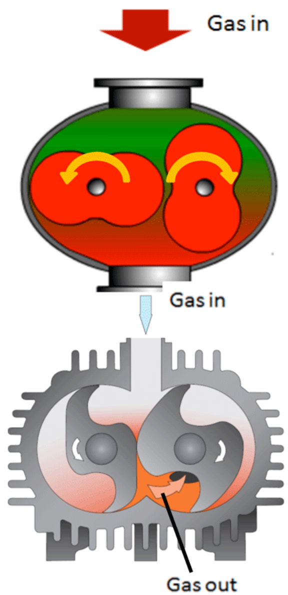
Primary pumps: from atm to medium vacuum

https://vacaero.com/information-resources/vacuum-pump-technology-education-and-training/1039-an-introduction-to-vacuum-pumps.html

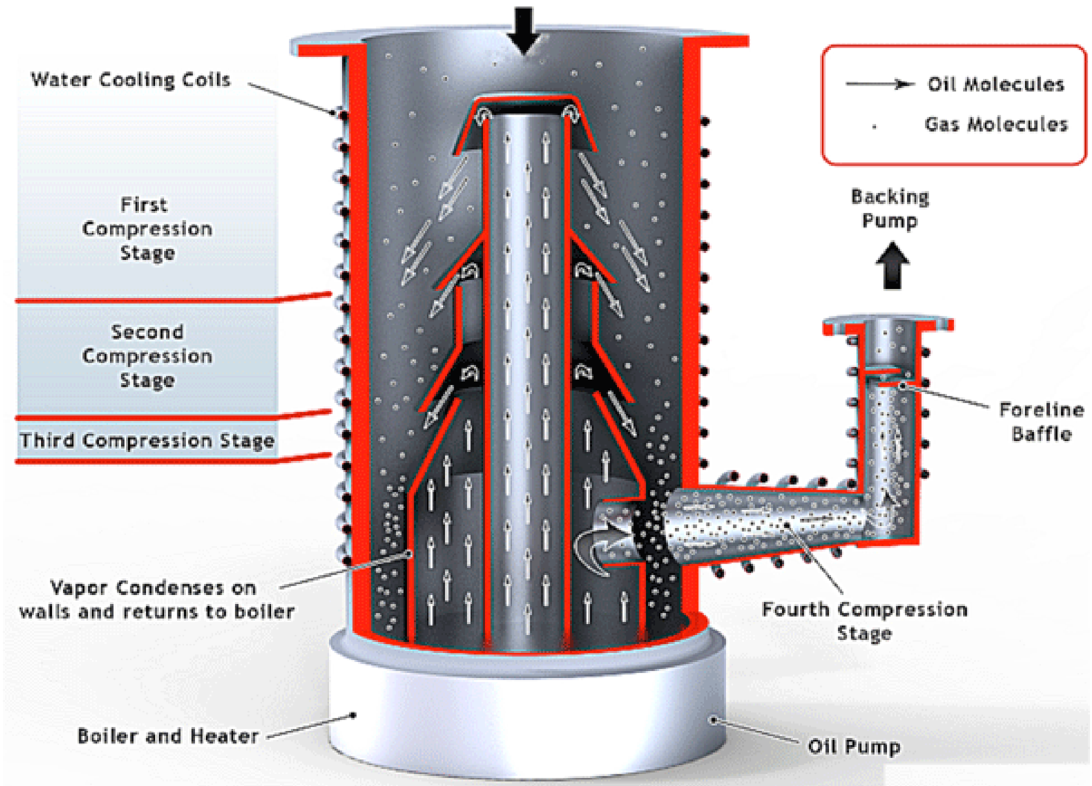
Vacuum pumps



Mechanical (rotary) oil or dry pumps

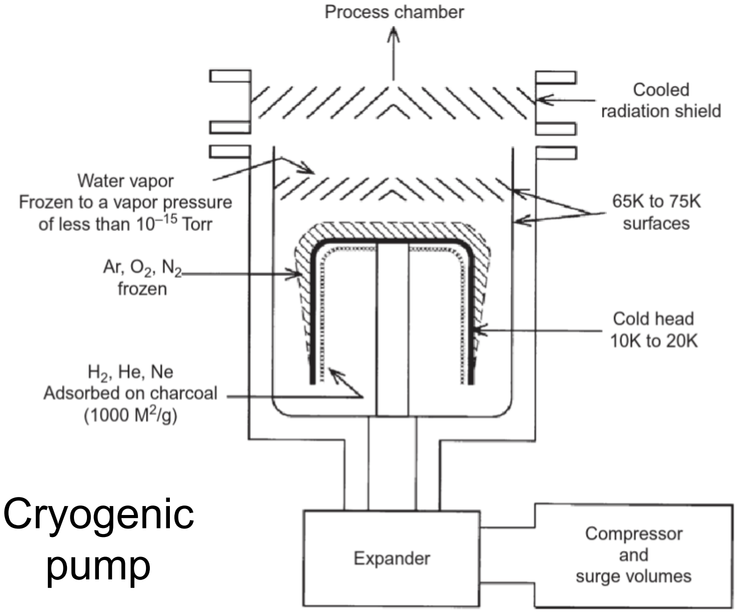


Roots pump



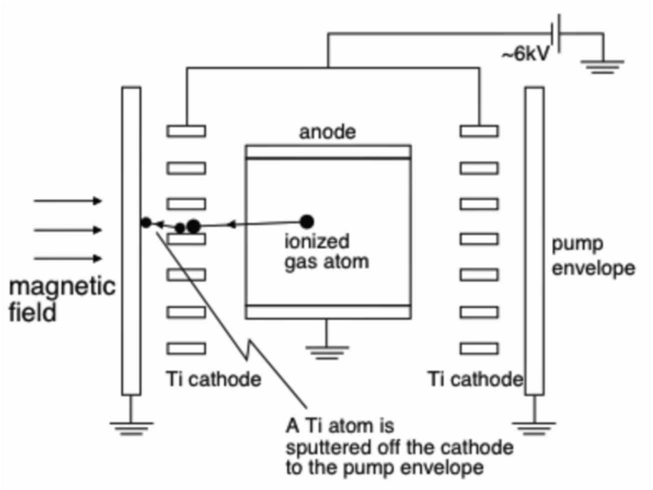
Diffusion pump: mercury, oil

Vacuum pumps



Cryogenic pump

Figure 3.18: A Cryopump



Ionization pump

Pumping speed and pressure

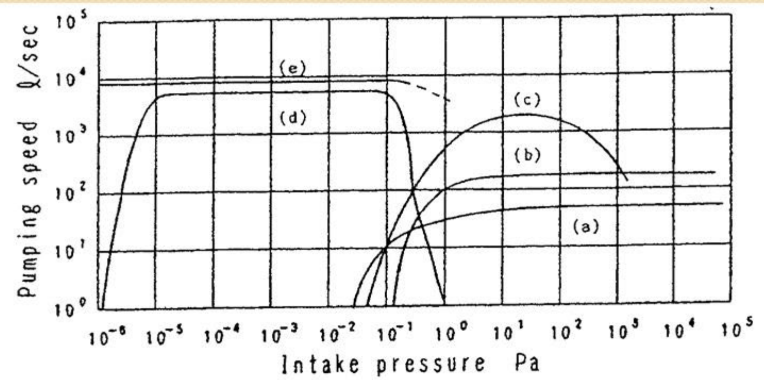
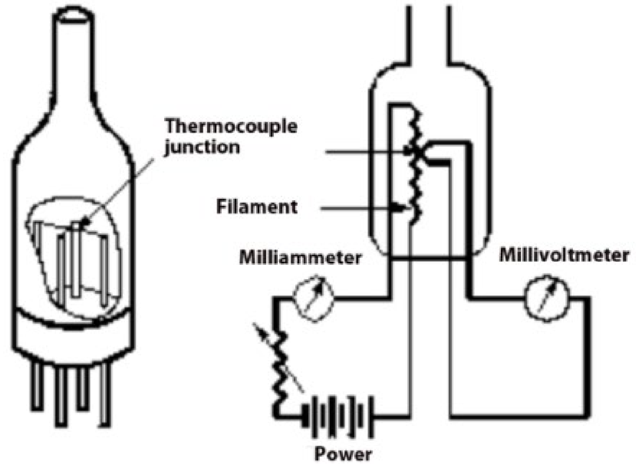
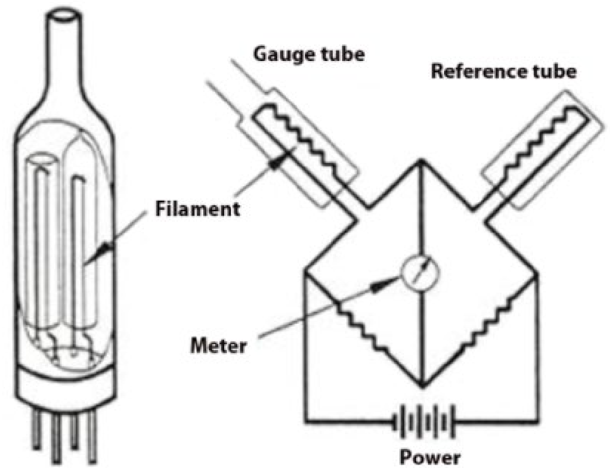


Fig. 3 Typical pumping speed as a function of intake pressure. (a) Rotary vane pump, (b) Kinney pump, (c) Roots pump, (d) Diffusion pump, (e) Turbo molecular pump.

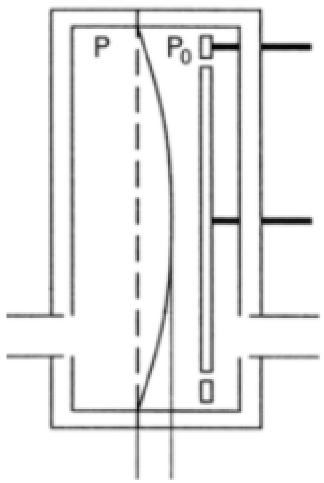
Vacuum gauges – medium vacuum (0.1 mTorr+)



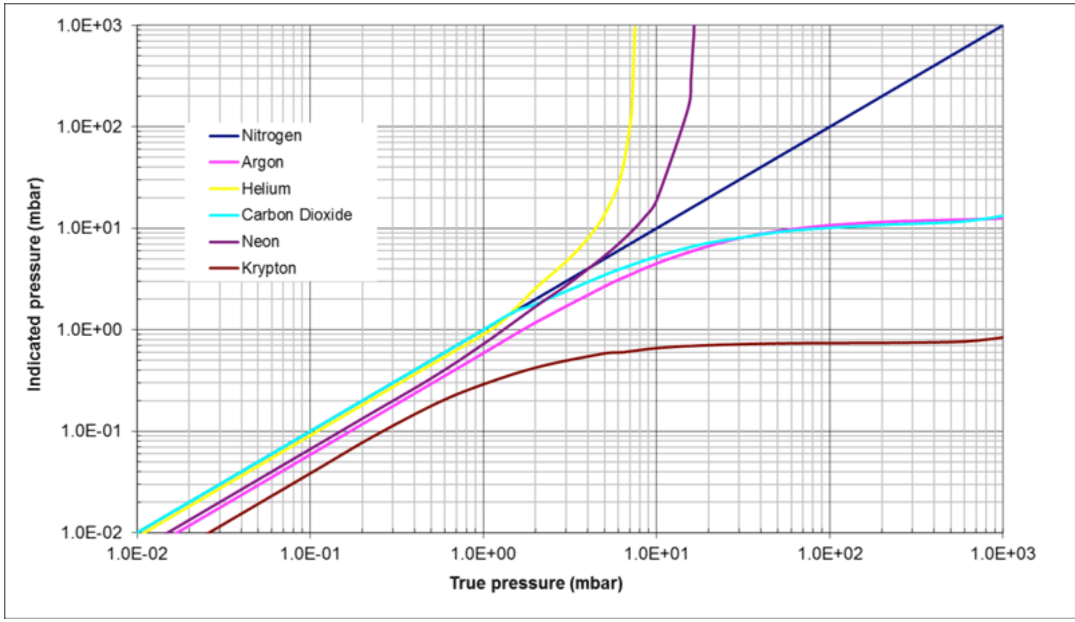
Thermocouple gauge



Pirani gauge



Capacitace (diaphragm) gauge



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Vacuum gauges – high/ultrahigh vacuum (< 1 mTorr)

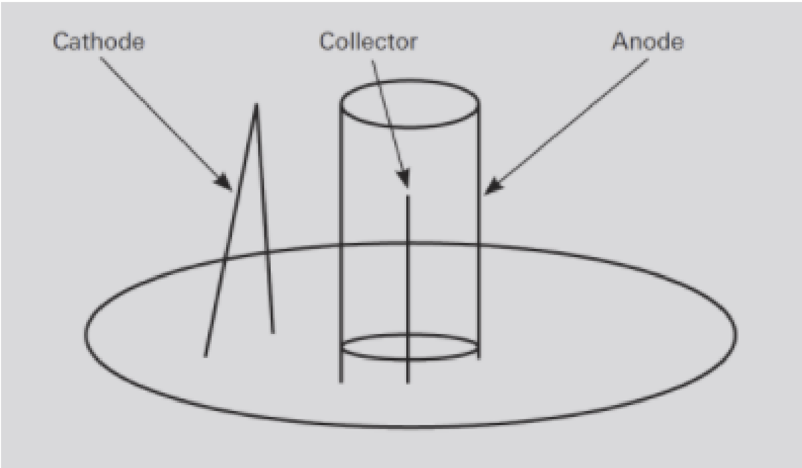


Figure 5.7: Design of a Bayard-Alpert vacuum gauge

Hot cathode ion gauge

Cold cathode ion gauge (Penning)

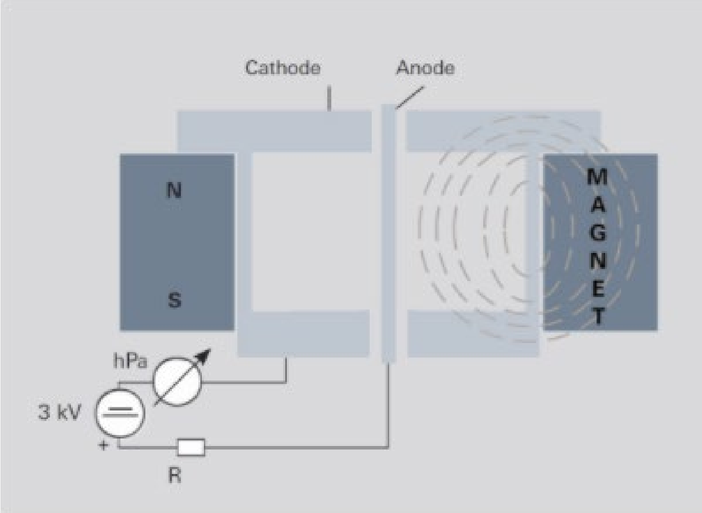
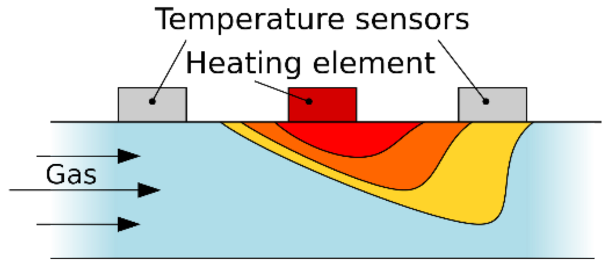
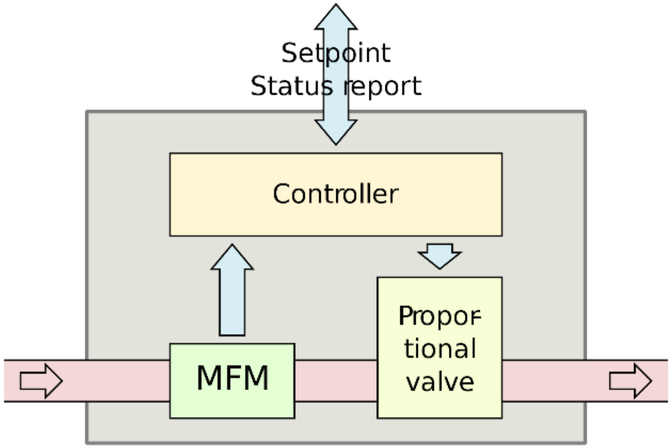
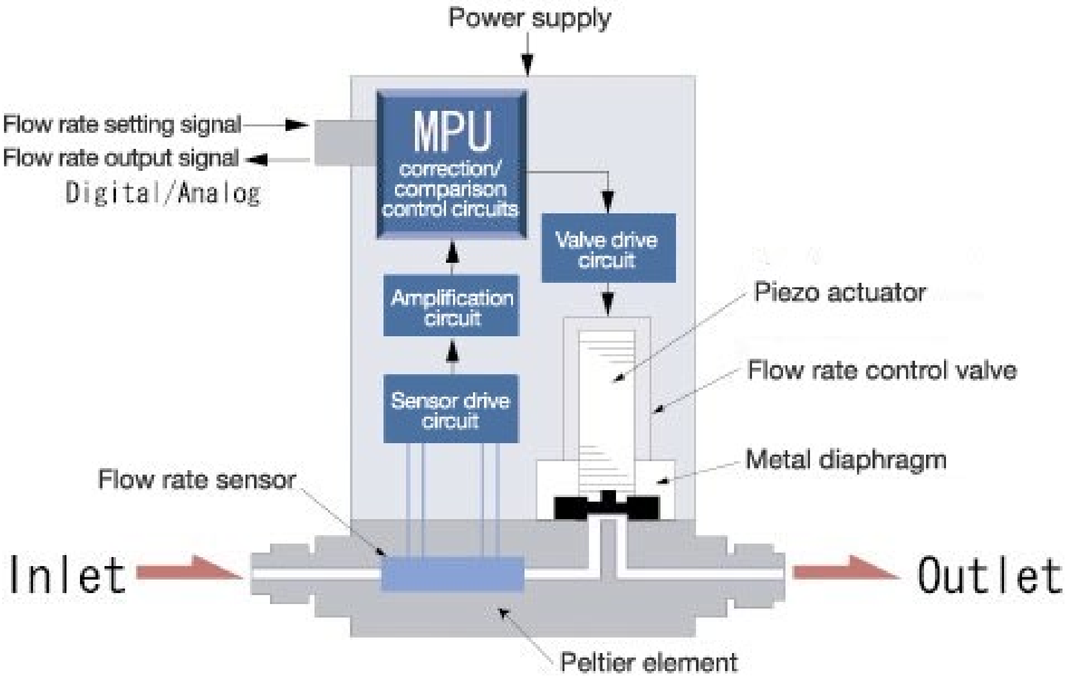


Figure 5.5: Design of an inverted magnetron

Mass flow controller







Gas flow units:

[sccm – standard cubic cm at atmospheric pressure per minute] …. Typical values: 10-100 sccm

Deposition system – process performance

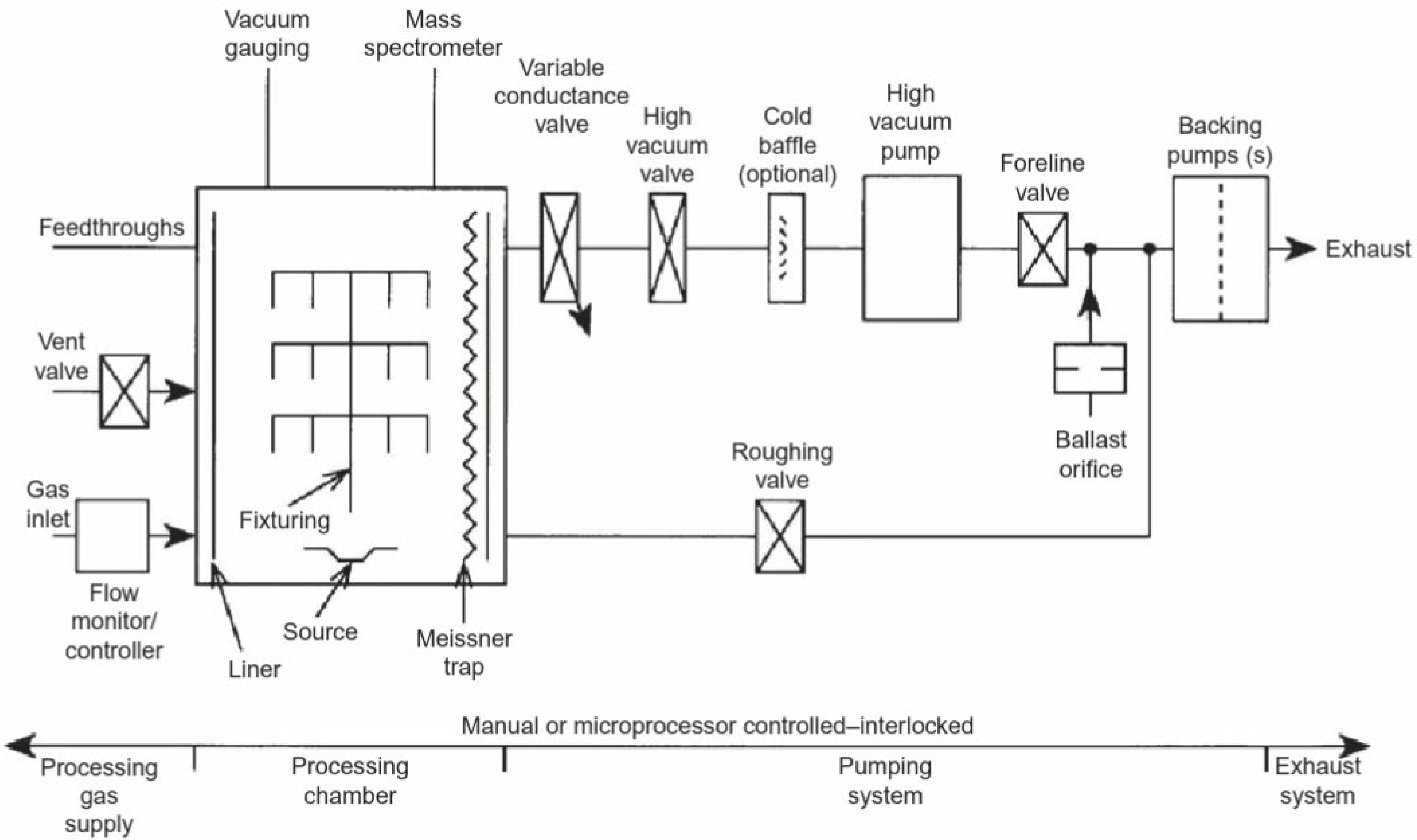
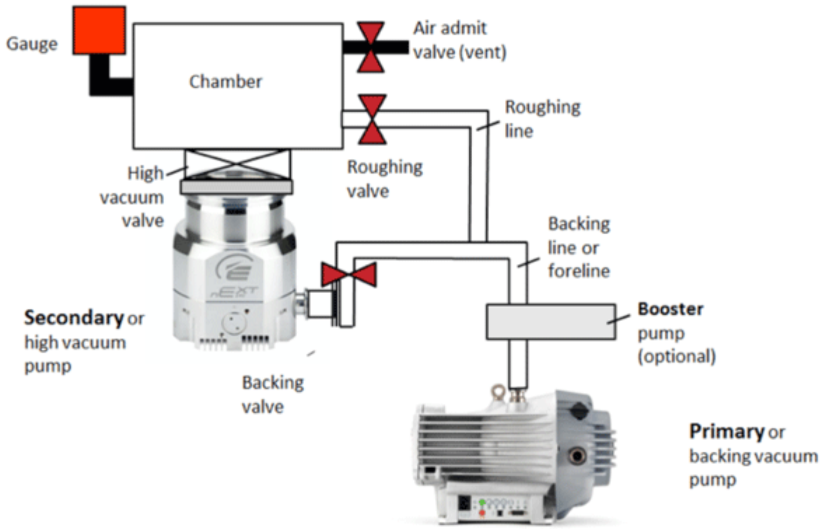


Figure 3.9: Vacuum/Plasma Processing System

Deposition system – Leak rate



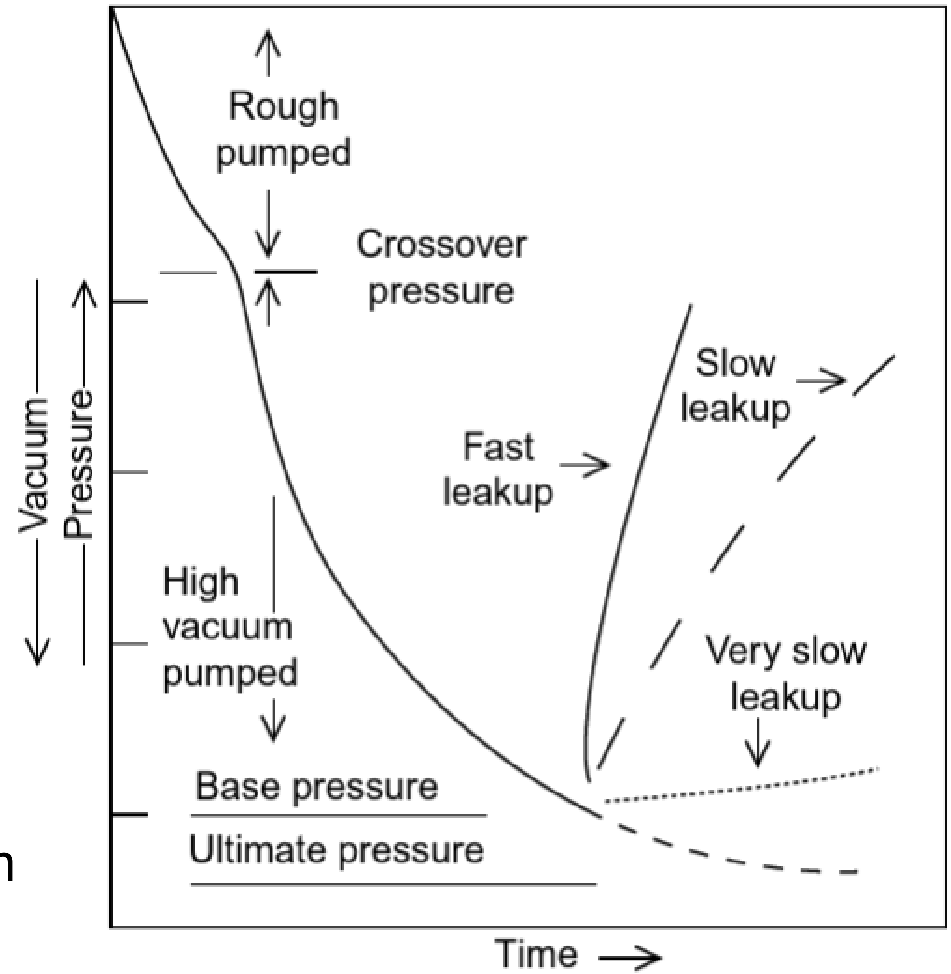


Figure 3.6: Leakup Rates

$$L_R = (\Delta p/\Delta t)\, V \text{ [torr-l per sec.]}$$

Needs to be well below
10-3 torr-l/s, i.e., less than 0.1 sccm

Thin film and coating fabrication techniques: Surface engineering

Materials added to the surface (deposition)

