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 and process optimization
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**

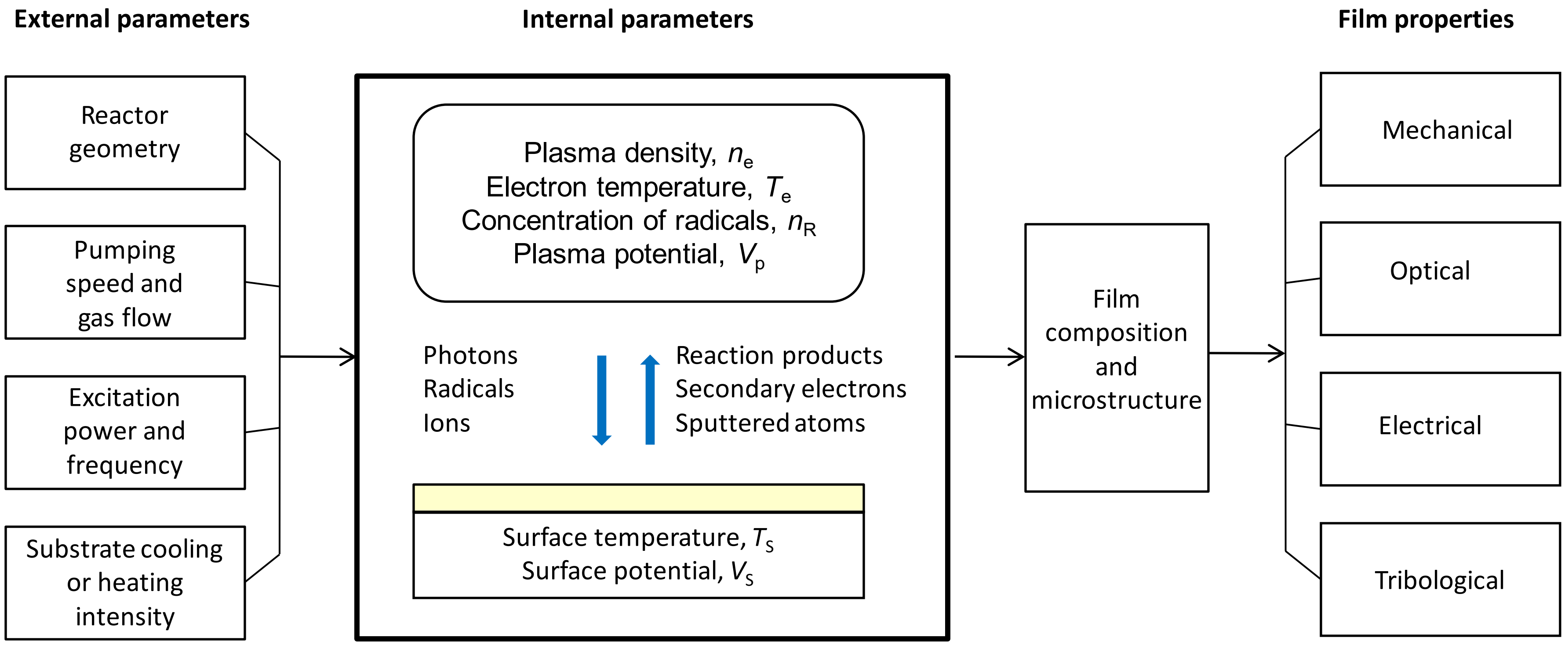
Report and presentation: **19 April**

Project #1: Techniques for the fabrication of nanostructured films and coatings

Mohamed Ammari – HiPIMS (High Plasma Impulse Magnetron Sputtering)
Veronika Cervenkova - Atomic layer deposition (ALD)
Emilien Martel – HVOF
Alexandre Lussier – DIBS
Gabriel Juteau - OMBE
Thomas Lapointe – Supersonic MBE
Luc Montpetit - …
Alexandre Fall - …
Arghavan Yazdanpanah Ardakani - ”PECVD”
Alexandre Pinel – ….
Izacard Bastien – Cold spray