Surface modification

Origin of the source material: a) Solid phase – Physical vapor deposition (PVD)
b) Gas phase – Chemical vapor deposition (CVD)

Process	Physical	Hybrid	Chemical
Vacuum	Evaporation • Joule effect • Electron beam	Reactive evaporation	Chemical vapor deposition (CVD) Organo-metallic vapor phase epitaxy (OMVPE)
	Sputtering • Magnetron • Ion beam	Ion-assisted deposition • Ion beams • Surface biasing Reactive sputtering	
	Molecular beam epitaxy Pulsed laser deposition (PLD)	Surface cleaning Surface functionalization Nitriding, carburizing, boriding, … Implantation	Plasma enhanced CVD (PECVD) Laser assisted CVD (Laser CVD) Atomic layer deposition (ALD)

Process:	**Physical**	**Hybrid**	**Chemical**
		Corona discharge: Surface cleaning/activation	
Non-vacuum (atmospheric pressure)	<u>Spraying</u> • Thermally assisted • Plasma assisted • Flame assisted • Laser assisted		<u>Solution-based deposition</u> • Electroplating • Electroless plating • Anodization • Langmuir – Blodgett
	<u>Polymer deposition</u> • Electrostatic • Solvent evaporation		<u>Sol-gel deposition</u> • Immersion • Spin coating • Spray deposition
	<u>Surface modification</u> • Diffusion • Implantation		<u>Liquid phase epitaxy</u>

Classification of Thin-Film Deposition Technologies

EVAPORATIVE METHODS

- ***Vacuum Evaporation***

Conventional vacuum evaporation
Molecular-beam epitaxy (MBE)
Electron-beam evaporation
Reactive evaporation

GAS-PHASE CHEMICAL PROCESSES

- ***Chemical Vapor Deposition (CVD)***

CVD epitaxy
Atmospheric-pressure CVD (APCVD)
Low-pressure CVD (LPCVD)
Metalorganic CVD (MOCVD)
Photo-enhanced CVD (PHCVD)
Laser-induced CVD (LCVD)
Electron-enhanced CVD

GLOW-DISCHARGE PROCESSES

- ***Sputtering***

Diode sputtering
Reactive sputtering
Bias sputtering (ion plating)
Magnetron sputtering
Ion beam deposition
Ion beam sputter deposition
Reactive ion plating
Cluster beam deposition

- ***Plasma Processes***

Plasma-enhanced CVD
Plasma oxidation
Plasma anodization
Plasma polymerization
Plasma nitriding
Plasma reduction
ECR plasma CVD
Cathodic arc deposition

LIQUID-PHASE CHEMICAL TECHNIQUES

- ***Electro Processes***

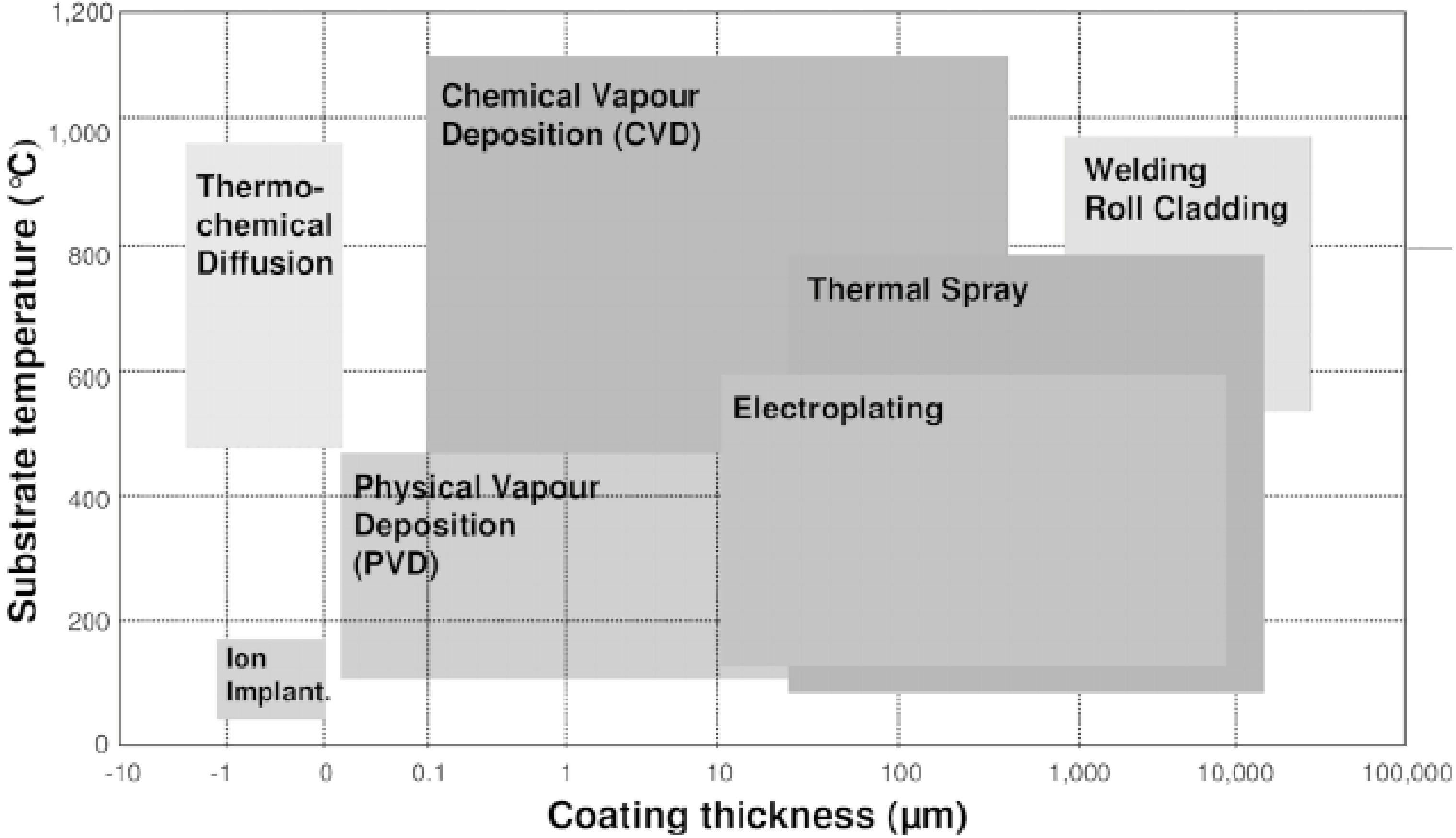
Electroplating
Electroless plating
Electrolytic anodization
Chemical reduction plating
Chemical displacement plating
Electrophoretic deposition

- ***Mechanical Techniques***

Spray pyrolysis
Spray-on techniques
Spin-on techniques
Liquid phase epitaxy

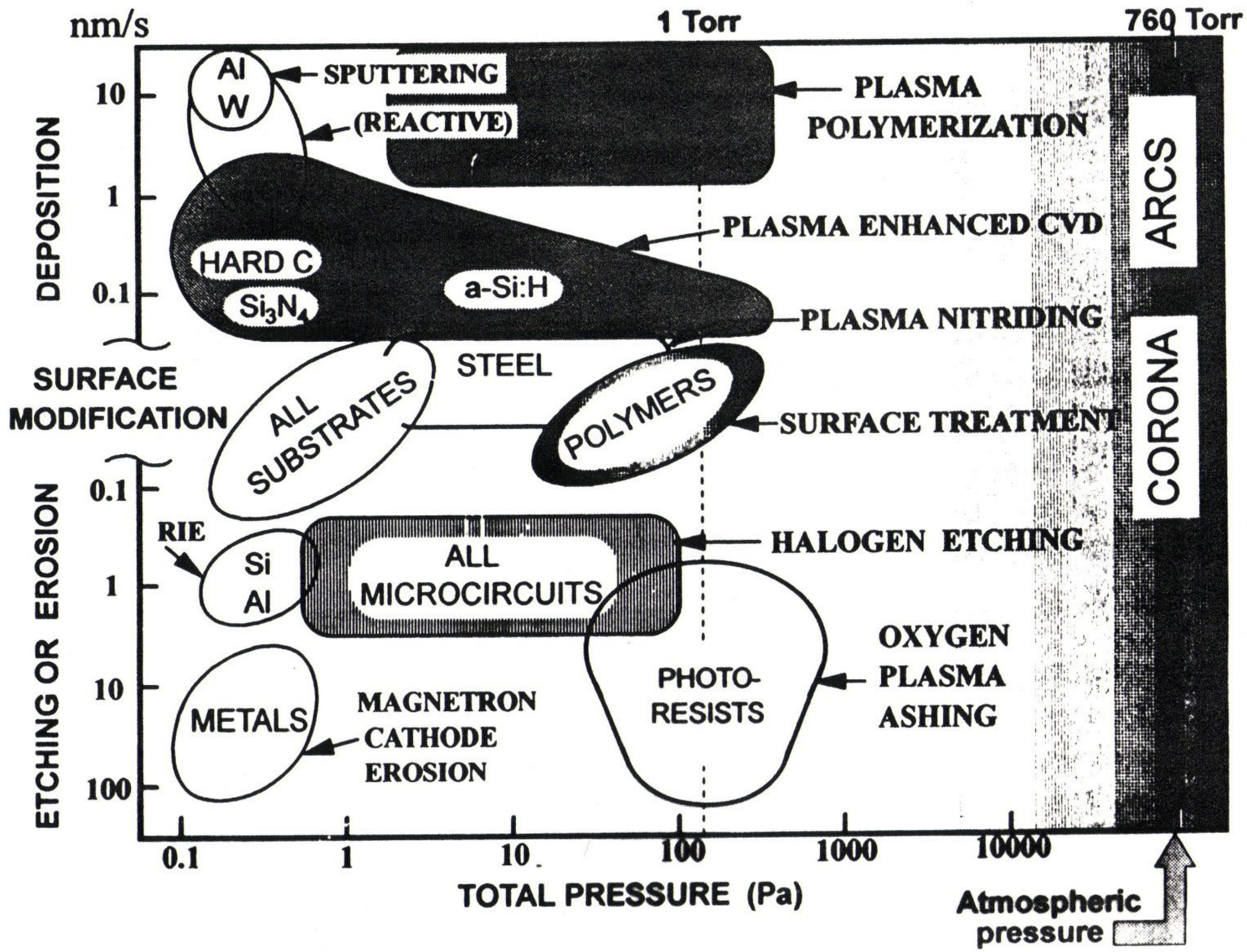
Vacuum vs Atmospheric pressure deposition techniques:

Thin and thick coatings



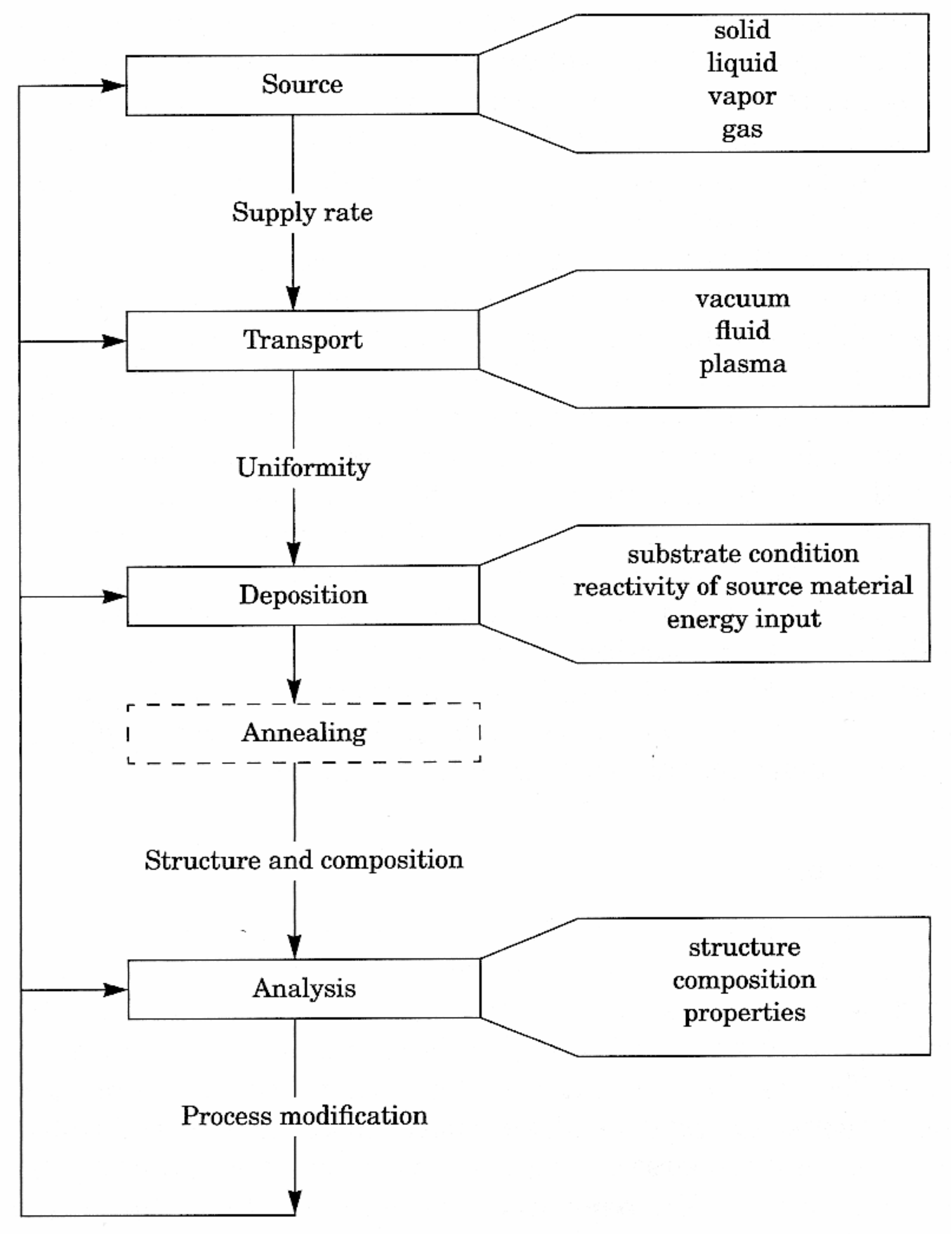
Introduction to powder metallurgy, F. Thümmler, ed., London 1993

Plasma processing of materials – pressure ranges



Steps in thin film deposition

Monitoring
Contamination



Electron beam evaporation

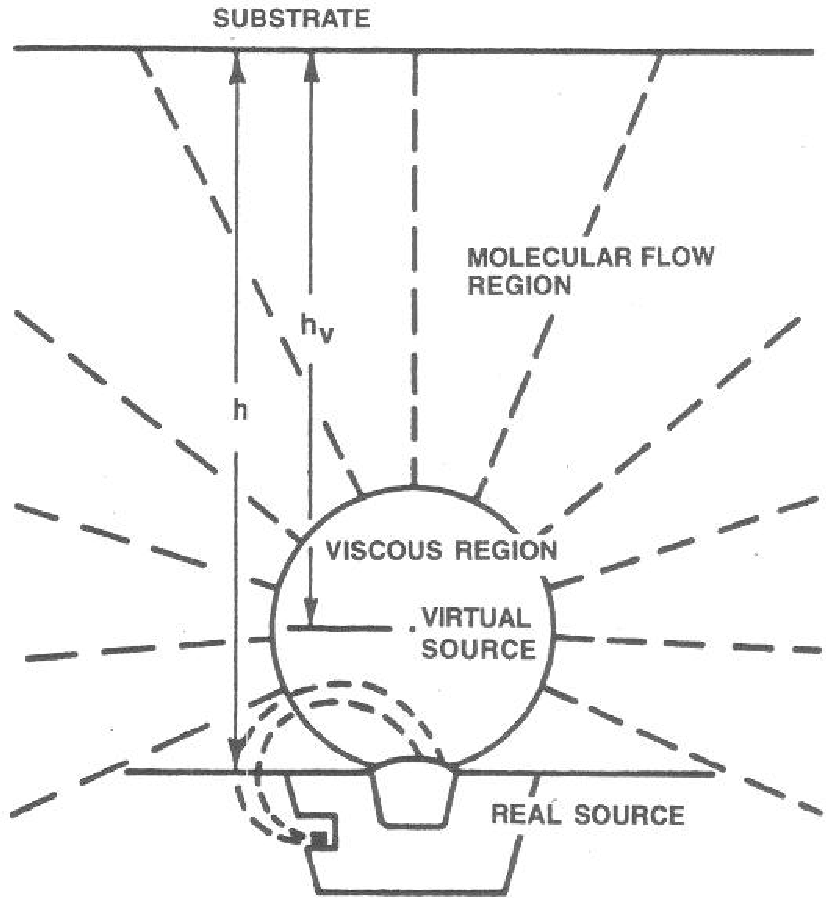


Figure 3-14 Schematic depiction of the regions of viscous and molecular flow around an electron-beam evaporation source. (From *Physical Vapor Deposition*, edited by R. J. Hill. Temescal, BOC Group, 1986. Reprinted with the permission of Russell J. Hill.)

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Film growth

Effect of substrate temperature

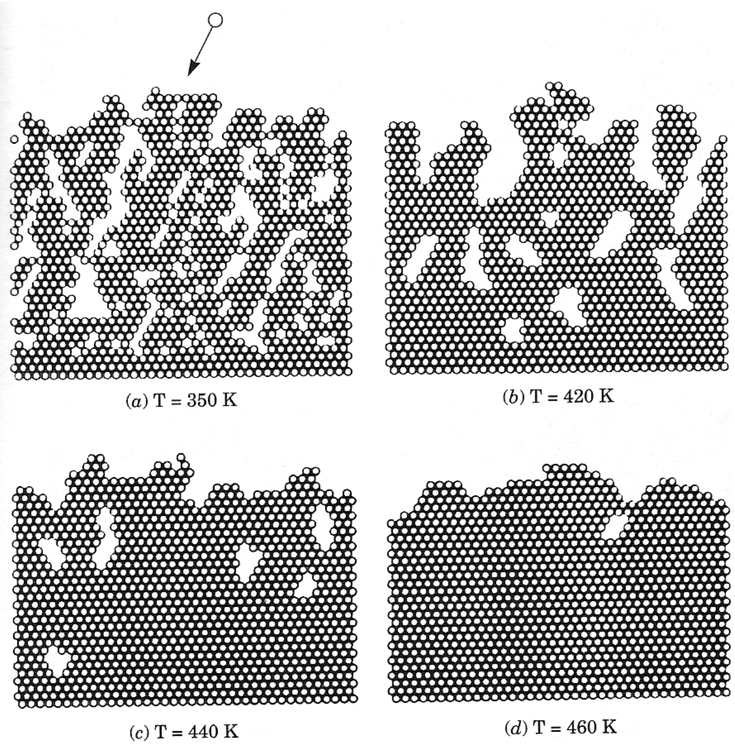

Figure 5.20 Two-dimensional computer simulation of the effect of substrate T on void filling by surface diffusion. (Source: Reprinted from Ref. 22 by permission.)

D.L. Smith: Thin-film deposition: principles and practice

Effect of ion bombardment

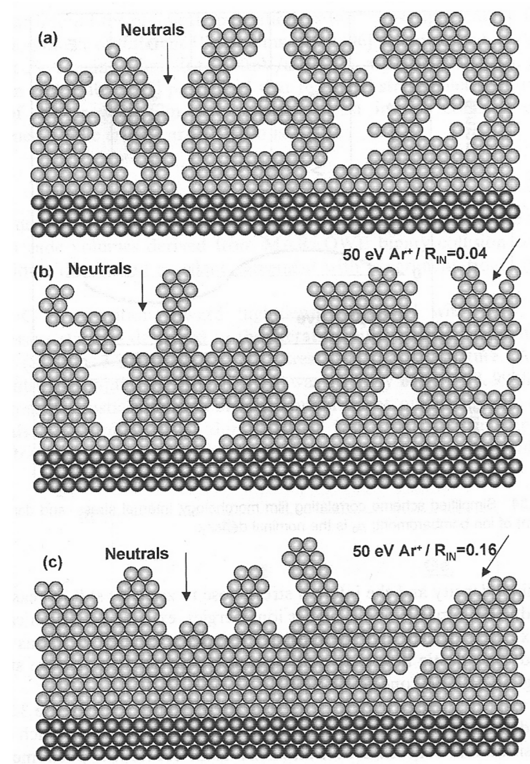

Figure 3.33 Morphology of a growing metal film as obtained from an early two-dimensional MD computer simulation using a Lennard-Jones interatomic potential, (*a*) without ion bombardment, (*b*) and (*c*) for IBAD using Ar^+ ions at E_i=50 eV and R_{in}=0.04 and 0.16, respectively. The directions of the incoming neutral and ion fluxes are indicated by arrows; After [187].

A. Anders:
Handbook of ion immersion ion implantation and deposition

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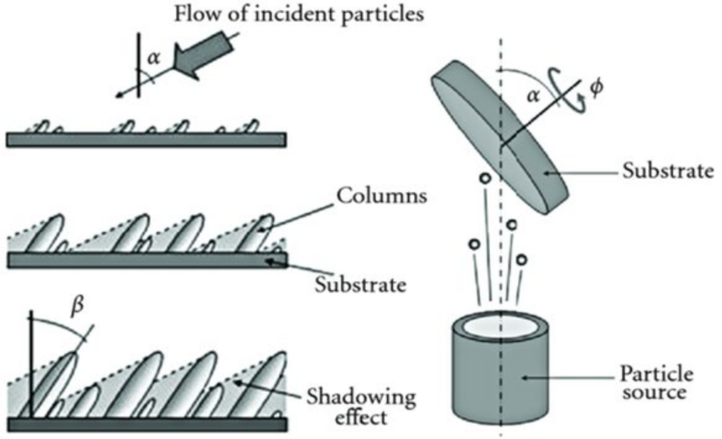
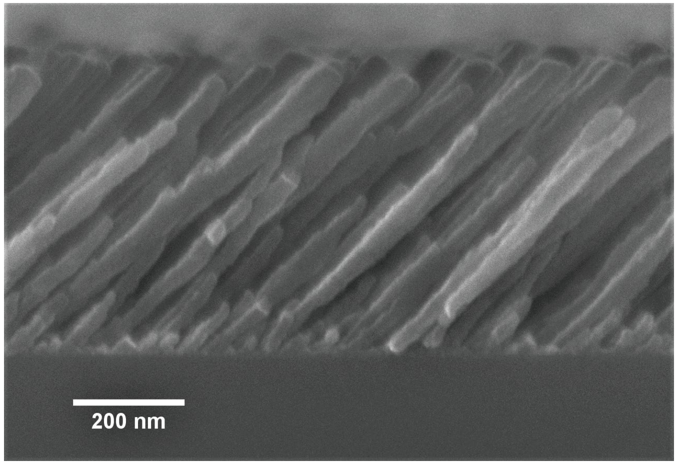
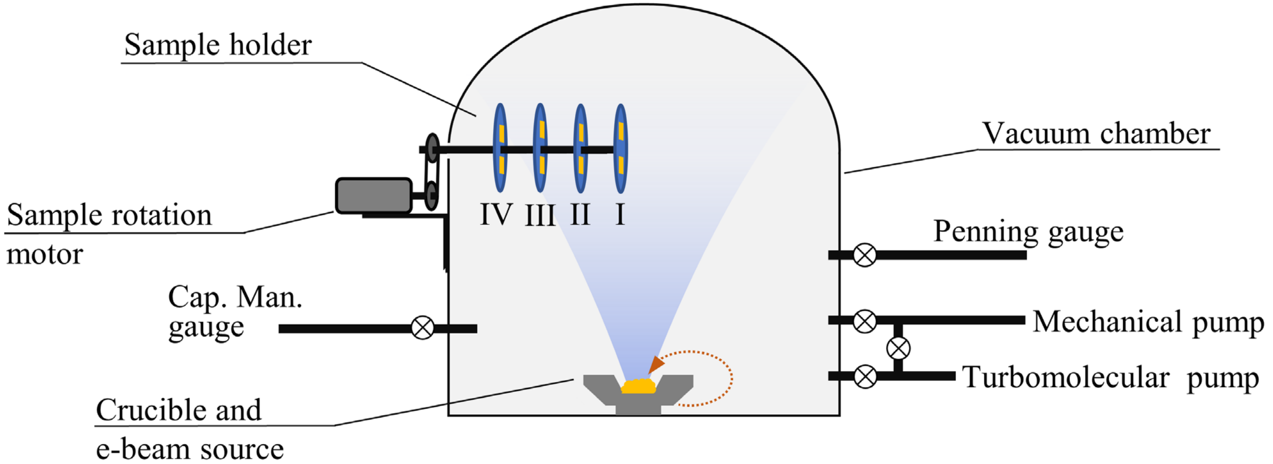
Glancing Angle Deposition - GLAD

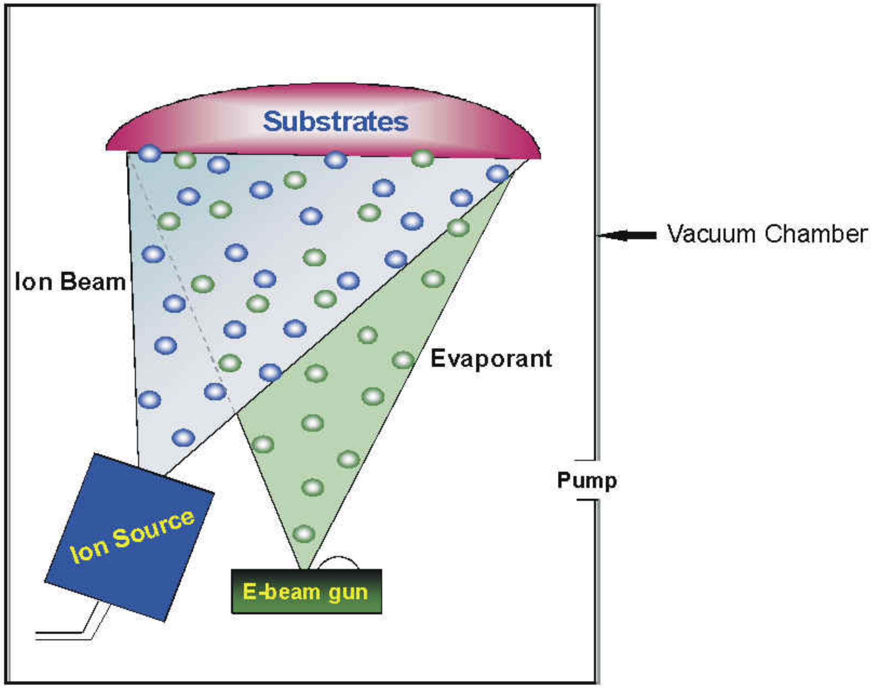






Ion beam assisted evaporation (IAD, IBAD) in a box coater

Leybold Optics BOXER Pro

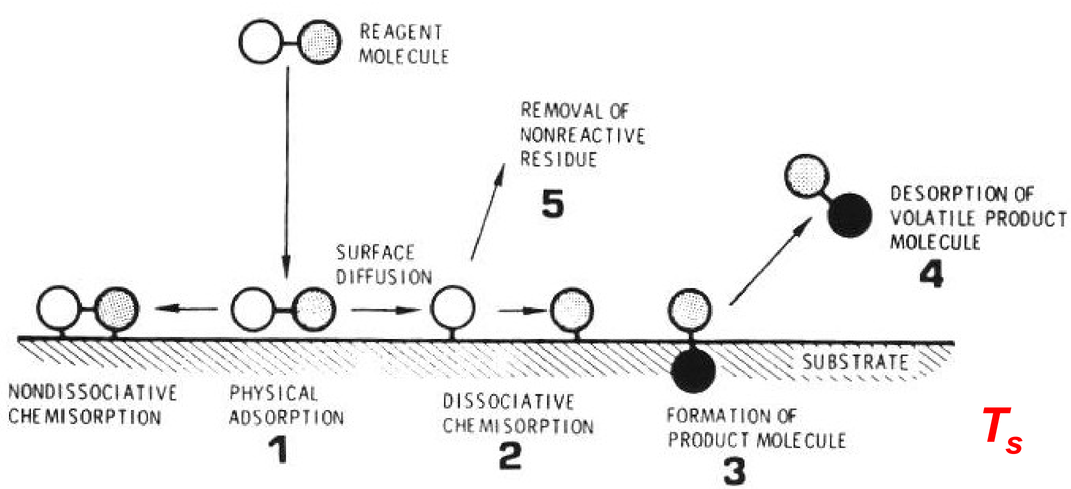


- Electron beam or thermal evaporation (e.g., Si, Ta, Ti…)
- Energetic and reactive oxygen ion beam from a broad beam ion source
- Ion beam is neutralized with an independent electron source
- Base pressure is ~ 10^{-7} Torr

Film growth from vapor phase

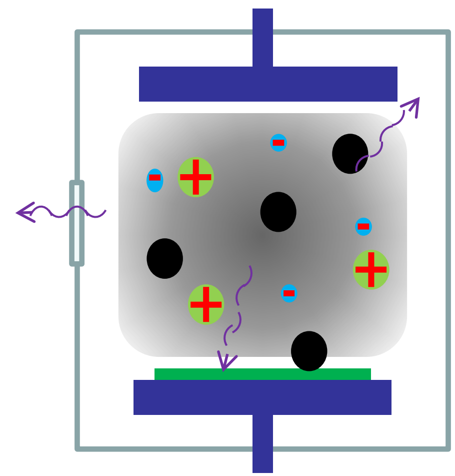
Energy and flux of (condensing) neutrals: E_n , Φ_n

Energy and flux of ions: E_i , Φ_i



T_s

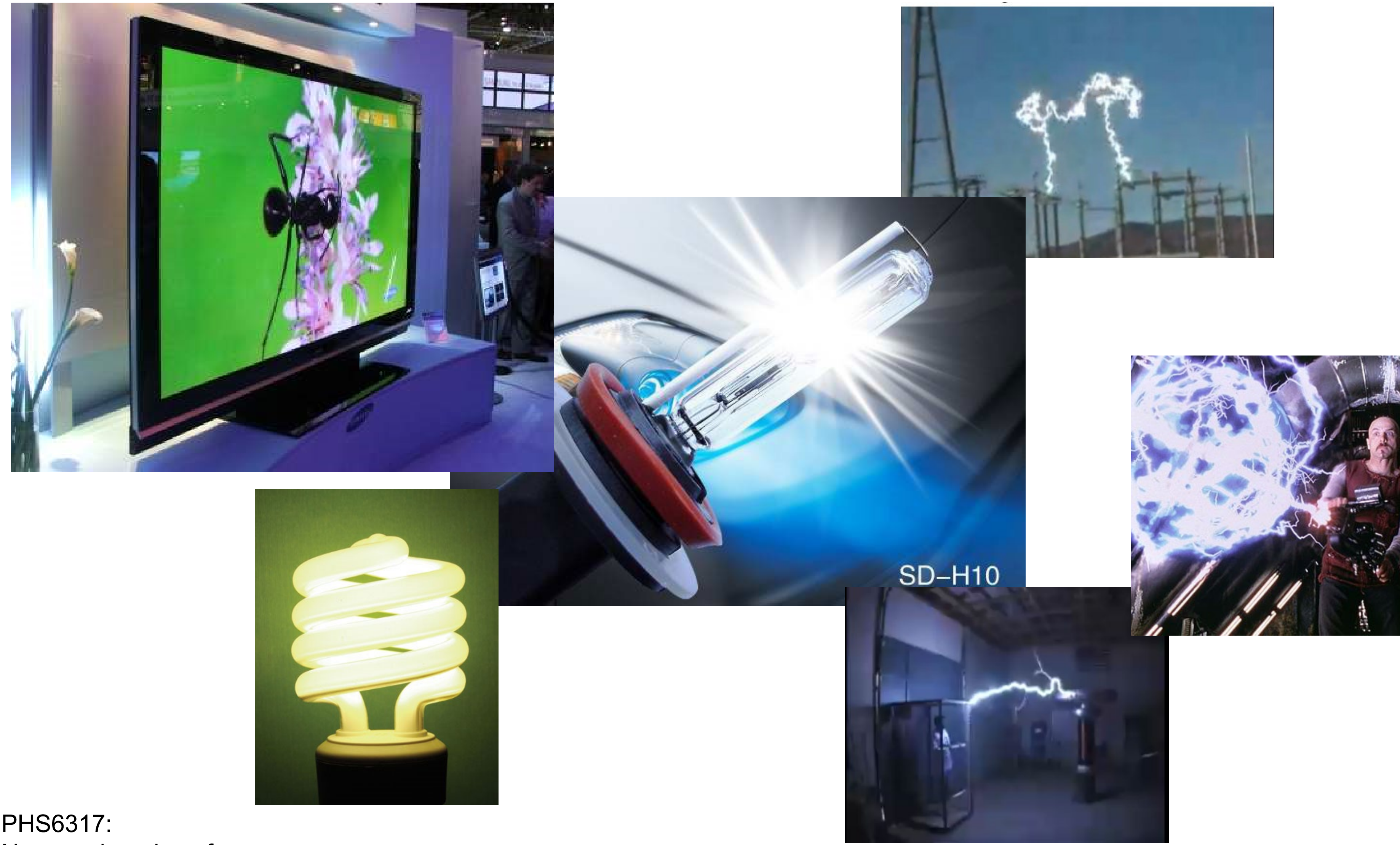
Figure 2.25. Schematic representation of surface chemisorption and volatile compound formation during dry etching.



Low pressure plasma

Electrons, ions, radicals, photons
Quasi-neutrality
Collective behavior

Plasmas around us



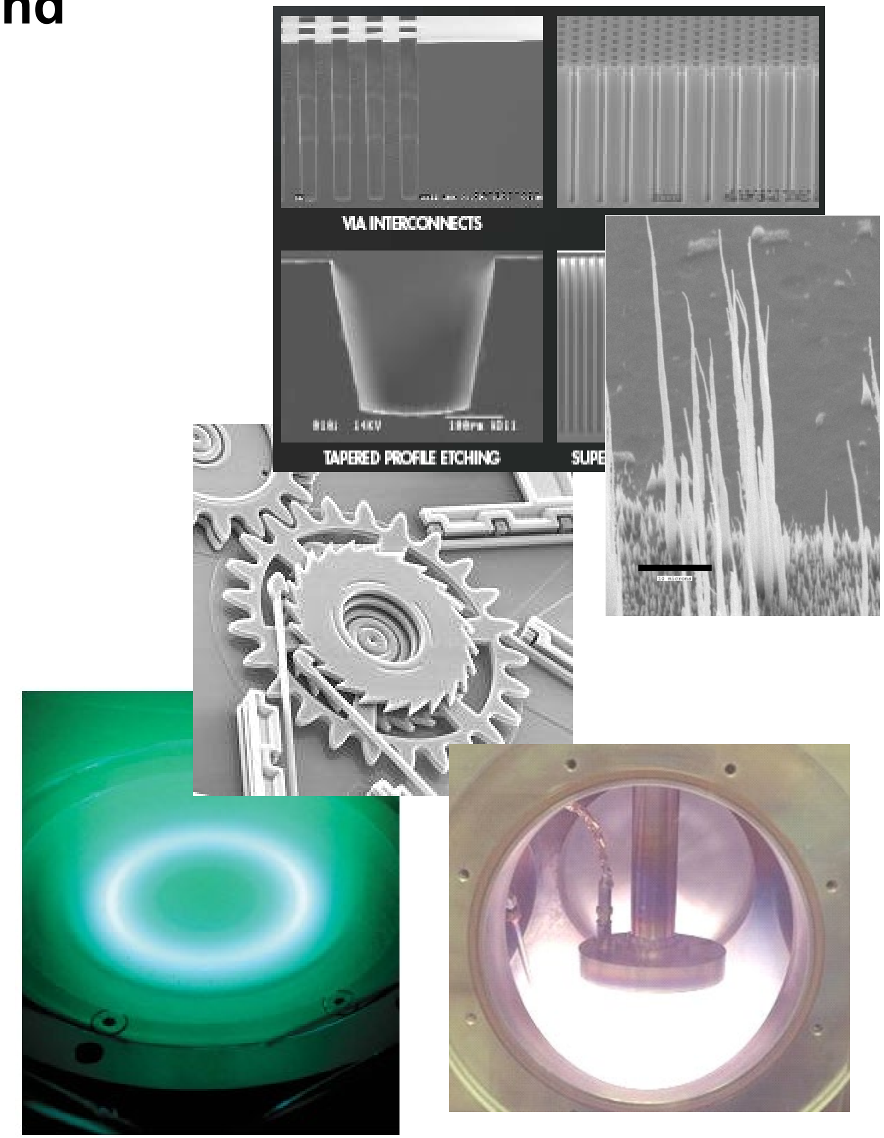
Plasma processes applied in micro- and nano-fabrication

Applications

- PECVD
- Plasma etching (incl. “ashing”)
- Surface functionalization
- Magnetron sputtering (MS)
- Ion beam sputtering (IBS)
- Ion assisted evaporation (IBAD, IAE, IBD)
- Ion implantation
- Plasma-enhanced ALD

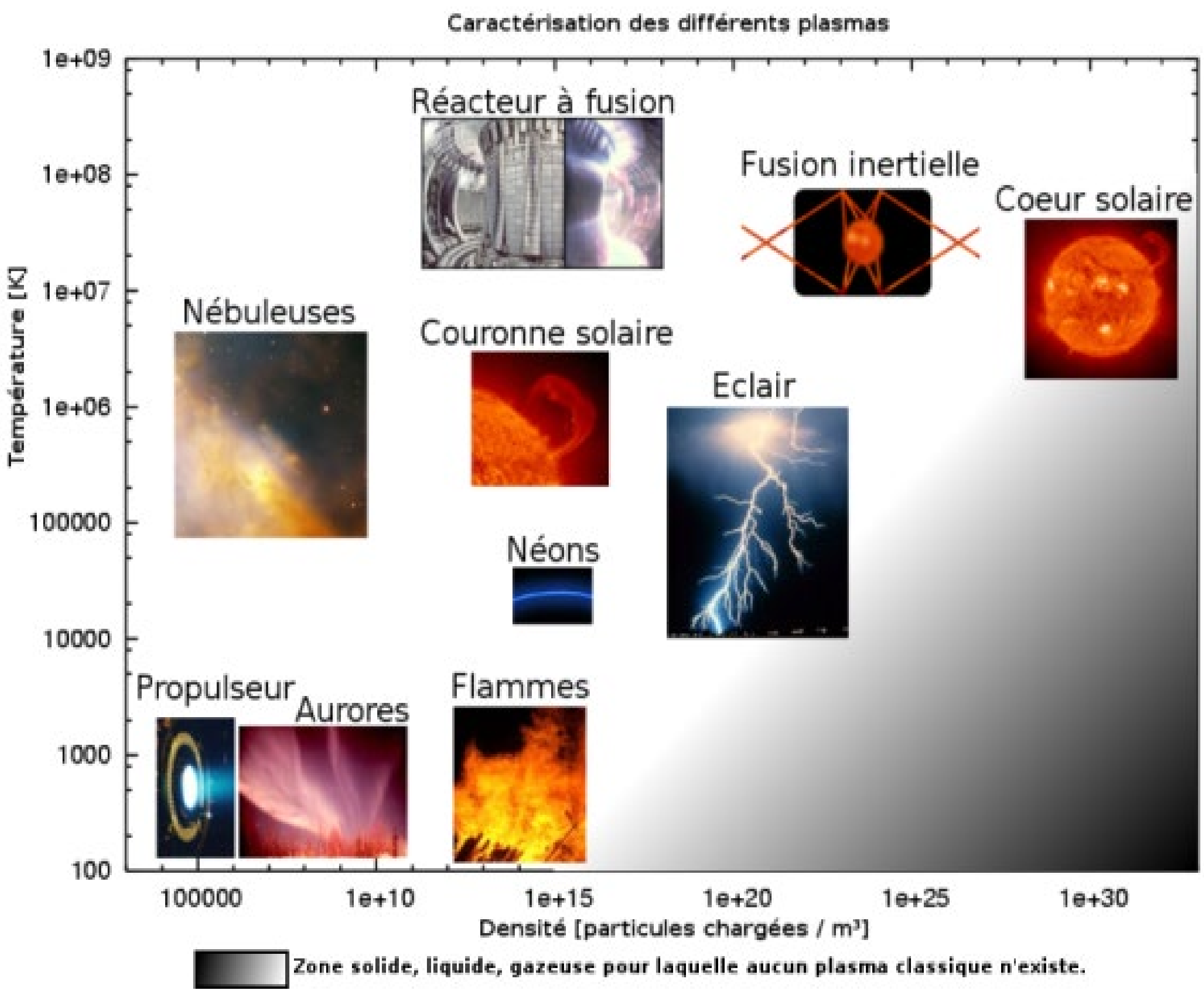
Approaches (configurations)

- Electron cyclotron resonance (ECR)
- DC, p-DC, AC, and magnetrons
- High Power Impulse Magnetron Sputtering - HiPIMS
- Frequences: DC, p-DC, AC, RF, MW
- Capacitive or inductive coupling
- Pulsed plasmas
- Surface waves
- …..



Pulvérisation magnétron d'une cible de cuivre pour le dépôt de couches minces

Plasmas around us



<u>Definition:</u>
Plasma is a quasi-neutral gas of charged and neutral particles which exhibits a collective behavior.

Irwing Langmuir, 1929

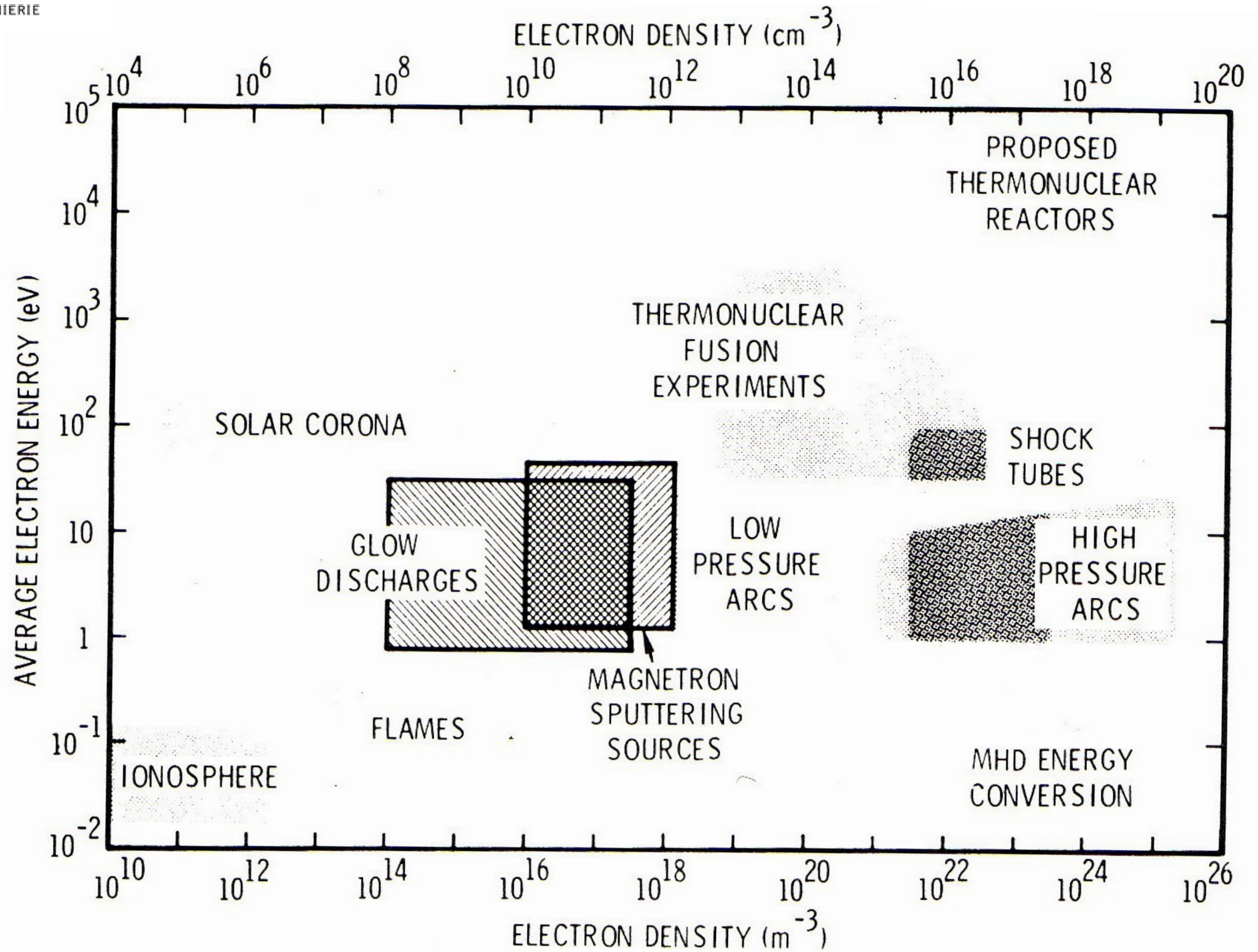


Figure 2.17. Regions of average electron density and energy representative of various types of plasmas (from Ref. 7).

Challenges in low pressure plasma processing of materials

Despite a remarkable progress in the plasma-assisted synthesis of nanomaterials and functional nanostructures, the current use of the plasma-based techniques in nanotechnology is still quite limited; this mostly includes:

- synthesis of relatively simple nanoparticles,
- nanometer-thin and micrometers thick functional coatings,
- nanocrystalline films, and
- post-processing of nanostructures.

Basic plasma characteristics:

Electric discharges, electron density and temperature, Debye length, mouvement of charged particles in the E and B fields.

Elastique and inelastic collisions, interaction cross-section, diffusion and mobility of electrons.

Wave propagation in the plasmas, breakdown – Paschen's law, DC, AC and HF discharges.

Power transfer and dissipation in the plasma, energetic balance, energy distributions.

Plasma-surface interactions, sheath, self-bias, ion bombardement, UV photons.

Design and operation of plasma reactors, RF coupling (capacitive and inductive), microwaves, magnetized plasma, pulsed plasma.

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References

- Course notes (Moodle web site)
- M. Ohring, *"Materials Science of Thin Films",* Academic Press, New York 1992 (1st edition), 2002 (2nd edition).
- M. A. Lieberman and A. J. Lichtenberg, "Principles of Plasma Discharges and Materials Processing", Wiley, New York, 1994.
- R.F. Bunshah, ed., *"Handbook of Deposition Technologies for Films and Coatings",* Noyes publications, Park Ridge, NJ, 1994. http://www.knovel.com/knovel2/Toc.jsp?BookID=57
- D.A. Glocker et S.I. Shah, ed.,"*Handbook of Thin Film Process technology*", Vol.1, IoP, Bristol 1995.
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- D.M. Mattox, *"Handbook of Physical Vapor Deposition (PVD) Processing",* William Andrew Publishing/Noyes, 1998. http://www.knovel.com/knovel2/Toc.jsp?BookID=63
- K. Seshan, ed., *"Handbook of Thin-Film Deposition Processes and Techniques - Principles, Methods, Equipment and Applications"* (2nd Edition), William Andrew Publishing/Noyes, 2002. http://www.knovel.com/knovel2/Toc.jsp?BookID=459
- ''Handbook of Deposition Technologies for Films and Coatings'', P.M. Martin, ed., Elsevier, 2010.
- High Power Impulse Magnetron Sputtering – Fundamentals, Technologies, Challenges and Applications, D. Lundin, T. Minea, J.T. Gudmundsson, eds., Elsevier 2019.

Main parameters of the low pressure (cold) plasma

n_e - electron density
n_g – gas density (neutrals)
n_i - ion density

$n_e + \Sigma n_{i-} = \Sigma n_{i+}$ - plasma quasi-neutrality

$\alpha_i = n_e / (n_e + n_g)$ - degree of ionisation (very low in usual processing plasmas)

T_e – electron temperature
T_g – gas temperature
T_i – ion temperature

$T_e >> T_i \gtrsim T_g \approx T_{wall}$ - plasma is stronly out of thermodynamic equilibrium (non-equilibrium)

$p = n_g k T_g << p_{atm}$ – low (reduced) pressure

In this part of the course:

Plasma = glow discharge = cold plasma = electric discharge =
= low pressure plasma

Non-equilibrium plasma

- Degree of ionisation α_i : $\alpha_i = n_e / (n_e + n_o)$ typically ~ 10^{-3} - 10^{-4}
- Energy and temperature: $E = kT$ $E_e = 2$ eV

$T_e = 23\,000$ K

neutrals: 0.025 eV

ions: 0.04 eV

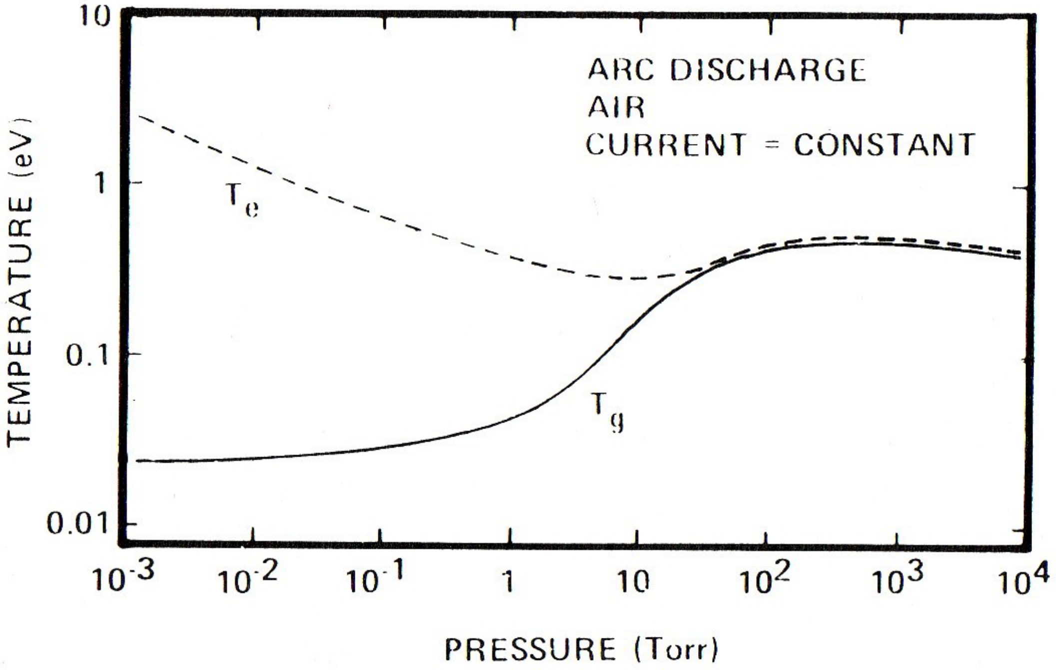
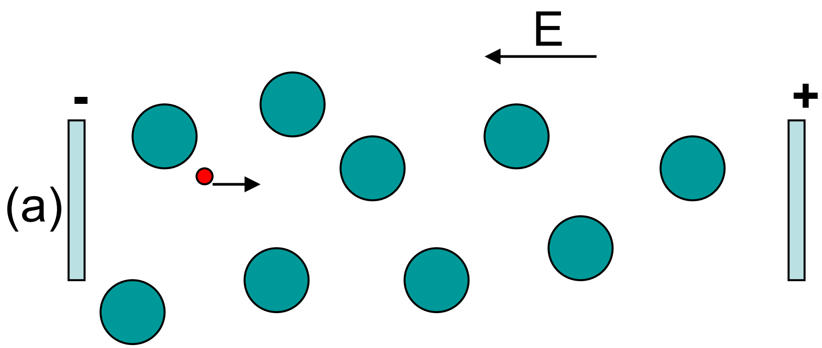


Figure 2.3. Electron (T_e) and gas temperatures (T_g) in an air arc as a function of pressure (from Ref. 5).