Etienne Tremblay-Nathan Sasseville – PIII
Alexandre Gamache-Thomas Sicotte – PLD
Alexandre Carrière-Yusef Ben Mami – Langmuir-Blodgett

Plasma system and process control



External parameters

Reactor geometry

Pumping speed and gas flow

Excitation power and frequency

Substrate cooling or heating intensity

Internal parameters

Plasma density, n_e
Electron temperature, T_e
Concentration of radicals, n_R
Plasma potential, V_p

Photons
Radicals
Ions

Reaction products
Secondary electrons
Sputtered atoms

Surface temperature, T_S
Surface potential, V_S

Film composition and microstructure

Film properties

Mechanical

Optical

Electrical

Tribological

Today:

Plasma-based processes and deposition approaches: PVD, CVD, PECVD
Plasma-based effect of frequency – DC, RF, MW
Atmospheric plasma processes

L. Martinu et al., Chapter 9 in "*Handbook of Thin Film Process Technology*", P.M. Martin, ed., Elsevier, 2010.

Inelastic collisions

Ionisation	$e + A \rightarrow A^{+} + 2\,e$	$e + N_2 \rightarrow N_2^{+} + 2\,e$
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	$e + AB \rightarrow 2\,e + A^{+} + B$	$e + TiCl_4 \rightarrow 2\,e + TiCl_3^{+} + Cl$
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)

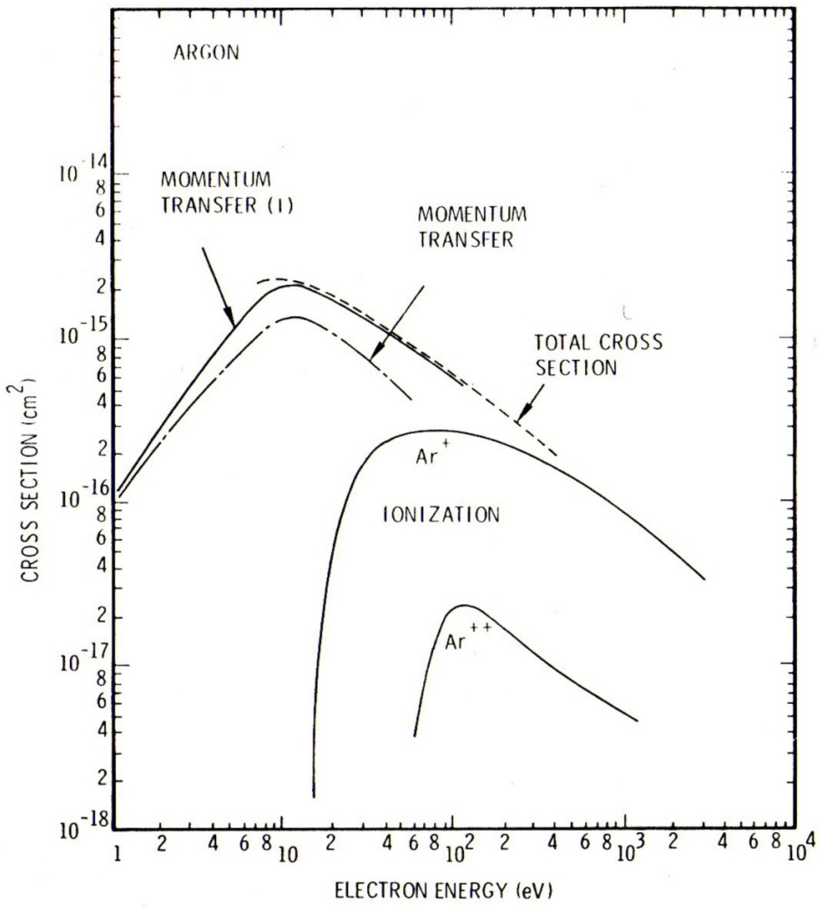


Figure 2.1. Collision cross sections for electrons in Ar gas (from Ref. 1).