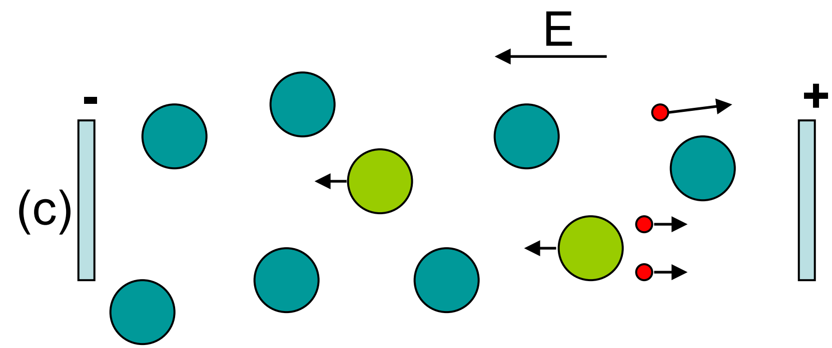
Ex. for 10 mtorr:
$n_0 = 10^{14}$ cm^{-3}
$n_e = n_i = 10^{10}$ cm^{-3}

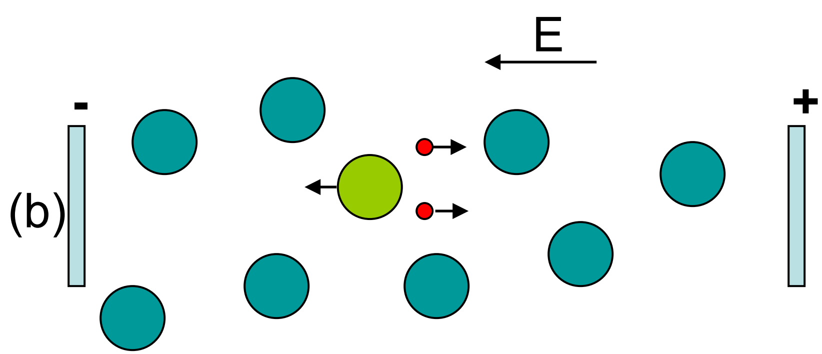
T_{transl} ~ 1000 K
T_{rot} ~ 2800 K
T_{vib} ~ 3800 K

Plasma initiation – Electric breakdown

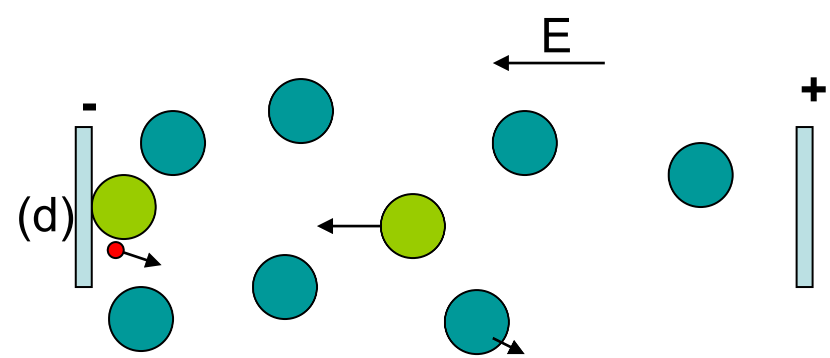


Spontaneous acceleration of an electron





Ionisation, multiplication of electrons



Ion arrives at the cathode: Secondary electron emission from the cathode

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Townsend's discharge

- Ionisation process by electron impact: **$e^- + A = 2e^- + A^+$**

Townsend's equation

$$i = i_0 \frac{\exp \alpha d}{[1 - \gamma_e(\exp \alpha d - 1)]}.$$

α – Townsend's coefficient of ionisation (ionisation probability per unit of length during an electron-atom collision)

$$\alpha = \frac{1}{\lambda} \exp^{-\frac{Vi}{q\mathscr{E}\lambda}}.$$

γ_e – Townsend coefficient of secondary electron emission

(number of secondary electrons emitted from the cathode per incident ion)

V_i – ionisation potential, q – electronic charge, λ – mean free path, p – pressure,

d – inter-electrode distance

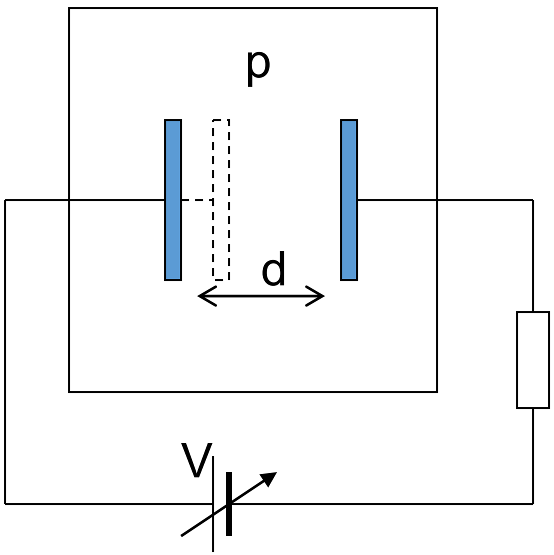
Paschen's law:

$$V_B = \frac{Bpd}{\ln Apd - \ln\left[\ln\left(1 + 1/\gamma_{se}\right)\right]}$$

V_B – breakdown voltage

A, B - constants

Paschen's law



$$V_B = \frac{Bpd}{\ln Apd - \ln\left[\ln\left(1 + 1/\gamma_{se}\right)\right]}$$

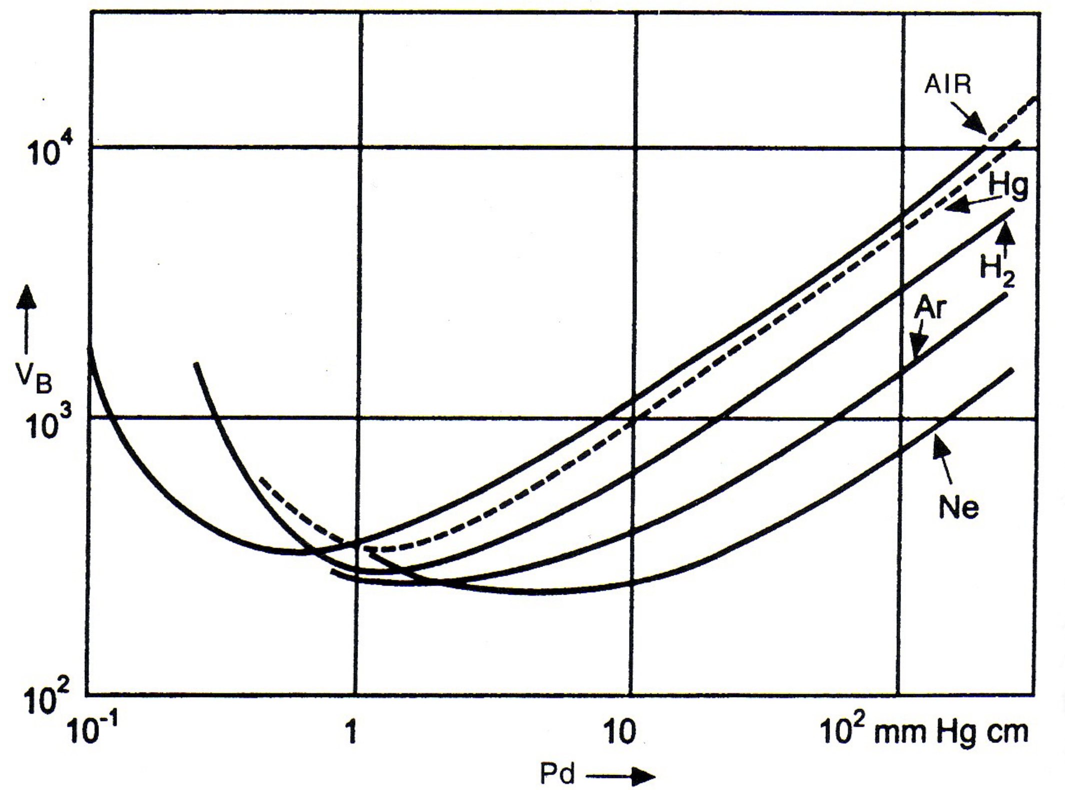


Figure 4-2 Paschen curves for a number of gases. (From A. von Engel, *Ionized Gases*. Oxford University Press, Oxford, 1965. Reprinted with permission.)

p – pressure
d – distance between the electrodes
V_B – breakdown voltage
A, B – characteristic constants for a specific gas

Electric discharge – cold cathode

- secondary electrons induced by ion bombardment
- typically $\gamma_e \sim 0.1$ (Ar^+)
- $f_e(E)$ multimode electron energy distribution function (EEDF)

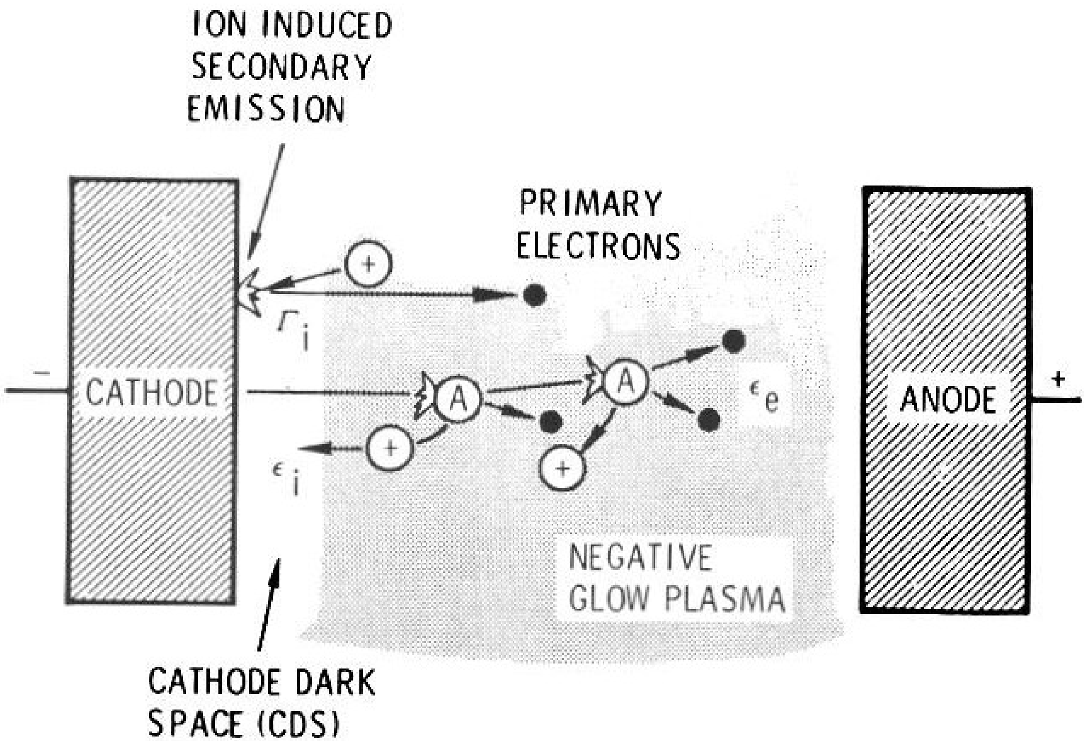


Figure 2.18. Schematic illustration of a cold-cathode discharge.

Example:
Ar, 75 mTorr
d = 4.5 cm
i = 1 mA/cm^2
V = 3 kV

Structure of an electric DC discharge

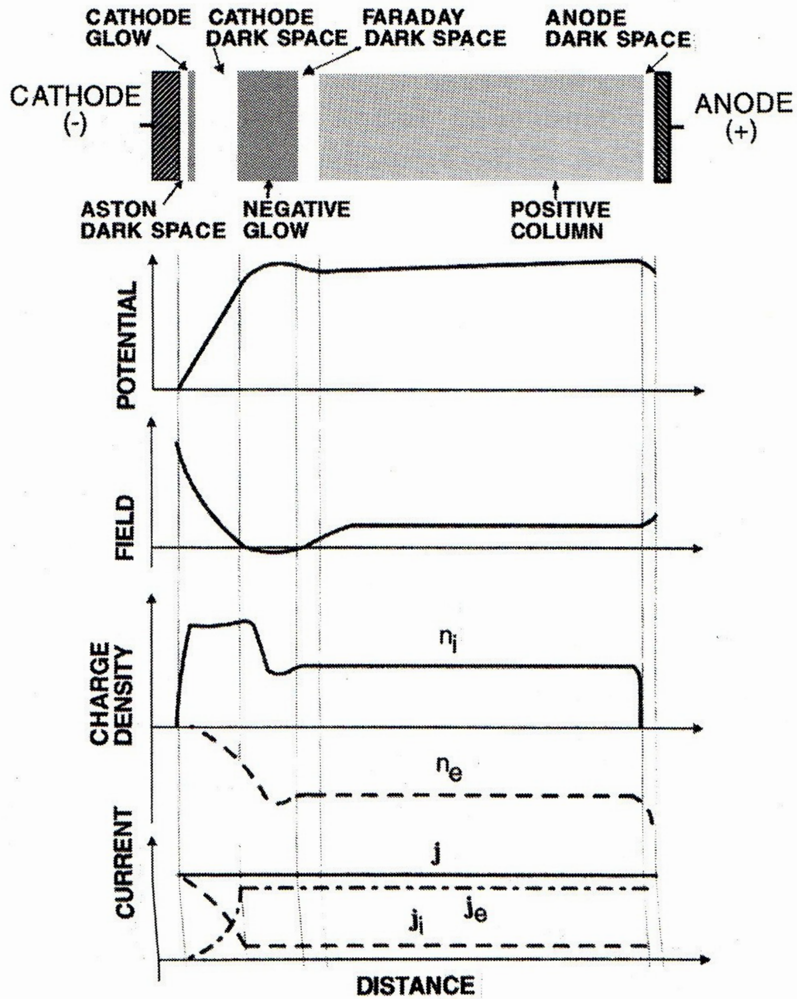


Figure 4-3 Structure of a DC glow discharge with corresponding potential, electric field, charge, and current distributions.

Types of discharges according to their I-V characteristics (schematic)

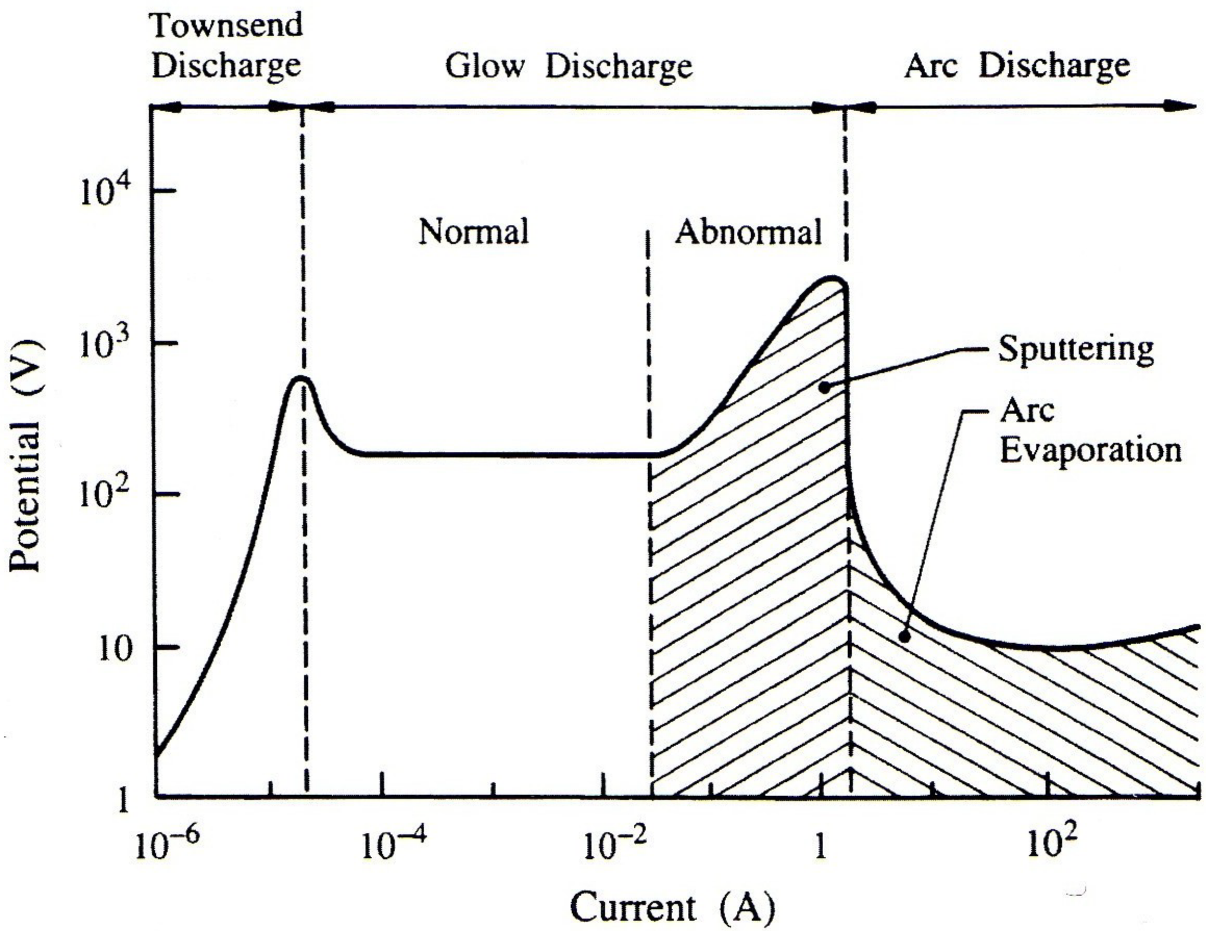


Figure A1.4.1. The voltage–current characteristics of discharges [1].

Charged particles mouvement in the plasmas

Effective current density: $j = nvq/4$

Mean velocity: $v = (8kT/\pi m)^{1/2}$

Mobility: $\mu = v/\mathcal{E}$

Typical value: $10^2 - 10^4$ cm^2/ V-s

$m\, dv/dt = q\,\mathcal{E} + m\,[\delta v/\delta t]_{coll}$

Mouvement due to diffusion (Fick's law) and $\mathcal{E}$

$$J_e = -n_e \mu_e \mathcal{E} - D_e\, dn_e/dx$$

$$J_i = n_i \mu_i \mathcal{E} - D_i\, dn_i/dx.$$

El. field due to diffusion:

$n_e = n_i = n$

$J_e = J_i = J$

$$\mathcal{E} = \frac{(D_i - D_e)}{n(\mu_e + \mu_i)} \frac{dn}{dx}.$$

Ambipolar diffusion:

$$D_a = \frac{(D_i \mu_e + D_e \mu_i)}{(\mu_e + \mu_i)}.$$

$D_i < D_a < D_e$

Mouvement of electrons in E and B

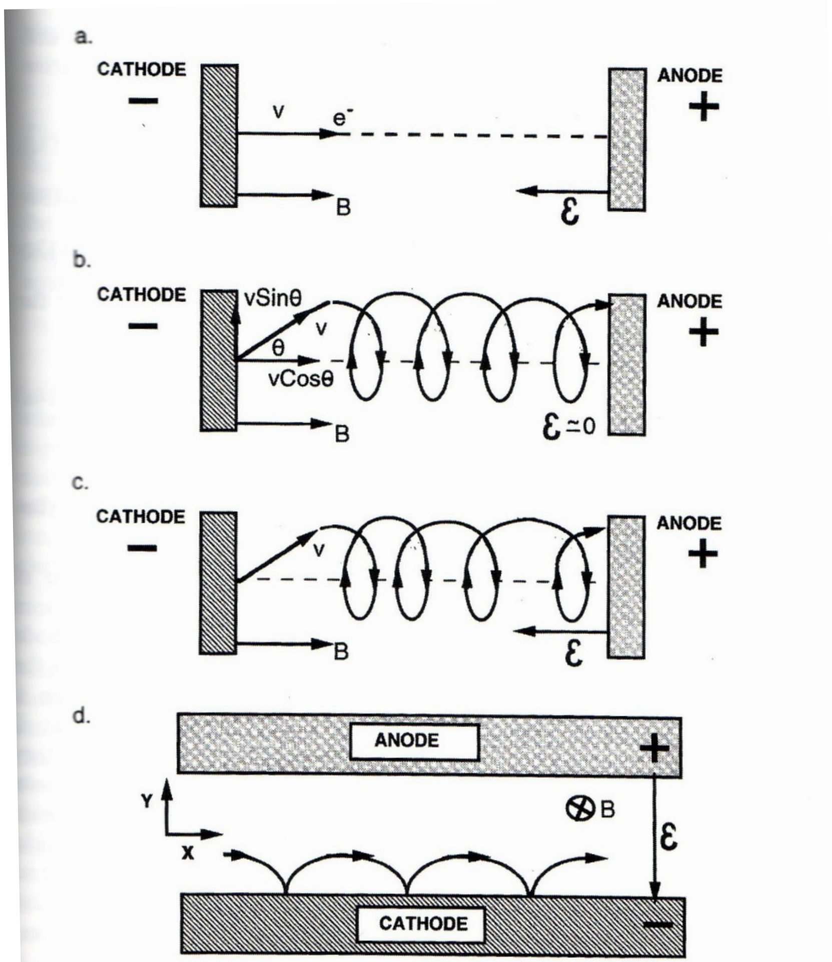


Figure 4-4 Effect of $\mathscr{E}$ and B on electron motion. (a) Linear electron trajectory when $\mathscr{E} \parallel B(\theta = 0)$. (b) Helical orbit of constant pitch when $B \neq 0$, $\mathscr{E} = 0(\theta \neq 0)$. (c) Helical orbit of variable pitch when $\mathscr{E} \parallel B(\theta \neq 0)$. (d) Cycloidal electron motion on cathode when $\mathscr{E} \perp B(\theta = 0)$.

$r = m v \sin\theta / qB$

$\omega_c = qB / m_e$

$\omega_c = 2.8 \times 10^6$ B (gauss) [Hz]

Typical B: 50-100 G
r (cyclotron): 0.1 cm

Collisional diffusion of electrons across B

Translation velocity:
$v_d = 10^8$ E (V/cm)/B (gauss)

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Collective effects

- Electron density around an ion

$$n_e(r) = n_i \exp qV(r)/k_B T.$$

$$n_e = n_i (1 + V(r)) / kT$$

- Poisson's equation

$$\frac{1}{r^2}\left[\left(\frac{d}{dr}\frac{[r^2\, dV(r)]}{dr}\right)\right] = -\frac{q(n_i - n_e)}{\varepsilon_0} = \frac{n_i q^2 V(r)}{\varepsilon_0 k_B T}$$

$$V(r) = q/r \exp - (r/\lambda_D)$$

- Debye length

$$\lambda_D = (\varepsilon_0 k_B T/n_i q^2)^{1/2}$$

- Plasma frequency

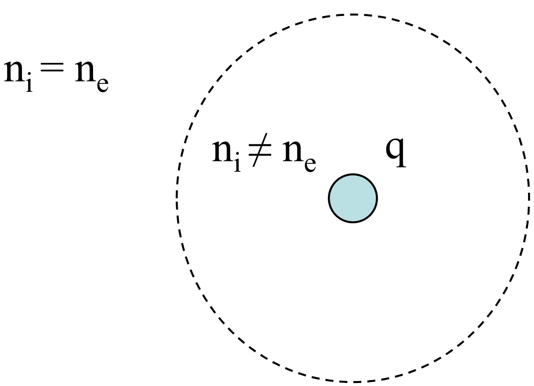
$$\omega_e = (q^2 n_e/m_e \varepsilon_0)^{1/2} = 8.98 \times 10^3 n_e^{1/2}\ \text{Hz},$$

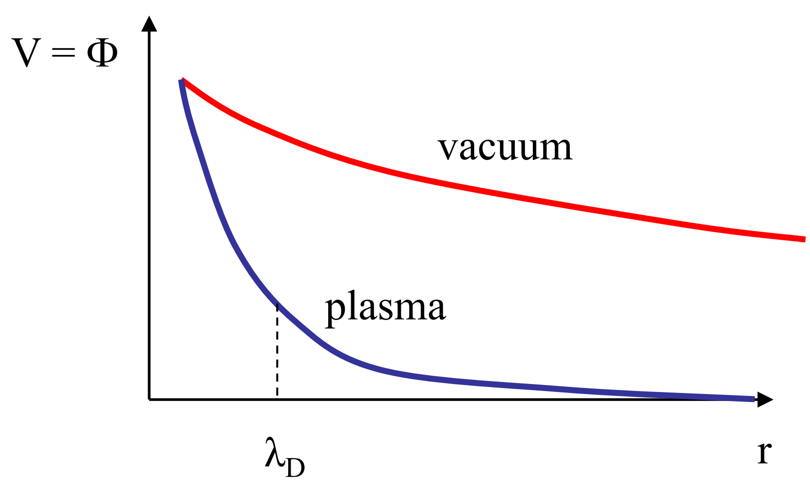
Debye length

Characteristic distance in the plasma: beyond λ_D, the electric field created by a charged particle is effectively shielded.

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k T_e}{n_e e^2}}$$

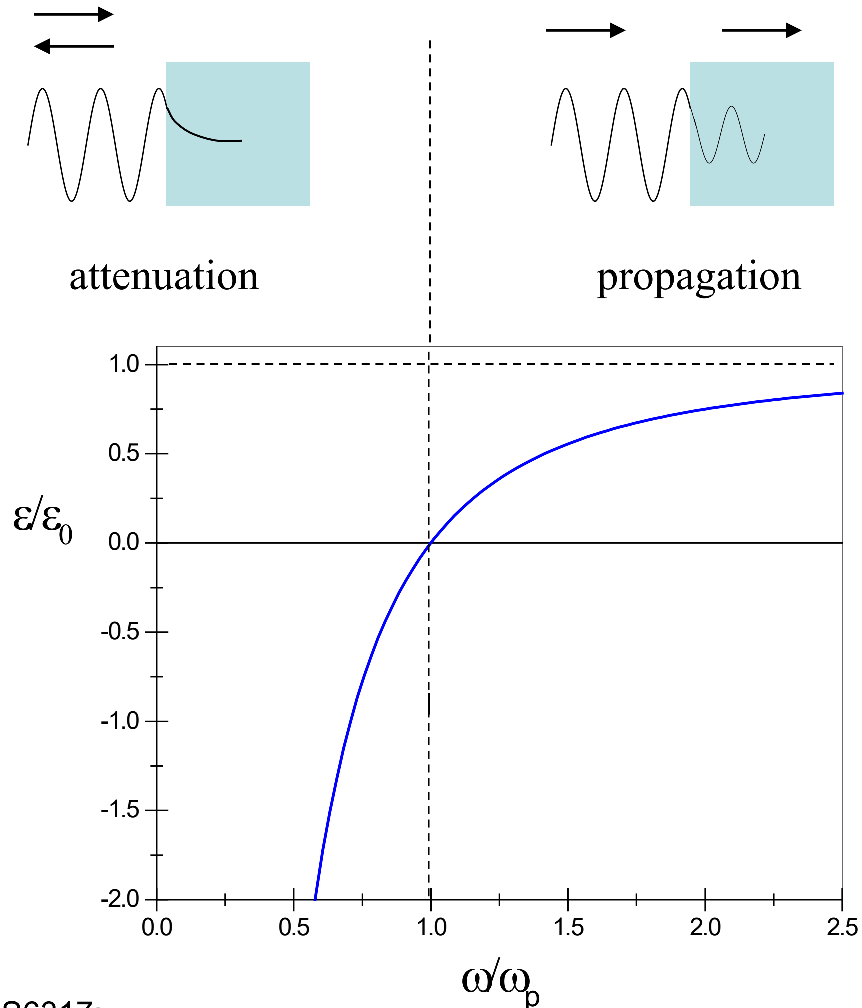
$$\Phi = \Phi_0 \exp\left(-\frac{r}{\lambda_D}\right)$$





Plasma frequency

Alternative E: $\mathbf{E} = \mathbf{i}\, E_0 \cos(\omega t)$



$$\omega_p = \sqrt{\frac{n_e e^2}{m_e \varepsilon_0}}$$

$$\lambda_D \omega_p = \sqrt{\frac{kT_e}{m_e}} \approx \bar{v}_e$$

$$\varepsilon_p = \varepsilon_0 \left(1 - \frac{\omega_p^{\ 2}}{\omega^2} \right)$$

For $\omega > \omega_p$ plasma acts as a dielectric

For $\omega < \omega_p$ - plasma acts as a metal

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Criteria for plasma creation:

1. System dimension: $\mathbf{D \gg \lambda_D}$

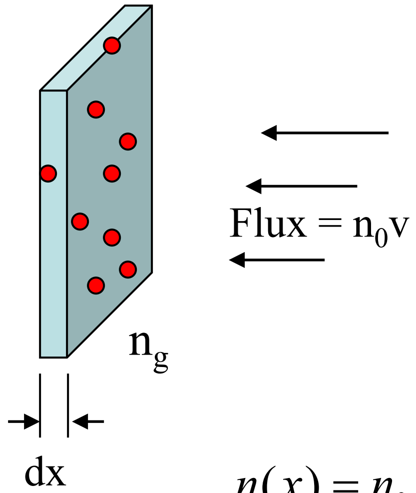
2. Sufficient plasma density:

$$N_D = 4/3\, \pi\, \lambda_D^3\, n_e \gg 1$$

   $N_D \sim 10^4$ … nb. of electrons around an ion

3. Dominant electron collisions - plasma is controlled by electromagnetic forces

Inter-particle collisions

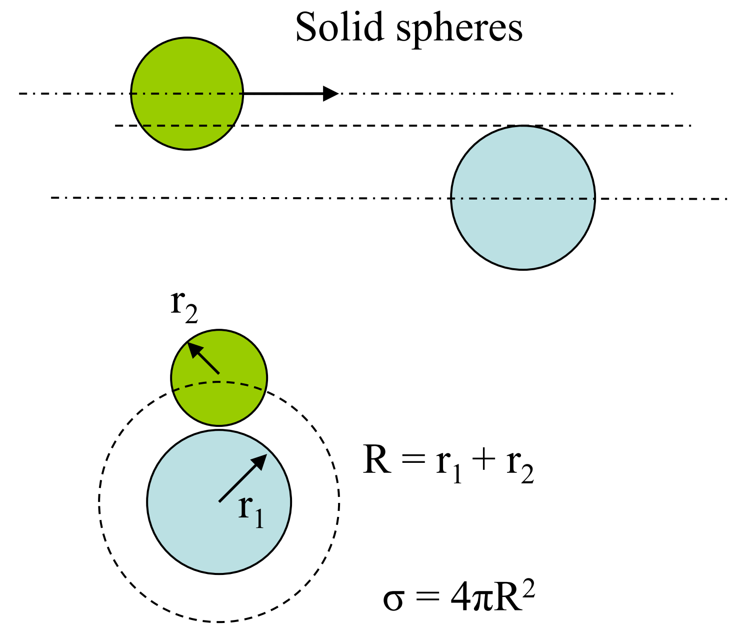


Number of particles incident per unit volume at position x that undergo interaction within dx (removing them from the incident beam):

$dn = -\sigma\, n\, n_g\, dx$

Uncollided density:

$$n(x) = n_0 \exp\left(-n_g \sigma x\right) = n_0 \exp\left(-\frac{x}{\lambda}\right)$$



σ – interaction cross-section (cm^2):
ionisation, excitation, scattering, …

$\lambda = \dfrac{1}{n_g \sigma}$ **Mean free path** (distance over which the uncollided density decreased by 1/e from its initial value n_0 at $x = 0$)

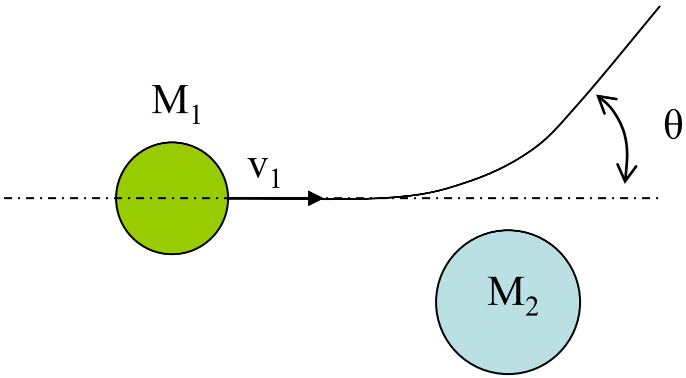
$\tau = \dfrac{\lambda}{v}$ Time between collisions

$\upsilon \equiv \tau^{-1} = \dfrac{v}{\lambda} = n_g \sigma v$ **Collision (interaction) frequency**

Lieberman, page 46

Elastic collisions

Elastic collisions :
M_1 moving, M_2 stationary



Kinetic energy is conserved

Energy transferred in one collision

$$\frac{E_2}{E_1} = \frac{\frac{1}{2}M_2 v_2^2}{\frac{1}{2}M_1 v_1^2} = \frac{4M_1 M_2}{(M_1 + M_2)^2}\cos^2\theta.$$

(a) $M_1 = M_2 \Longrightarrow E_{2\ max} = E_1$

(b) $M_1 << M_2 \Longrightarrow E_{2\ max} = E_1(M_1/M_2)$

$m_e = 9.10 \cdot 10^{-31}$ kg

$M_{Ar} = 40 \times 1.66 \cdot 10^{-27}$ kg $= 6.64 \cdot 10^{-26}$ kg

$m_e / M_{Ar} = 1.37 \cdot 10^{-5}$ → energy transfer during elastic electron collisions with neutral gas particles (and with ions) is negligible.