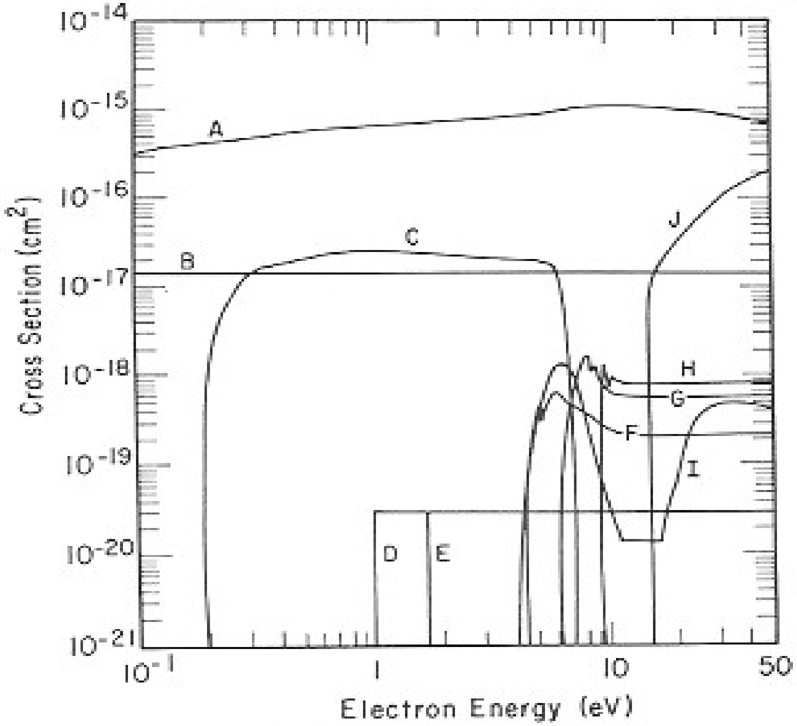


FIGURE 1.10. Elastic and inelastic collision cross-sections for electrons in oxygen; (A) elastic scattering; (B) rotational excitation; (C) vibrational excitation; (D) excitation to the $a^1\Delta_g$ state; (E) excitation of the $b^1\sum_g^+$ state; (F) excitation of the $A^3\sum_u^+$ state; (G) excitation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