Inelastic collisions

Ionisation	$e + A \rightarrow A^+ + 2e$	$e + N_2 \rightarrow N_2^+ + 2e$
Excitation	$e + A \rightarrow A^* + e$	$e + O_2 \rightarrow O_2^* + e$
Dissociation	$e + AB \rightarrow e + A + B$	$e + SiH_4 \rightarrow e + SiH_3 + H$
Dissociative ionisation	$e + AB \rightarrow 2e + A^+ + B$	$e + TiCl_4 \rightarrow 2e + TiCl_3^+ + Cl$
Dissociative attachement	$e + AB \rightarrow A^- + B$	$e + SiCl_4 \rightarrow Cl^- + SiCl_3$
3-body recombination	$e + A^+ + B \rightarrow A + B$	$e + A^+ + B \rightarrow A + B$
Radiative recombinaison	$e + A^+ \rightarrow A + h\nu$	$e + A^+ \rightarrow A + h\nu$
Charge transfer	$A^+ + B \rightarrow A + B^+$	$Ar^+ (f) + Ar (s) \rightarrow Ar(f) + Ar^+(s)$
Penning ionisation	$A^* + B \rightarrow A + B^+ + e$	$He^* + O_2 \rightarrow He + O_2^+ + e$

Cross-sections (Ar, O_2)

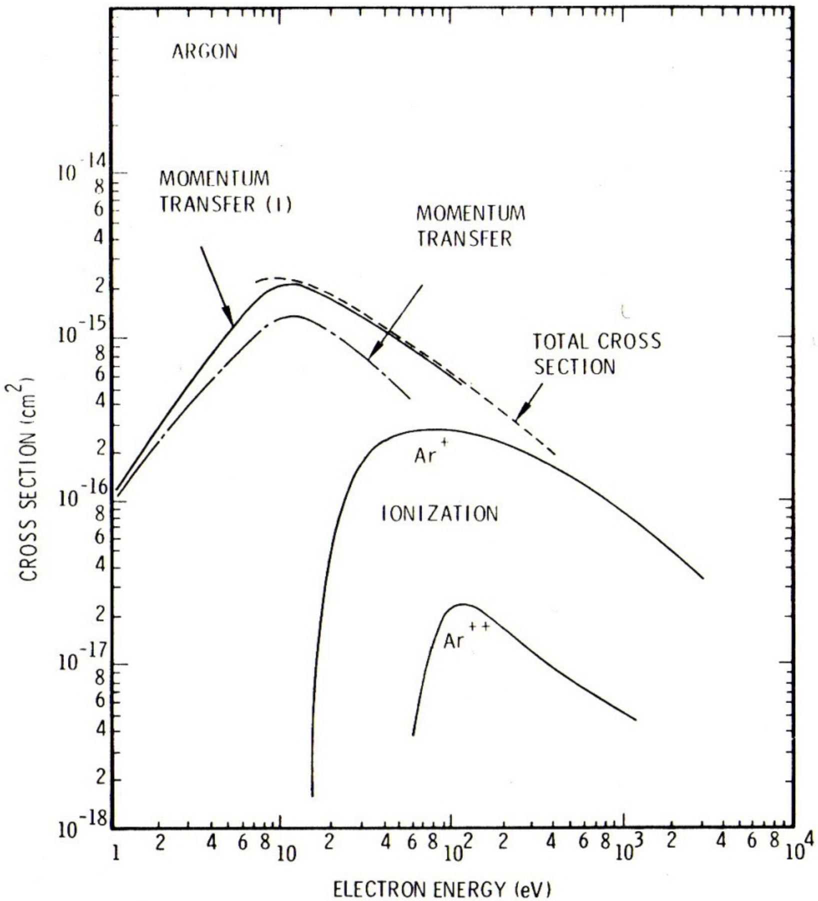


Figure 2.1. Collision cross sections for electrons in Ar gas (from Ref. 1).

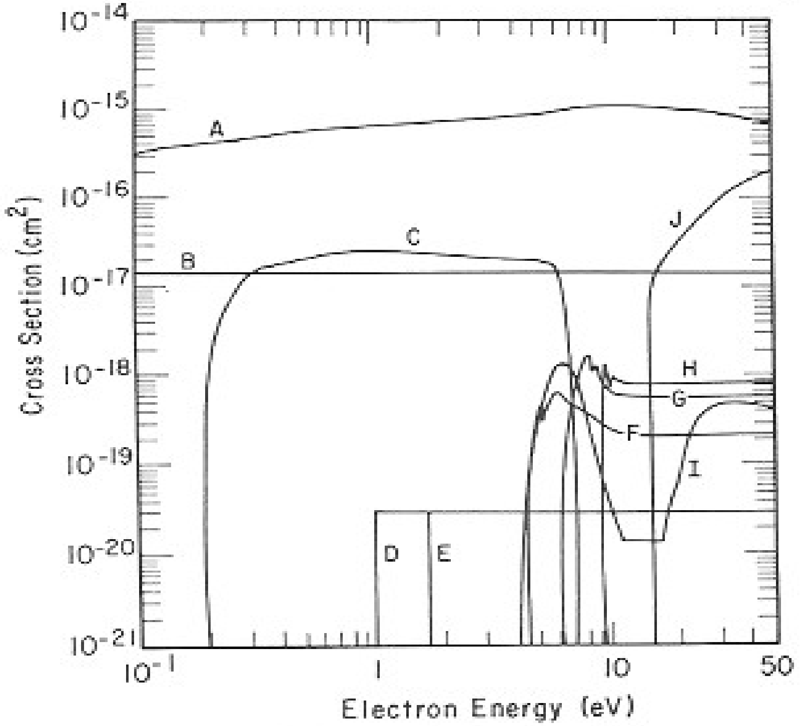


FIGURE 1.10. Elastic and inelastic collision cross-sections for electrons in oxygen; (A) elastic scattering; (B) rotational excitation; (C) vibrational excitation; (D) excitation to the $a^1\Delta_g$ state; (E) excitation of the $b^1\sum_u^+$ state; (F) excitation of the $A^3\sum_u^+$ state; (G) excitation of the $B^3\sum_u^-$ state; (H) excitation of higher electronic states; (I) dissociative attachment; (J) ionization [13].

Total cross-section: $\sigma_t = \sigma_{el} + \sigma_{ex} + \sigma_{ion} + \sigma_a + \sigma_\mu$

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Ionisation cross-sections in different gases

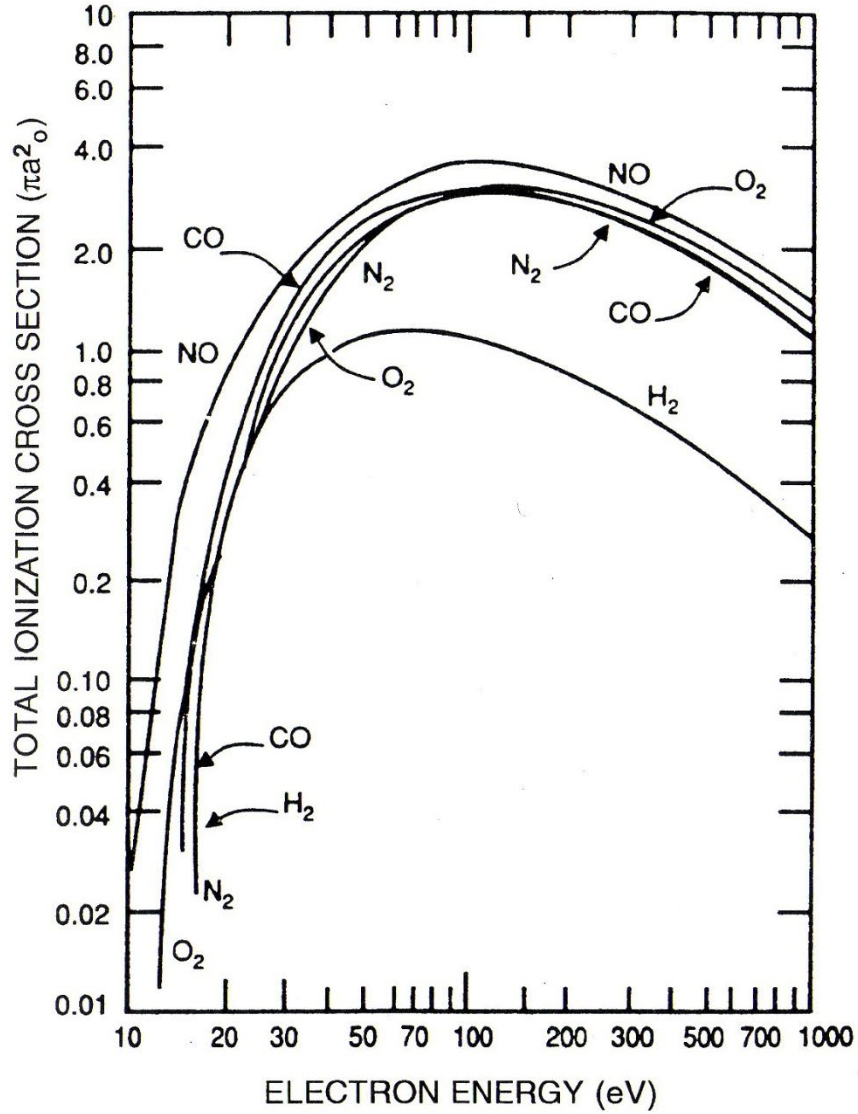


Figure 4-8 Total ionization cross sections for various gases plotted as a function of energy. (From S. C. Brown, *Basic Data of Plasma Physics*, 2nd ed. MIT, Cambridge, MA, 1967. Reprinted with the permission of The MIT Press.)

Electron energy distribution [$f_e(E)$, EEDF]

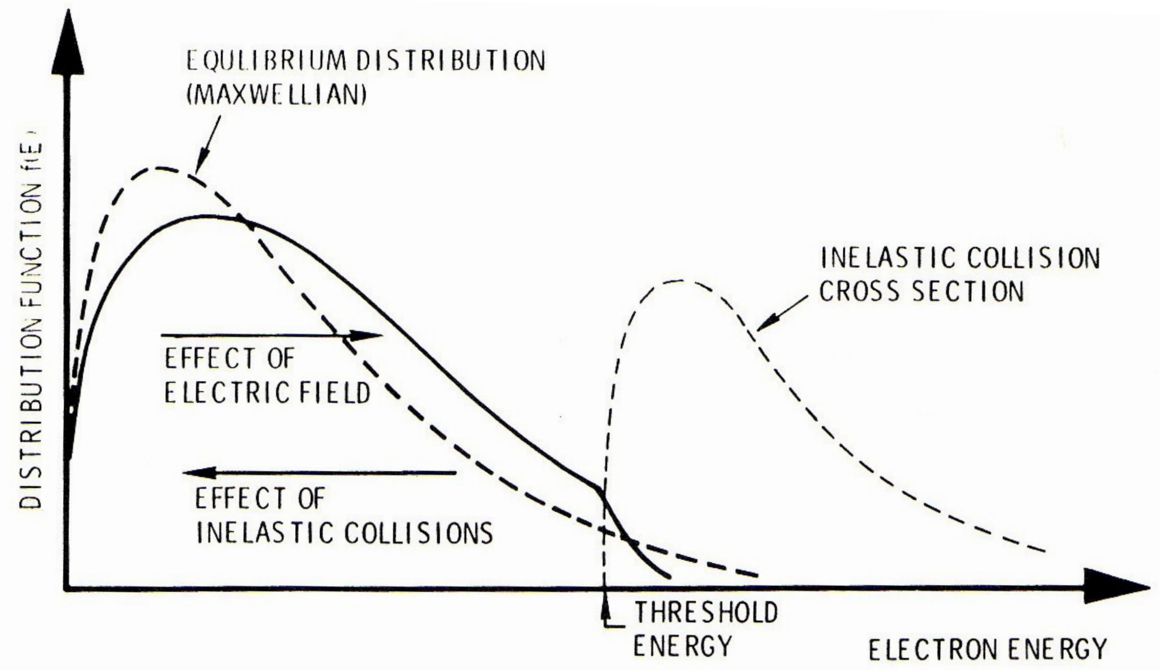


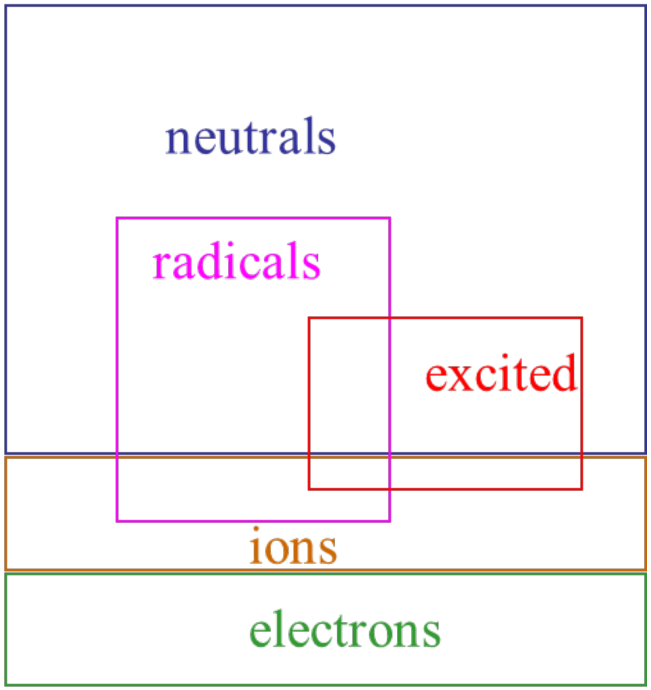
Figure 2.4. Schematic illustration of electron energy distribution function and inelastic collision cross section.

Example: Density of active species in a nitrogen discharge

Plasma parameters	Symbol	Value
Pressure	p	0.1 – 5 Torr
Current density	J	3.3 – 50 mA cm^{-1}
Temperature of		
Gas	T_g	300 – 700 K (0.03 – 0.06 eV)
Electrons	T_e	1-10 eV
Ions	T_i	0.03 – 0.3 eV
Density of		
Gaz	n_g	3 10^{15} – 10^{17} cm^{-3}
Electrons	n_e	10^9 – 10^{11} cm^{-3}
Ions (N2+)	n_i ($n_i = n_e$)	10^9 – 10^{11} cm^{-3}
Atomic nitrogen	n_N	10^{13} – 10^{15} cm^{-3}
Excited atomic nitrogen	n_N*	10^{10} – 10^{11} cm^{-3}
N_2, vibrational excit.	n_V (V=10)	10^{14} (p=2Torr, n_e = 1.7E10)
N_2, electronix excit.	n_A	10^{10} – 10^{11} cm^{-3}

1 eV ↔ 11 605 K

1 Torr = 133.32 Pa



A. Ricard, « Basic physics of plasmas/discharges: production of active species », in Plasma-Surface Interactions and Processing of Materials, Kluwer 1990.

Hybrid (combined) processes:

Ion plating

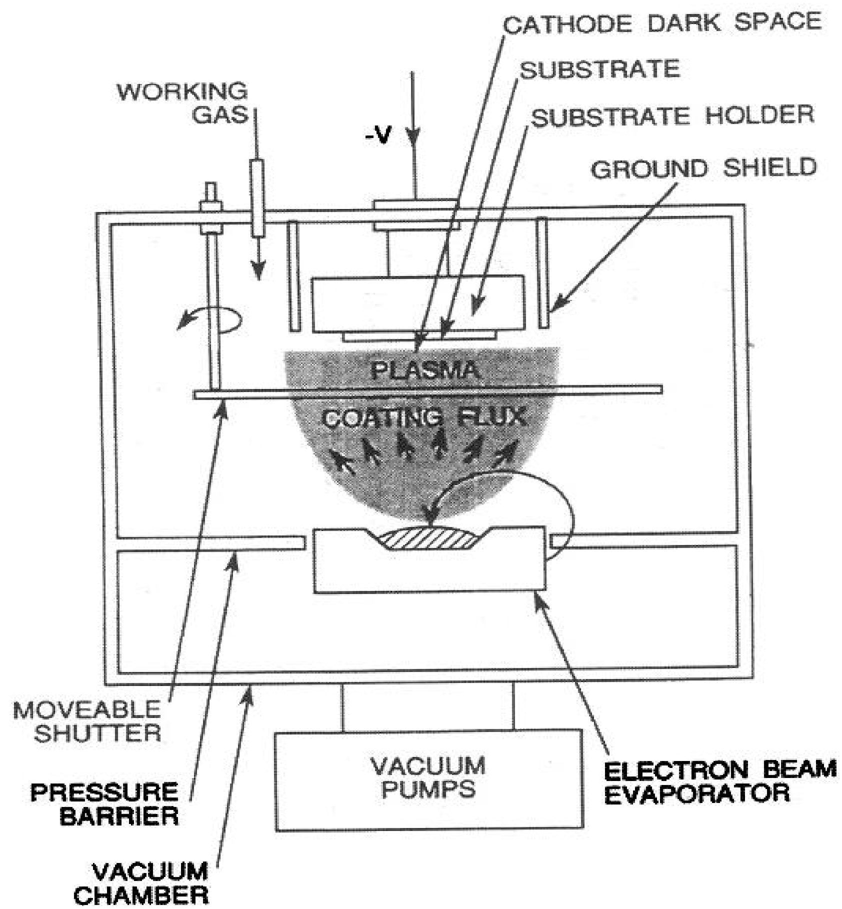


Figure 5-20 Ion plating system. (From Ref. 43.)

Activated reactive evaporation - ARE

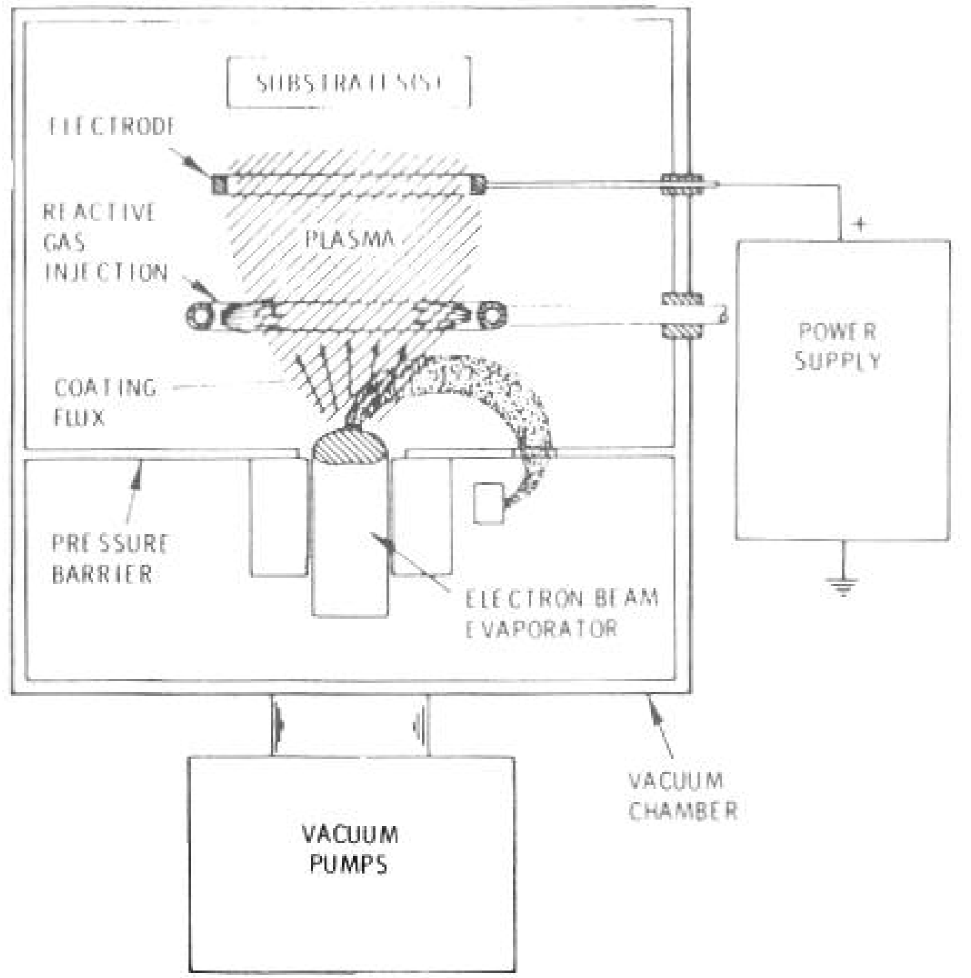


Figure 2.14. Schematic illustration of the activated reactive evaporation (ARE) process (see Ref. 49).

Ion sources – Kaufman type

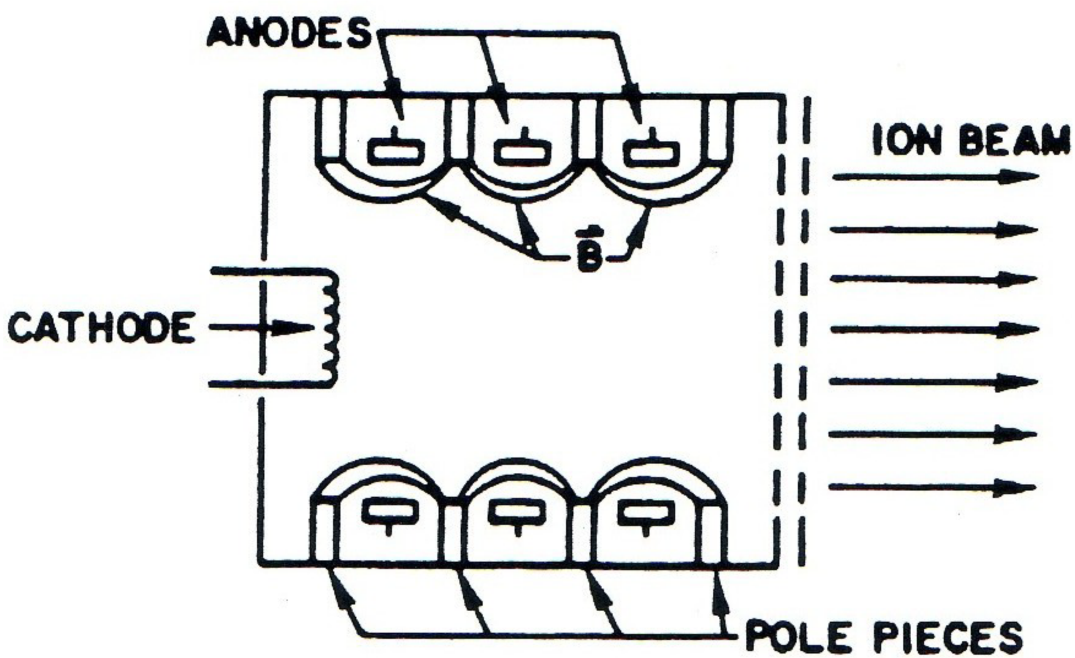
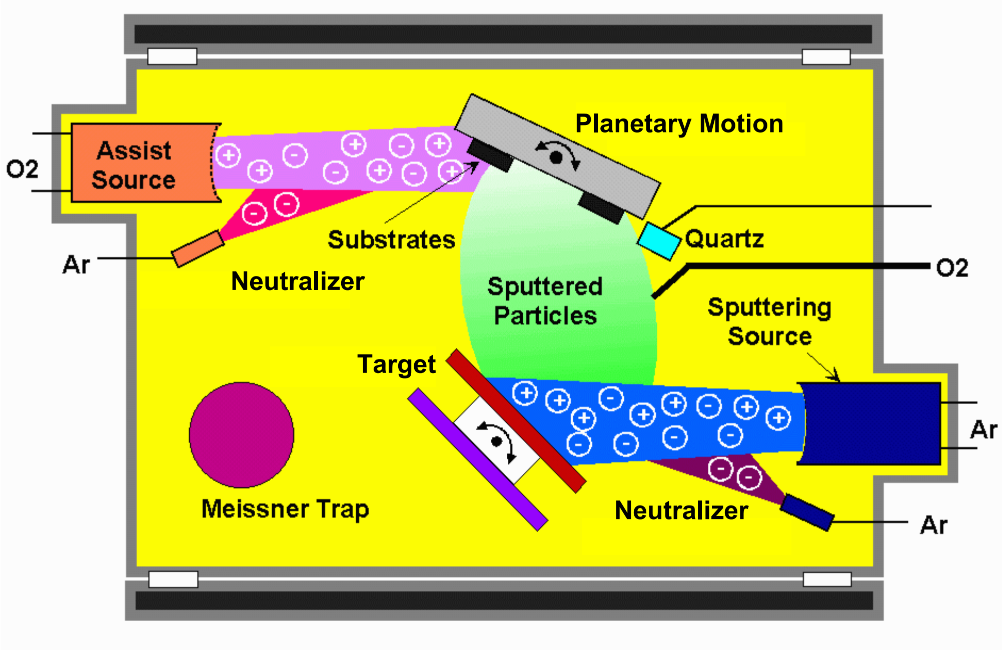


Figure E3.0.17. Kaufman-type ion source with multipole anode design. (After [73].)

M.R. Wertheimer, L. Martinu, T. Liston, in "*Handbook of Thin Film Process technology*", D.A. Glocker and S.I. Shah, eds.,IoP, Bristol 1995.

Dual ion beam sputtering (DIBS, IBS)



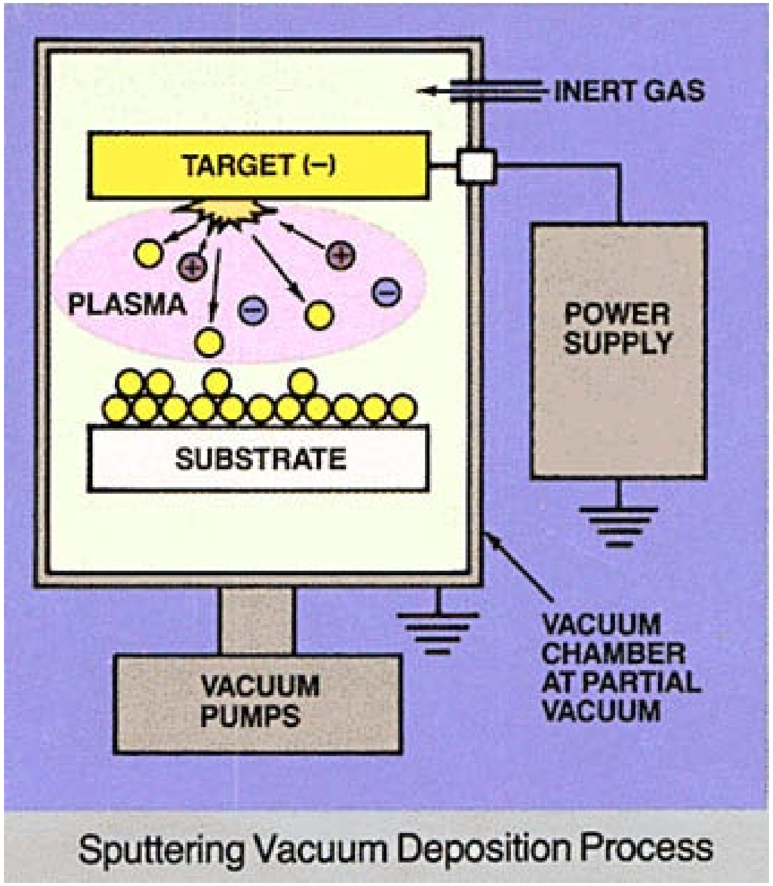
DIBS from Veeco at LaRFIS, Polytechnique

- Broad ion beam sputtering source
- Energetic beam is neutralized by electron injection
- Low energy oxygen ion source for the film bombardment
- Interchangeable targets : e.g., SiO_2 and Ta
- Base pressure ~10^{-7} Torr

Magnetron sputtering

- Non-reactive sputtering (Ar,…)
- Reactive sputtering (O_2, N_2, …)
- Target material (Si, Metals, ….)
- Target power (DC, AC, Pulsed DC, RF, …

- Base pressure 10^{-6} Torr
- Working pressure several mTorr



Magnetron sputtering

a) Planar magnetron

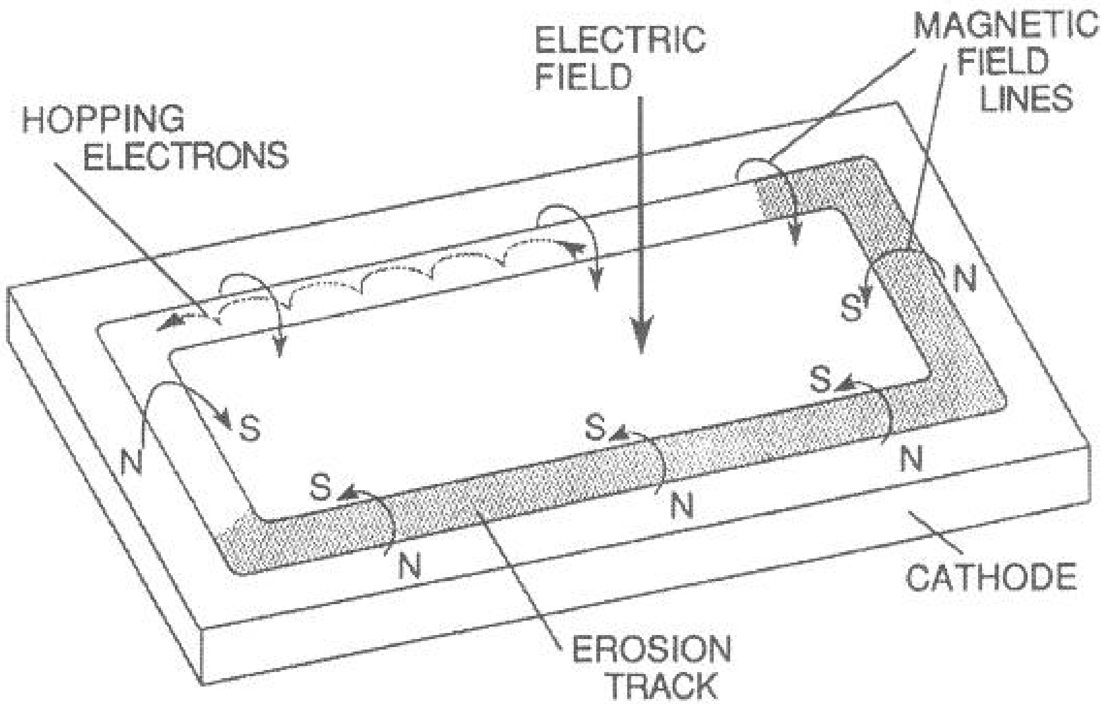


Figure 5-8 Applied fields and electron motion in the planar magnetron.

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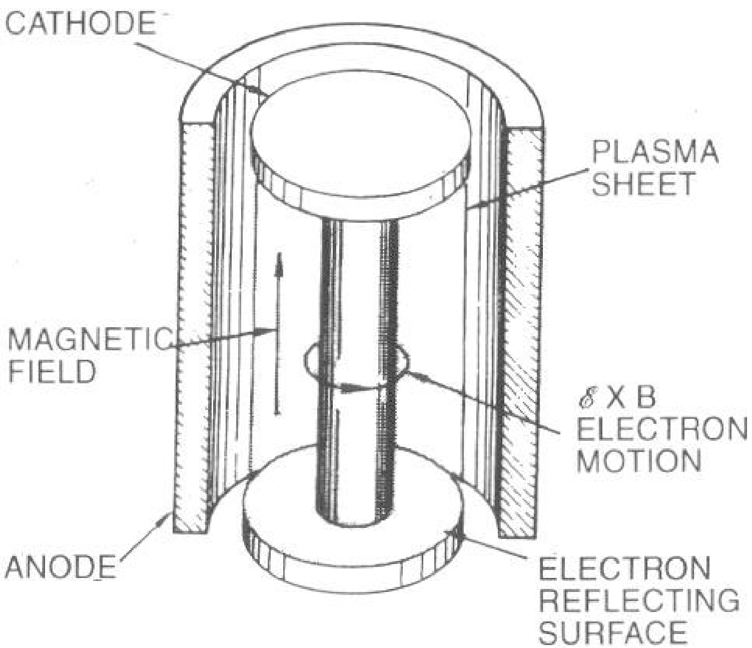
b) Cylindrical magnetron

c) Sputtering « gun »



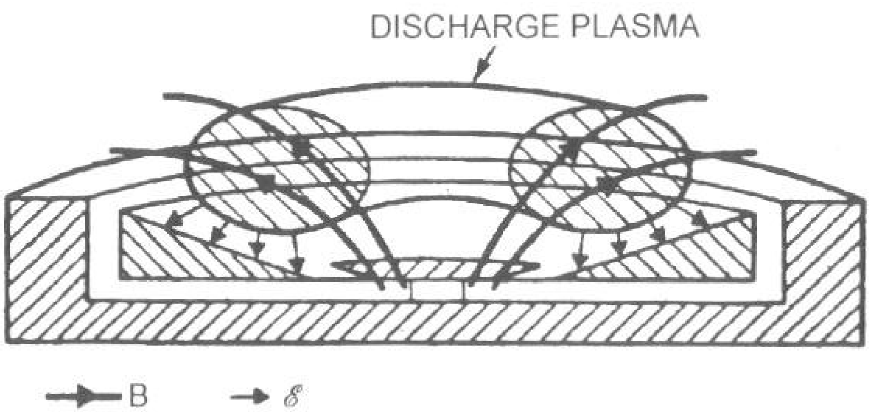


Figure 5-9 Nonplanar magnetron sputtering configurations. (Left) Cylindrical-post magnetron geometry. (From J. A. Thornton and A. S. Penfold, in J. L. Vossen and W. Kern, eds., *Thin Film Processes*. Academic Press, New York, 1978. Reprinted with the permission of Academic Press and A. S. Penfold.) (Right) Sputter-gun geometry. (Reprinted with the permission of S. M. Rossnagel.)

d) Different magnetron configurations:

- Triode system

- Hollow cathode:
Gas flow sputtering
Electron pendulum effect

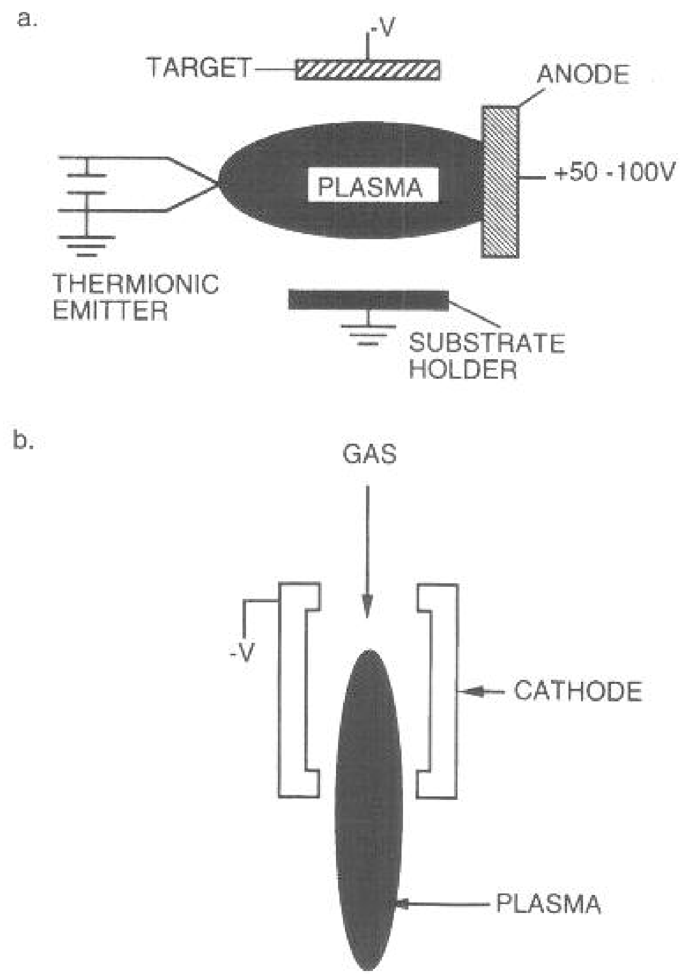
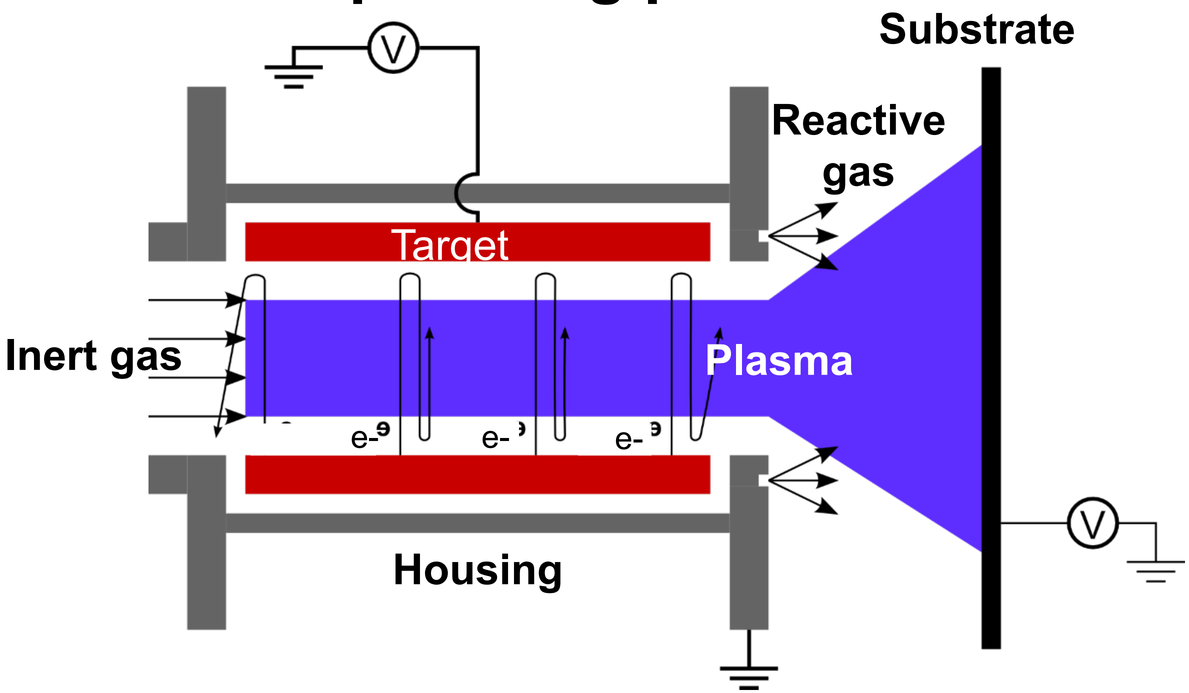
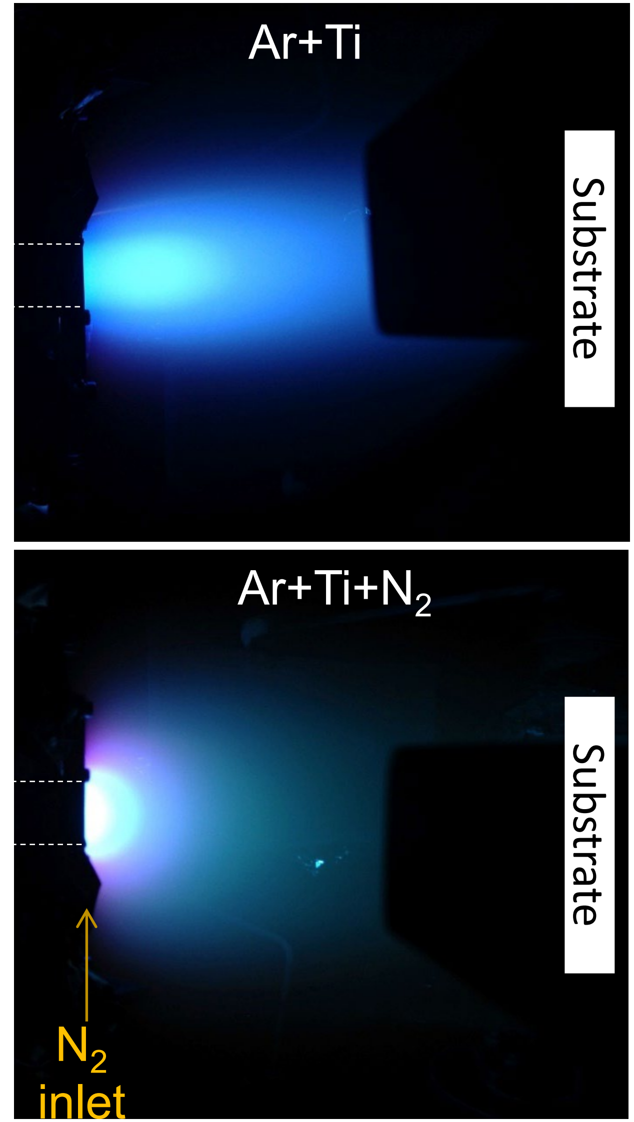


Figure 5-3 (a) Triode sputtering configuration utilizing a thermionic electron emitter. A magnetic field may be applied along the emitter–anode axis. (After L. I. Maissel in *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang, eds., McGraw-Hill, New York, 1970.) (b) Hollow cathode source. An axial magnetic field may also be applied.

Gas flow sputtering process





GFS system at LaRFIS, Polytechnique

Pendulum motion of electrons + restricted volume→ high discharge density, effective ionization of sputtered metal atoms, production of double-charged ions and metastables;
Pressure gradient pushes the high density, metal-rich plasma toward the substrate;
Reactive gas is added at the exit of the plasma plume.

Balanced and unbalanced magnetrons

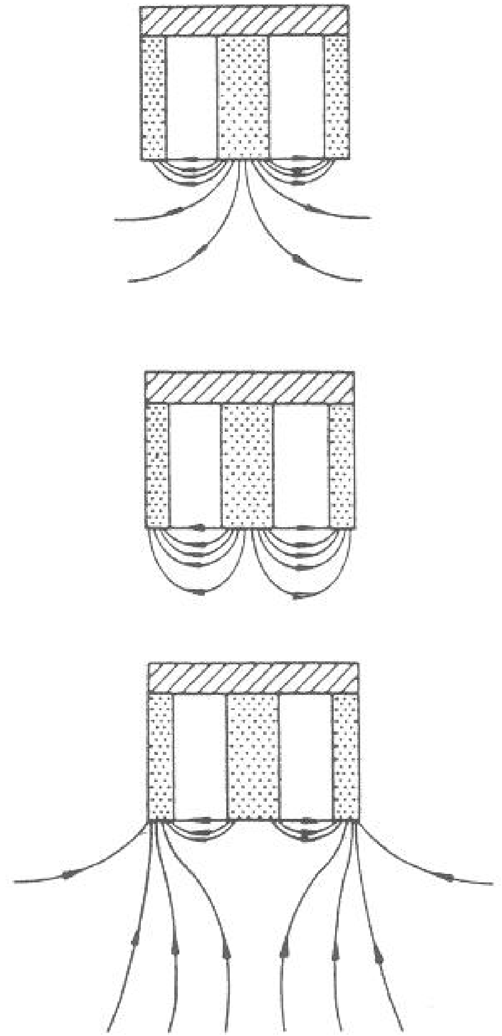


Figure 5-10 Planar magnetron configurations. (Top) Type-I (unbalanced). (Middle) Intermediate (balanced). (Bottom) Type-II (unbalanced). (From B. Window and N. Savvides, *J. Vac. Sci. Technol.* A4, 196, (1986). Reprinted with the permission of Dr. N. Savvides.)

Dual magnetron systems

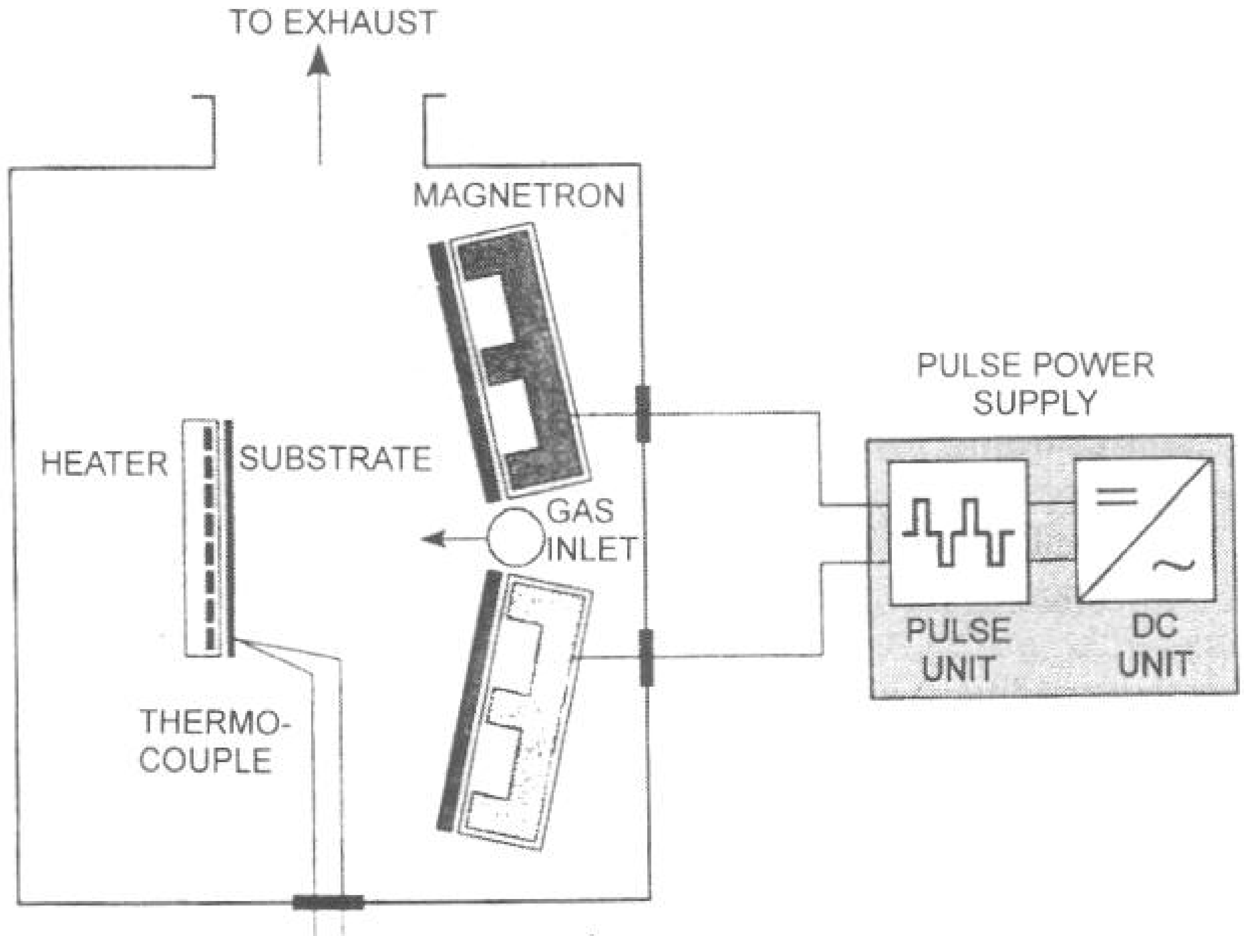


Figure 5-11 Arrangement for reactive pulsed-magnetron sputtering from dual Al targets. (From O. Zywitzki and G. Hoetzsch, International Conference on Metallurgical Coatings and Thin Films, San Diego, April 22–26, 1996). Reprinted with permission of the authors.

Cathodic arc deposition

(Arc evaporation)

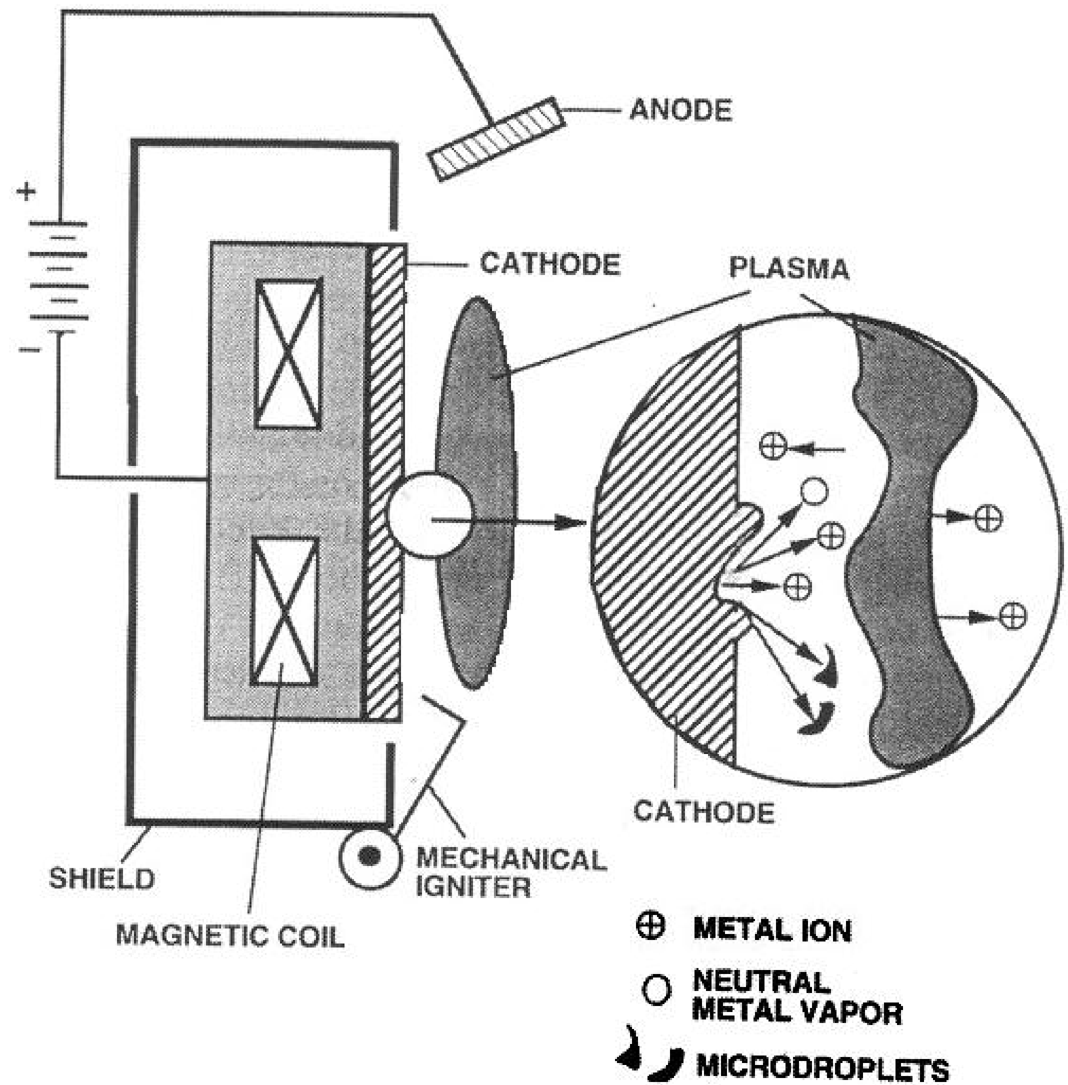
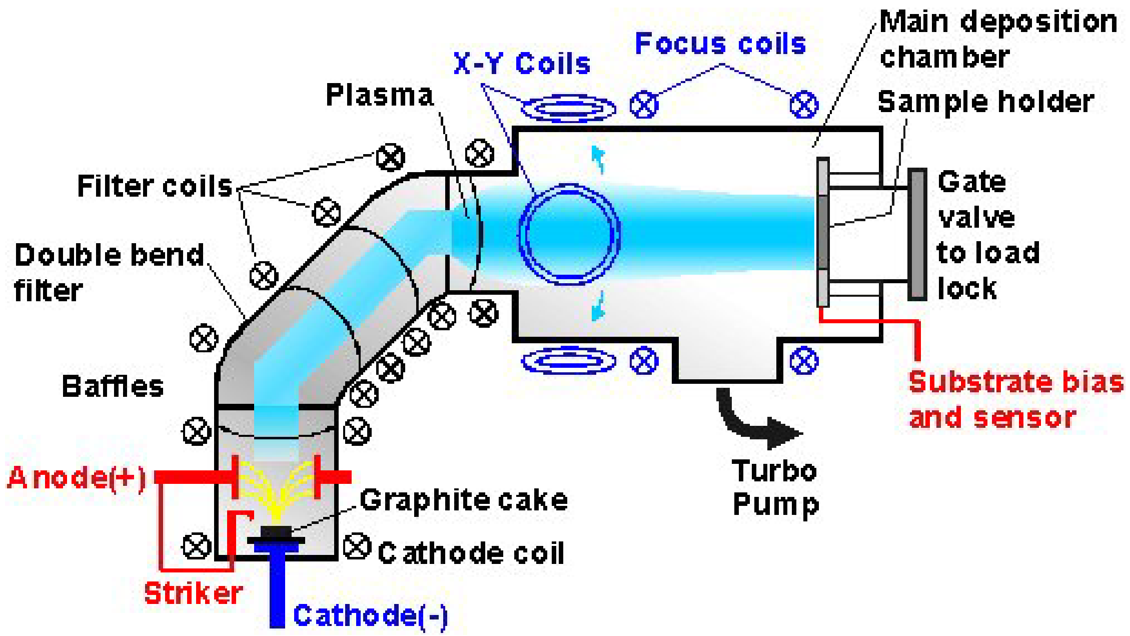


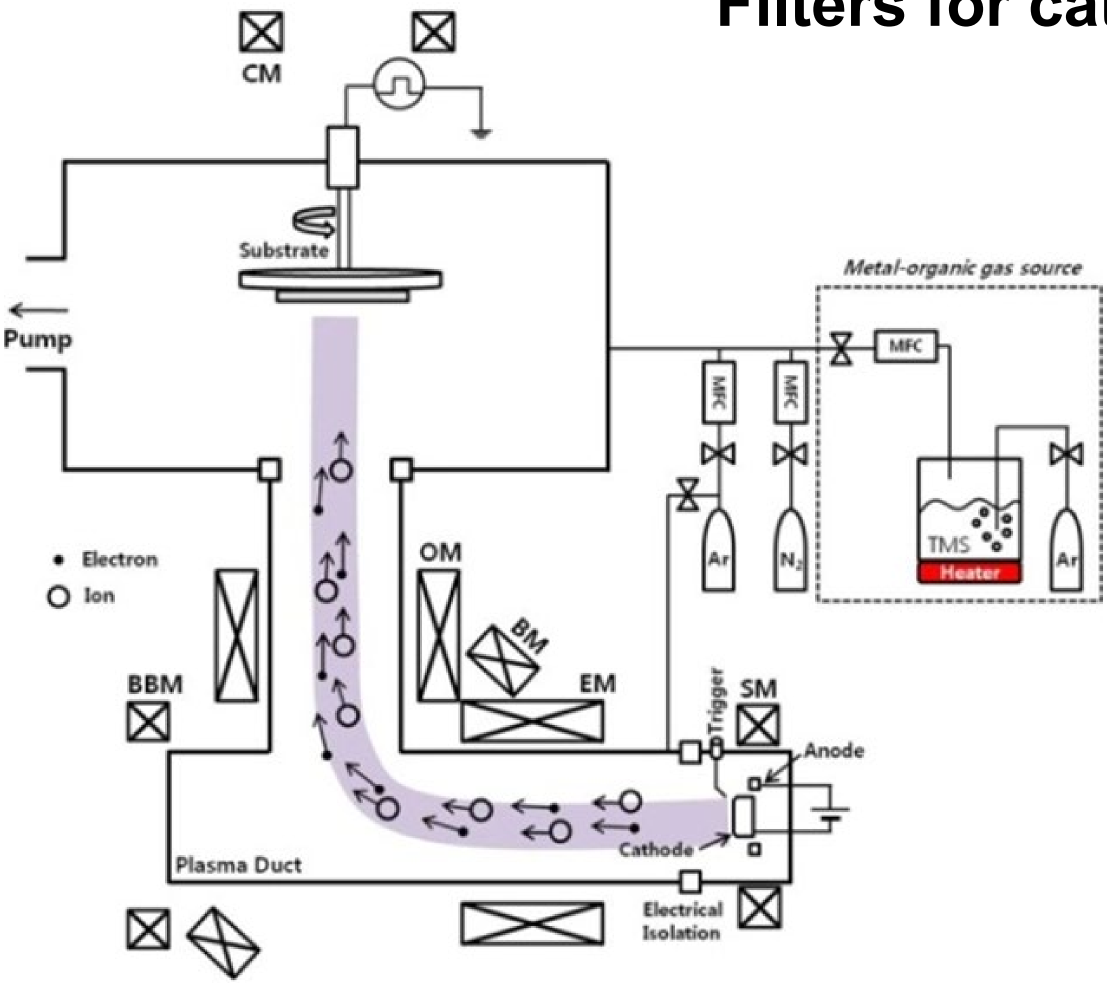
Figure 5-23 Cross section of cathodic-arc deposition system with a model of activity at a cathode spot. (From Ref. 48.)

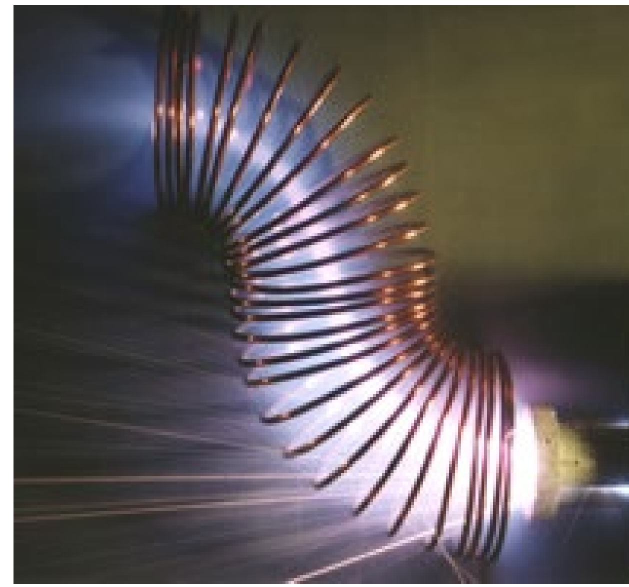
Filtered cathodic arc deposition



- The arc, cathode spot: 1- 10 μm size
- Current density in the spot: ~ 10^6 to 10^8 Acm^{-2}
- Solenoidal elbow with magnetic and electric fields, filtration of macroparticles
- Target: Ti….
- Base pressure: 10^{-6} Torr

Filters for cathodic arc deposition





S-shape filter
A. Anders

S. Lee, P.V. Bharathy, T. Elangovan, D. Kim, J.-K. Kim, Chapter 17 in Nanotechnology and nanomaterials, F. Ebrahimi, ed., ISBN 978-953-51-0762-0, 2012

Plasma impulse immersion implantation:

20-100 kV

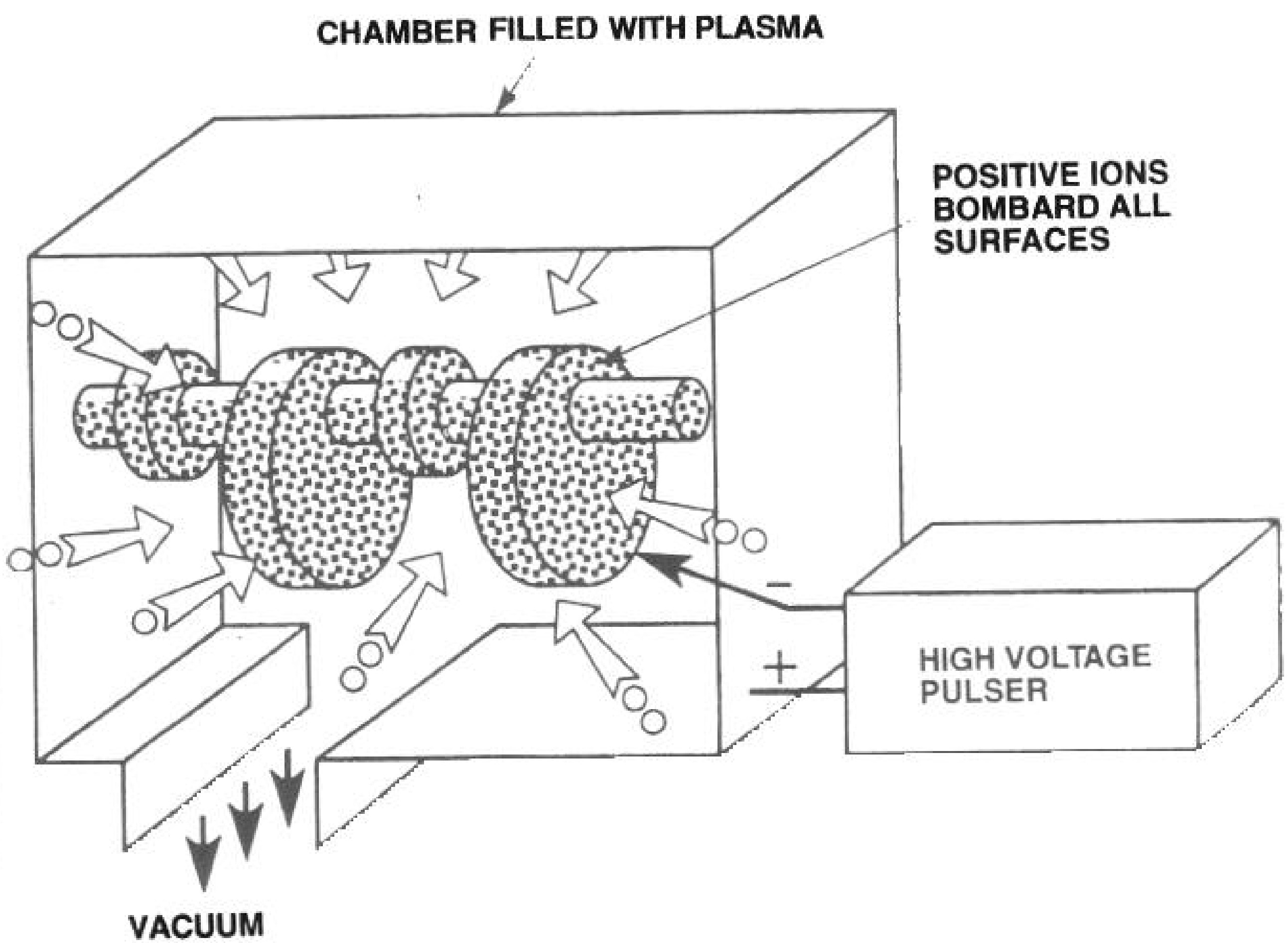


Figure 5-26 Illustration of the PIII process for automotive crankshafts. Because the plasma sheath surrounds the shaft, all of its surfaces are simultaneously ion bombarded without beam aiming or target manipulation. (From J. V. Mantese, I. G. Brown, N. W. Cheung, and G. A. Collins, *MRS Bulletin* **21**(8), 52 (1996). Reprinted with permission.)

Pulsed laser deposition - PLD

Deposition process:

a) Optical absorption depth

$$I(z) = I_0 \exp(-\alpha x)$$

b) Thermal diffusion

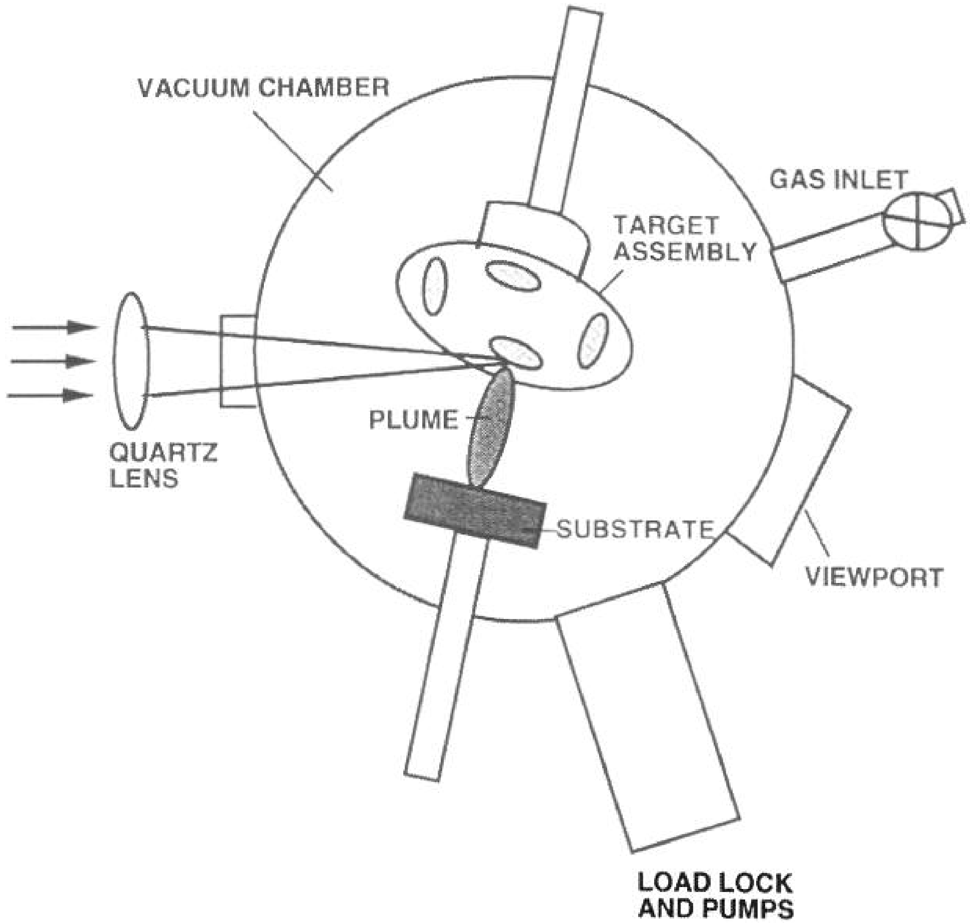


Figure 3-16 Schematic of PLD system for the deposition of metal oxide films. (From R. Ramesh, O. Auciello, V. G. Keramidas, and R. Dat in *Science and Technology of Electroceramic Thin Films*, O. Auciello and R. Waser, eds. Kluwer, Dordrecht, The Netherlands, 1995. Reprinted with the permission of the publisher.)

Surface engineering
Vapor deposition of thin films and coatings

Materials added to the surface - deposition

Surface modification – interface engineering

Origin of the source material: a) Solid phase – Physical Vapor Deposition (PVD)

b) Gas phase – Chemical Vapor Deposition (CVD)

Physical	**Hybrid**	**Chemical**
Evaporation • Joule effect • Electron beam	Reactive evaporation	Chemical vapor deposition (thermal CVD) Plasma-Enhanced CVD (PECVD)
Sputtering • Magnetron • Ion beam	Reactive sputtering Ion-assisted deposition (Plasma Immersion Ion Implantation –PIII)	Laser Assisted CVD (Laser CVD) Atomic Layer Deposition (ALD) New trends: - Atmospheric pressure CVD
Molecular beam epitaxy Pulsed laser deposition (PLD)	Surface cleaning Surface functionalization (nitriding, carburizing, boriding, … Implantation Patterning, …)	- Ion Beam Assisted CVD - Hybrid methods: a) PVD/CVD/PECVD b) Duplex – Thin-on-Thick

Thermal CVD Process

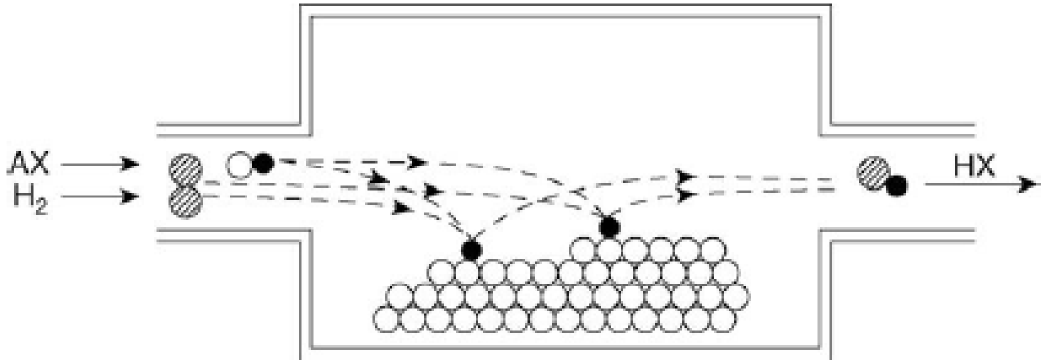


Figure 7.1: The principle of CVD.

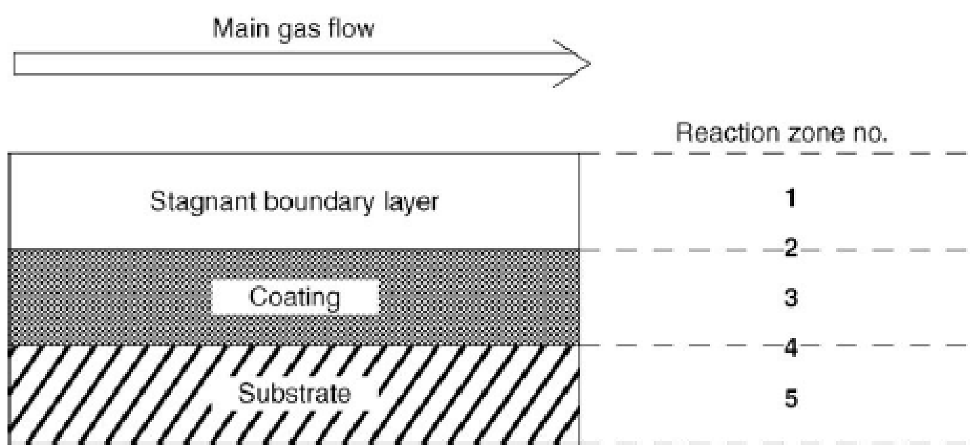


Figure 7.2: Important reaction zones in CVD.

Three step reaction:
- Initiation
- Propagation
- Termination

Rate-limiting steps during CVD

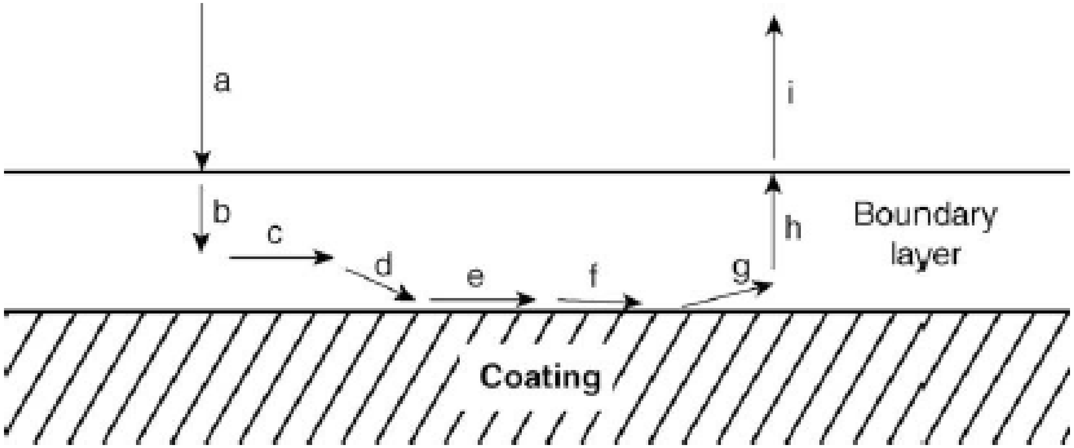


Figure 7.20: The various steps in a CVD process.

(a) Transport of gaseous reactants to the boundary layer surrounding the substrate (free and forced convection)
(b) Transport of gaseous reactants across the boundary layer to the surface of the substrate (diffusion and convection flows)
(c) Adsorption of reactants on the surface of the substrate
(d) Chemical reactions (surface reactions between adsorbed species, between adsorbed species and reactants in the vapor and or between reactants in the vapor)
(e and f) nucleation (at least at the initial stage) and growth
(g) Desorption of some of the reaction products from the surface of the substrate
(h) Transport of reaction products across the boundary layer to the bulk gas mixture
(i) Transport of reaction products away from the boundary layer

CVD-based processes

Table 7.1: Summary of chemical vapor deposition (CVD) process family

Type	Pressure range	Description
Atmospheric pressure CVD (APCVD)	High–atmospheric	Processes at atmospheric pressure
Low-pressure CVD (LPCVD)	Low	Processes at subatmospheric pressures
Ultrahigh vacuum CVD (UHVCVD)	Typically below 10^{-6} Pa ($\sim 10^{-8}$ torr)	Processes at a very low pressure
Aerosol-assisted CVD (AACVD)		Precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically
Direct liquid injection CVD (DLICVD)		Precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursor's vapors are transported to the substrate as in classical CVD process
Microwave plasma-assisted CVD (MPCVD)		

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CVD-based processes (continued)

Remote plasma-enhanced CVD (RPECVD)		Utilizes a plasma to enhance chemical reaction rates of the precursors, and allows deposition at lower temperatures
Atomic layer CVD (ALCVD) or ALD		Deposits successive layers of different substances to produce layered, crystalline films
Hot wire CVD (HWCVD)		Also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). Uses a hot filament to chemically decompose the source gases
Metal-organic chemical vapor deposition (MOCVD)		Based on metal-organic precursors
Hybrid physical–chemical vapor deposition (HPCVD)		Vapor deposition processes that involve both chemical decomposition of precursor gas and vaporization of a solid source
Rapid thermal CVD (RTCVD)		Uses heating lamps or other methods to rapidly heat the wafer substrate
Vapor-phase epitaxy (VPE)		

Ion beam assisted CVD – IBA-CVD
Fluidized bed CVD
Hollow cathode PECVD

Application: Microelectronics components

Structure of a DRAM memory

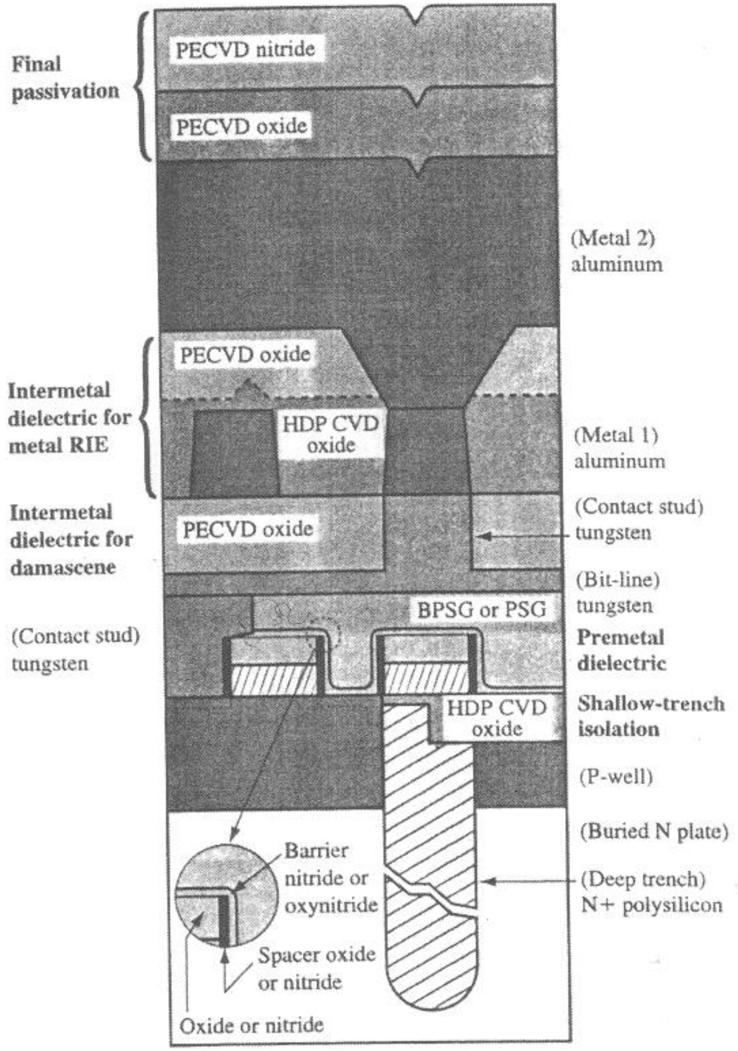

Figure 6-21 Schematic drawing of a three-level DRAM cell illustrating actual and potential (bold font) plasma CVD applications. (From Ref. 48. Copyright © 1999 by IBM Corp. Reprinted with permission.)

Structure of a MOS transistor

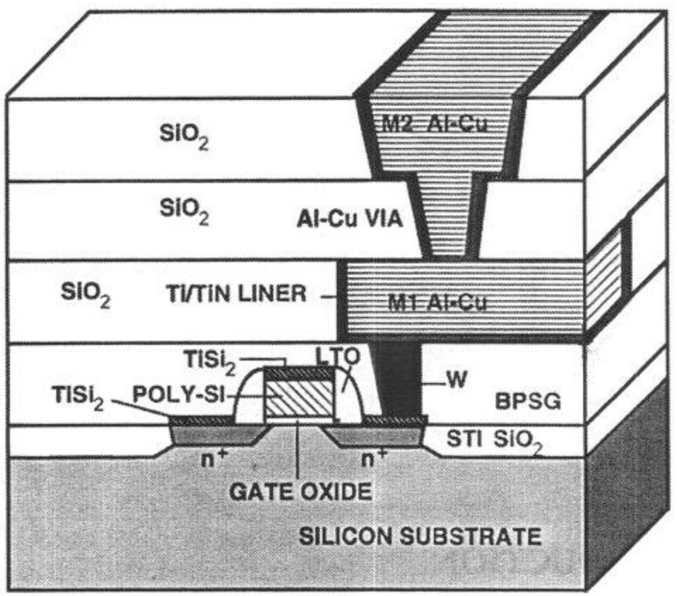

Figure 6-1 Schematic cross-sectional view of an MOS transistor structure with multilevel metallization scheme. Film materials deposited by CVD are indicated in the text. *Note:* LTO = low temperature oxide, BPSG = borophospho-silicate glass, STI = silicon trench insulator. After K. P. Rodbell, IBM, T. J. Watson Research Division.

Al-Cu, Ti/TiN, $TiSi_2$ - PVD
Si_3N_4, W, SiO_2 - CVD

Schematics of a CVD System

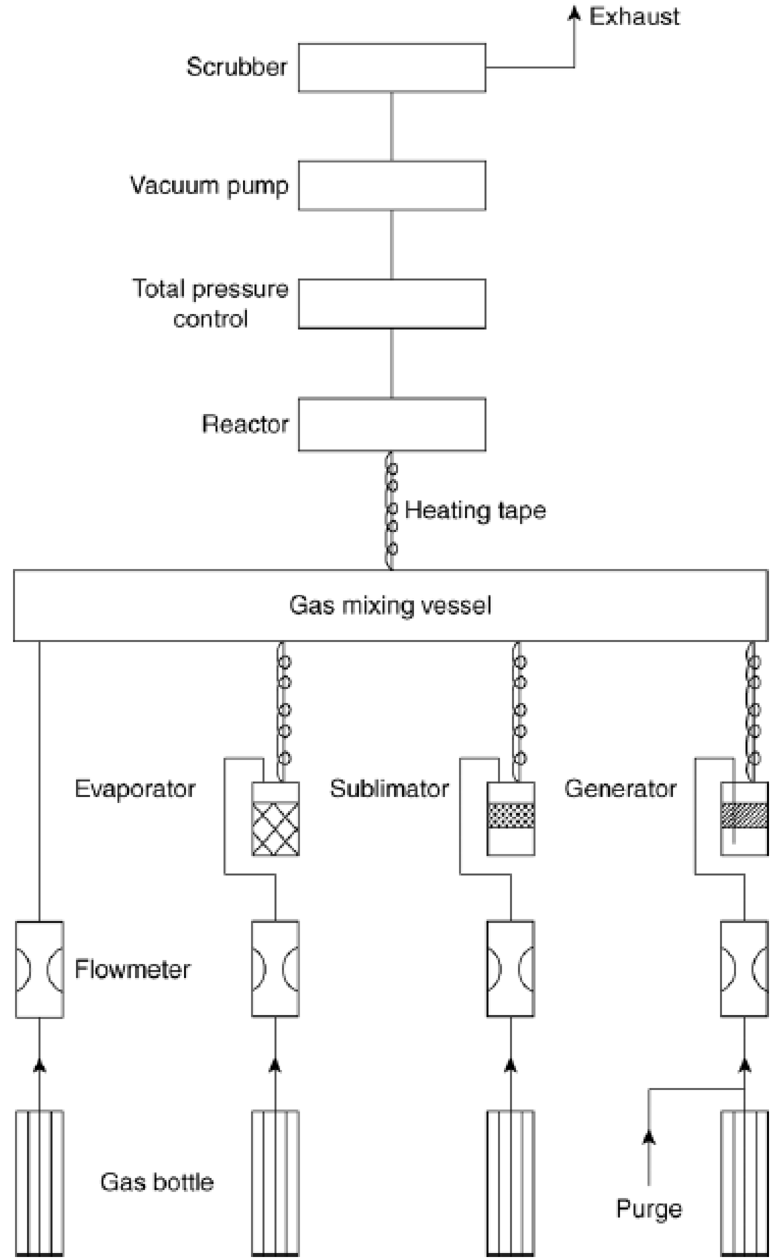

Figure 7.6: Sketch of a CVD system.

Types of reactors: hot and cold walls

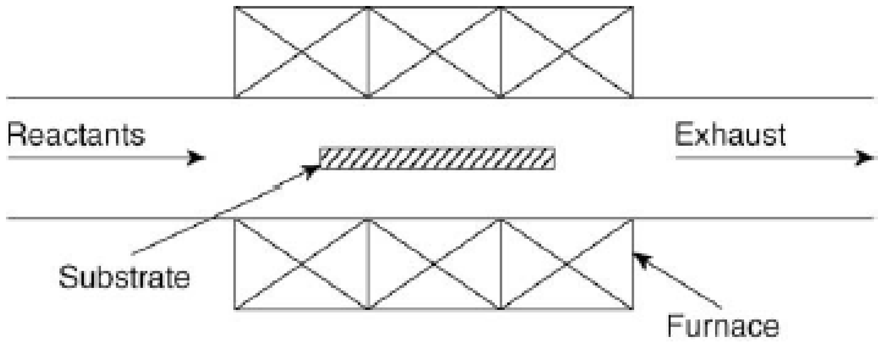

Figure 7.7: Hot wall CVD reactor.

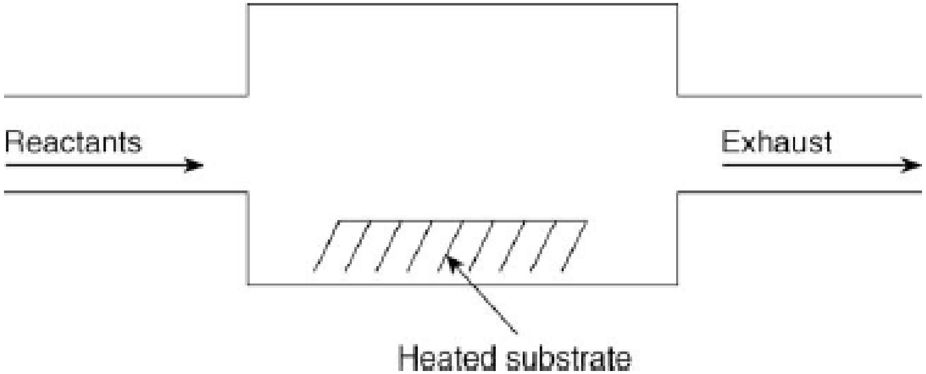

Figure 7.8: Cold wall CVD reactor.

Reactor configurations

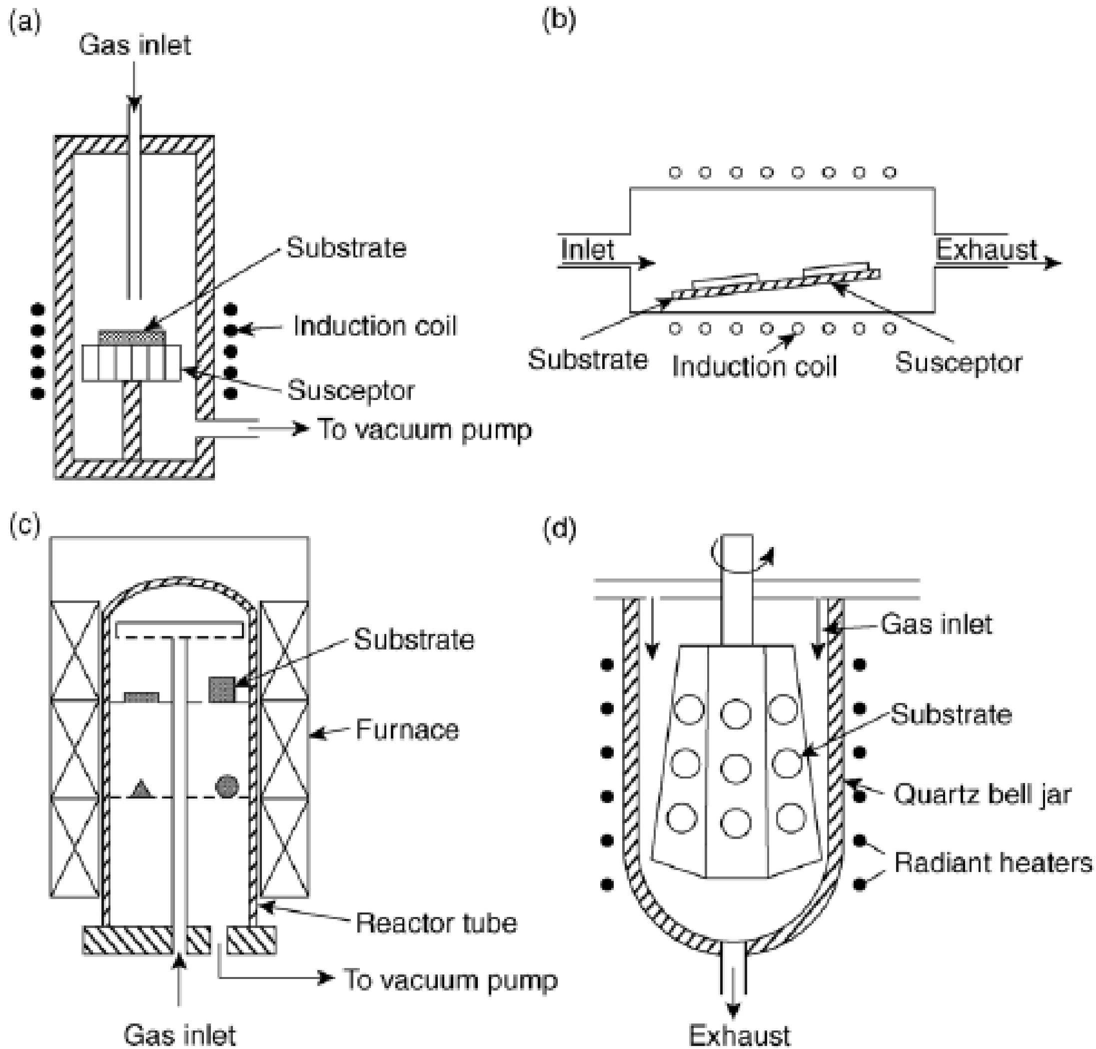

Figure 7.9: Examples of some CVD reactors: (a, b) RF heated cold wall reactors; (c) vertical hot wall reactor; (d) barrel reactor.

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AP direct liquid injection CVD

Surface & Coatings Technology 204 (2009) 887–892

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journal homepage: www.elsevier.com/locate/surfcoat

DLI-CVD of TiO_2–Cu antibacterial thin films: Growth and characterization

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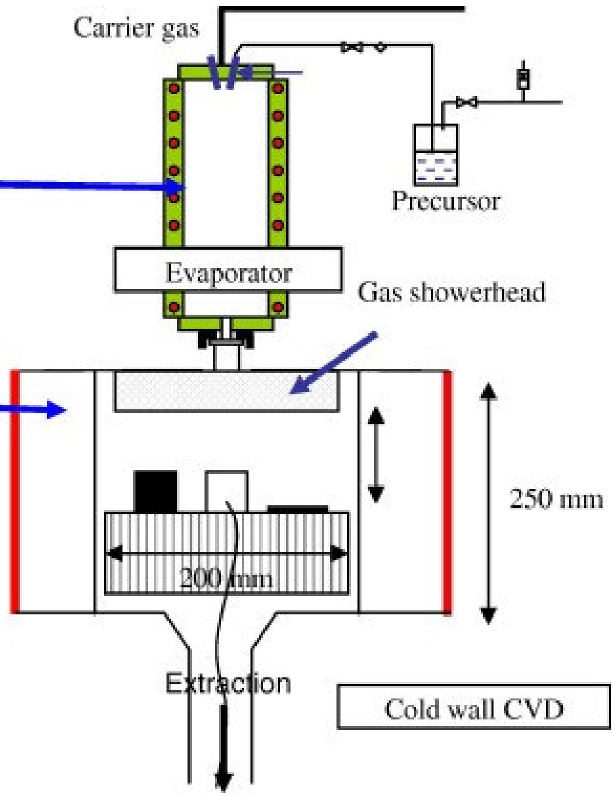
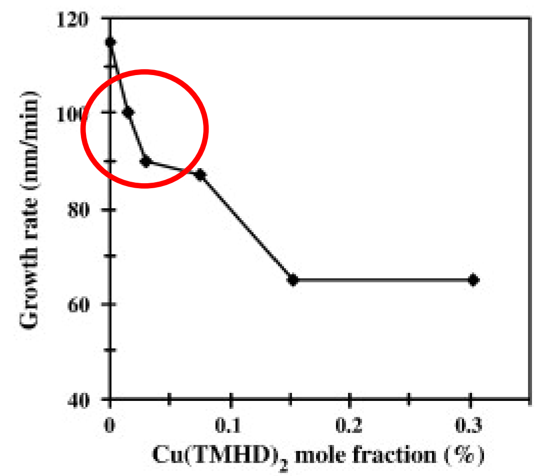
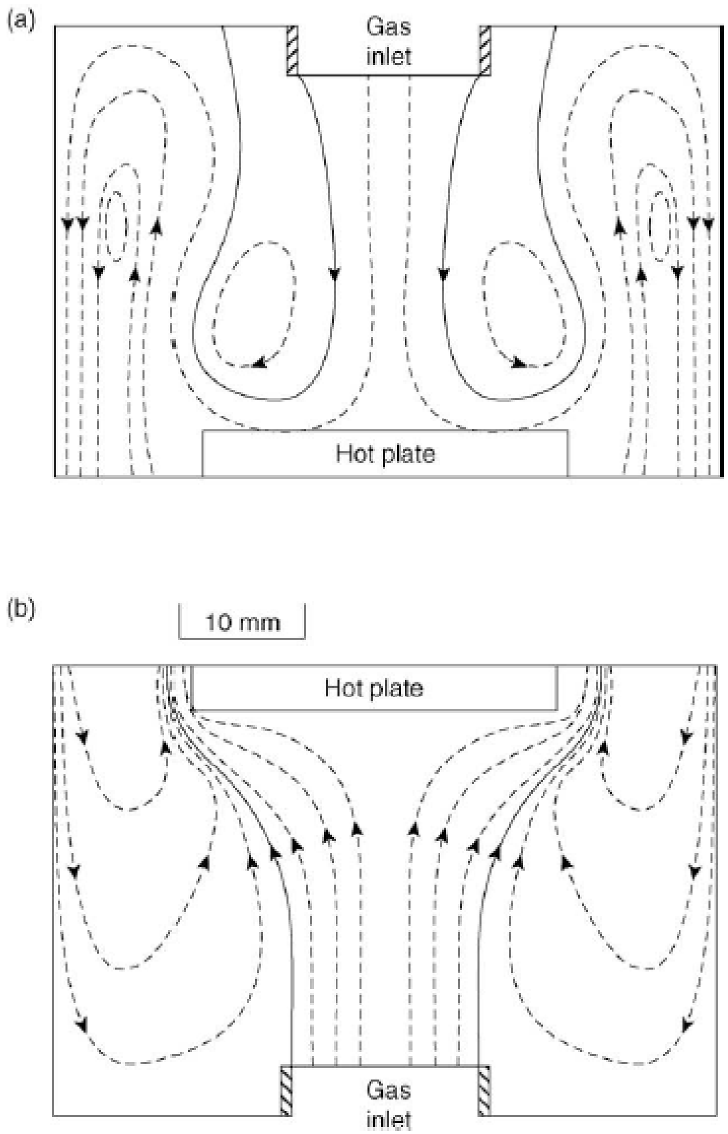




Influence of the $Cu(TMHD)_2$ mole fraction on the growth rate of TiO_2–Cu films (T = 683 K).

Gas flow patterns



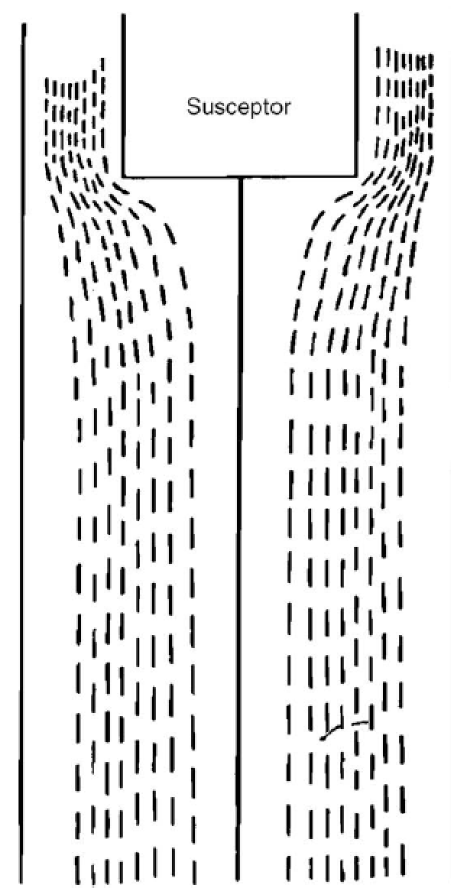


Figure 7.13: Gas flow pattern in a cold wall reactor with geometry different than that sh
Figure 12 [36].

Figure 7.12: Gas flow pattern in a cold wall reactor, where the forced and buoyance-driven convection (a) interact, and (b) counteract, substrate temperature 900 K, Re = 50 [35].

Control of the CVD film microstructure

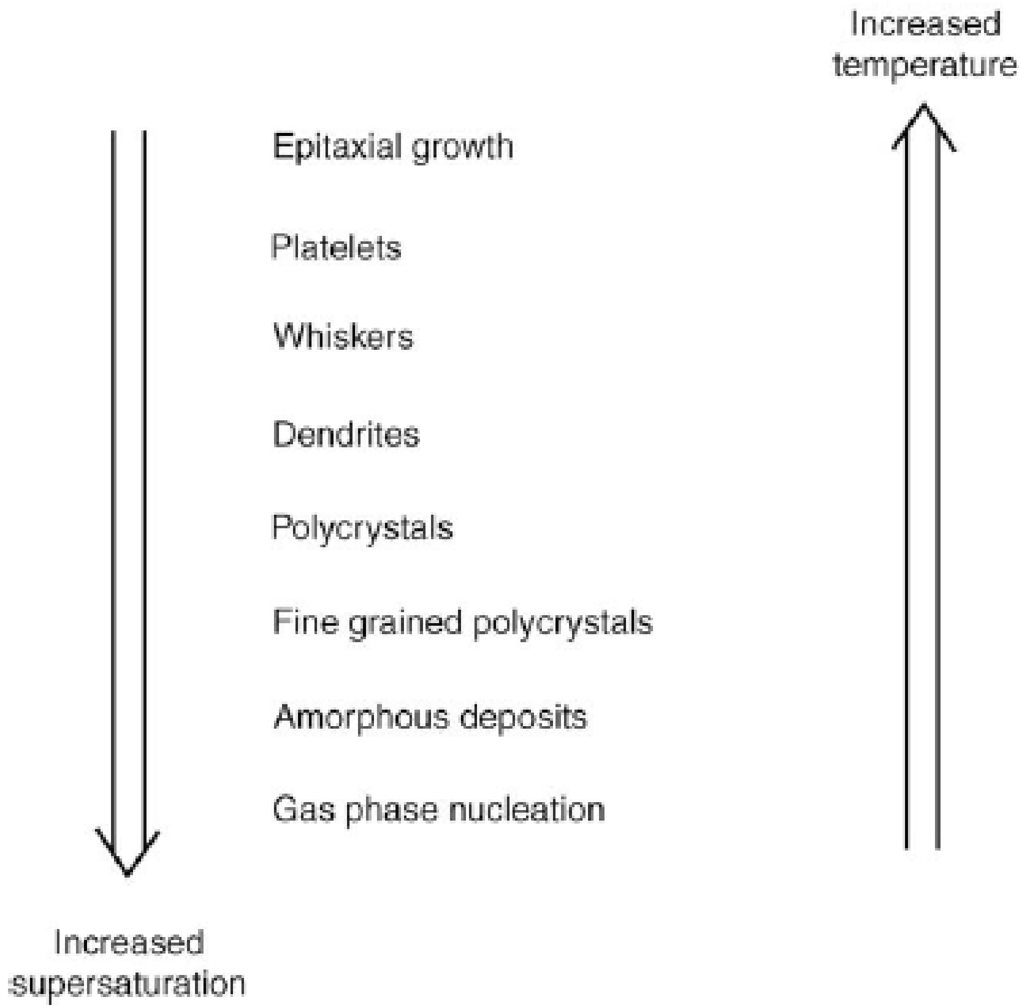


Figure 7.31: Microstructure sequence of CVD materials [55].

Example: CVD of hard coatings

APCVD TiN and TiCN

1. High temperature, $1200°C > T > 850°C$:

$$2TiCl_4 + N_2 + 4H_2 \rightarrow 2TiN + 8HCl$$

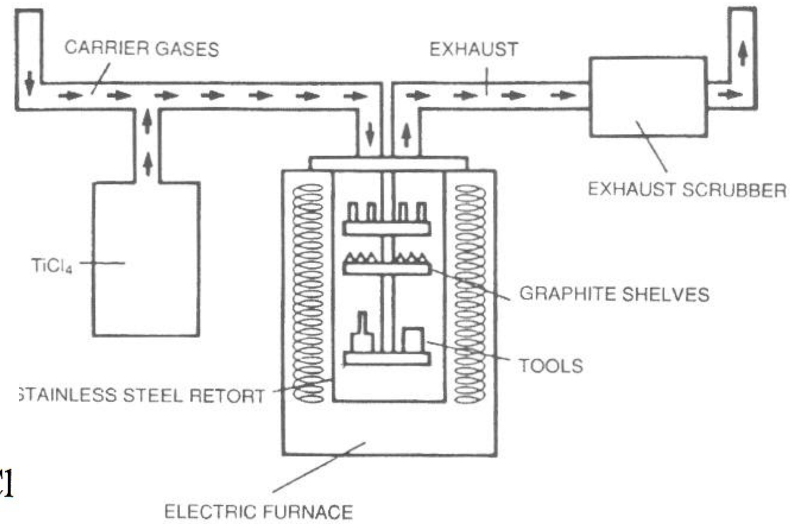
2. Moderate temperature, $850°C > T > 700°C$:

$$TiCl_4 + CH_3CN + 5/2H_2 \rightarrow Ti(C, N) + CH_4 + 4HCl$$

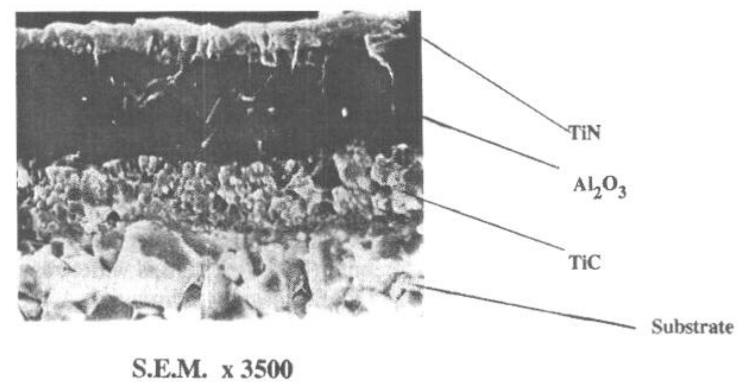
APCVD of SiO_2

$$Si(OC_2H_5)_4 \xrightarrow{700°C} SiO_2 + \text{by-products.}$$

$$SiH_4 + O_2 \xrightarrow{450°C} SiO_2 + 2H_2$$



(a)



(b)

Figure 6-16 Schematic view of a commercial CVD reactor for deposition of TiC, TiN, and Al_2O_3 on carbide cutting tools. (Courtesy of A. Gates, Multi-Arc Scientific Coatings Inc.) (b) SEM image of CVD multilayer coating for cutting tool inserts. Carbide substrate/TiC/Al_2O_3/TiN (3500 ×). Courtesy of S. Wertheimer, ISCAR Ltd.

Examples of applications of CVD films

- ***Microelectronics*** industries use CVD for growth of epitaxial layers (vapor-phase epitaxy (VPE)) and for making films serving as dielectrics (low and high *k*), conductors, passivation layers, diffusion barriers, oxidation barriers, etc.
- ***Semiconductor lasers*** of GaAs/(Ga,Al)As and InP/(In,Ga)As. These materials are also used in microwave devices and solar cells.
- ***Optical fibers*** for telecommunication. Optical fibers are produced by coating the inside of a fused silica tube with oxides of silicon, germanium, boron, etc., for obtaining the correct refractive index profile. After the deposition, a fused silica tube is collapsed to a rod and the rod is then drawn into a fiber.
- ***Solar energy*** conversion by the utilization of selective absorbers and of thin film solar cells of silicon and gallium arsenide, and dye sensitized solar cells.
- ***Carbon nanotubes*** for advance electronic, biological and chemical devices and detectors.
- ***Wear-resistant*** coatings have wide industrial applications. Coatings of TiC, TiN and Al_2O_3 on cemented carbide cutting-tool inserts and of TiC on steels (punches, nozzles, free wheels, etc.) are used extensively.
- ***Friction-reducing*** coatings for use in sliding and rolling contacts, for example.
- ***Corrosion-resistant*** coatings (Ta, Nb, Cr, etc.).
- ***Erosion-resistant*** coatings (TiC, Cr_7C_3, B_4C, etc.).
- ***Heat-resistant*** coatings (Al_2O_3, SiC, Si_3N_4, etc.).
- ***High temperature superconductors*** for use in medical, power grid, high-energy physics applications.
- ***Fibers*** for use in fiber-reinforced materials (fibers of boron, silicon carbide, boron carbide, etc.).
- ***Structural shapes*** (tubes, crucibles, heating elements, etc.) of, for example, tungsten and silicon carbide.
- ***Decorative coatings*** of TiN (gold color) on watches, for example.
- ***Conductive coatings*** for integrated circuit interconnects, display applications, solar control, electrochromic windows, automotive windows.

Advanced fabrication techniques for the deposition of the nanostructured thin films:

Examples of possible subjects for Project 1

- High power impulse magnetron sputtering (HIPIMS)
- Atomic layer deposition (ALD)
- Dual ion beam sputtering (DIBS)
- Distributed electron cyclotron resonance (DECR) PECVD
- Plasma impulse chemical vapor deposition (PICVD)
- Plasma immersion ion implantation (PIII)
- Hollow cathode plasma processing
- Cold spray deposition
- High velocity oxy-fuel (HVOF) deposition
- Flash evaporation
- Pulsed laser deposition
- Langmuir Blodgett (LB) film deposition
- Cluster beam deposition
- Filtered cathodic arc deposition
- Organic molecular beam epitaxy
- Supersonic molecular beam epitaxy
- Inkjet printing …

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PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes
2 February	Fabrication methods - Plasma-surfaces interactions and diagnostics
9*	Fabrication methods – Thermal/Plasma spray technologies
16***	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1* March	*Presentations – Emerging fabrication techniques (30%)*
	March 4-8 - Winter/Spring break
15***	Tribomechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact
19***	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

Projet #3 – Application of nanostructred thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Report and presentation: **19 April**