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

Ionisation cross-sections in different gases

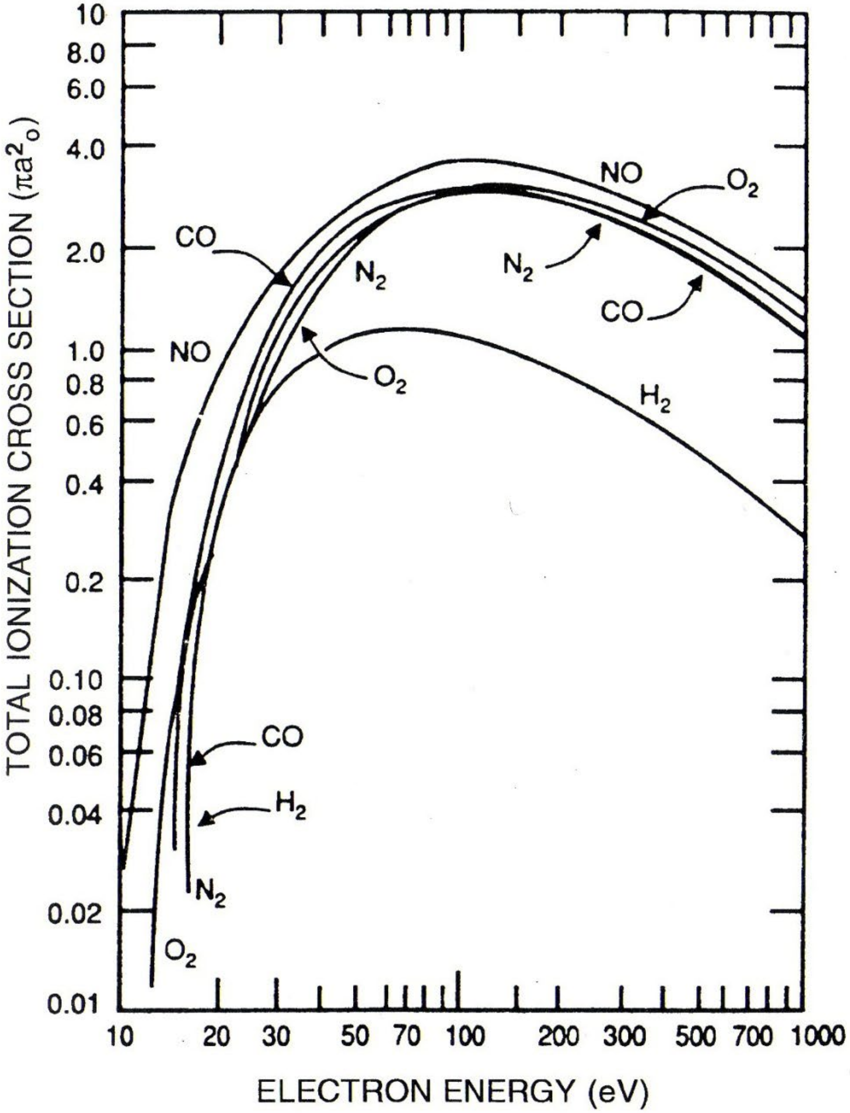


Figure 4-8 Total ionization cross sections for various gases plotted as a function of energy. (From S. C. Brown, *Basic Data of Plasma Physics*, 2nd ed. MIT, Cambridge, MA, 1967. Reprinted with the permission of The MIT Press.)

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

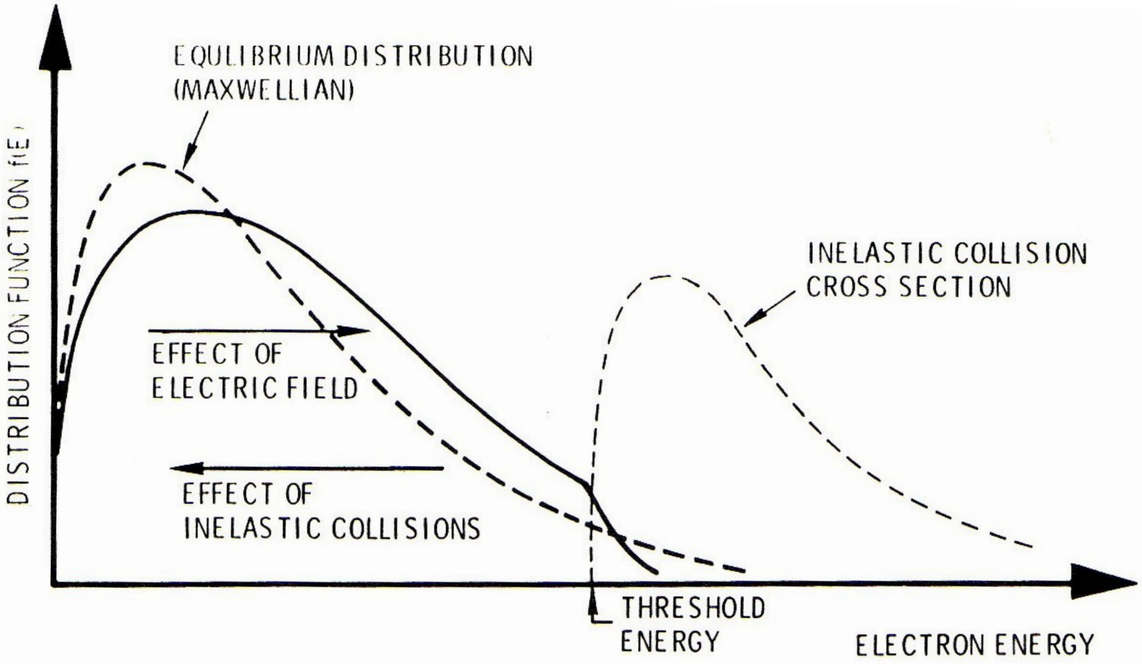


Figure 2.4. Schematic illustration of electron energy distribution function and inelastic collision cross section.

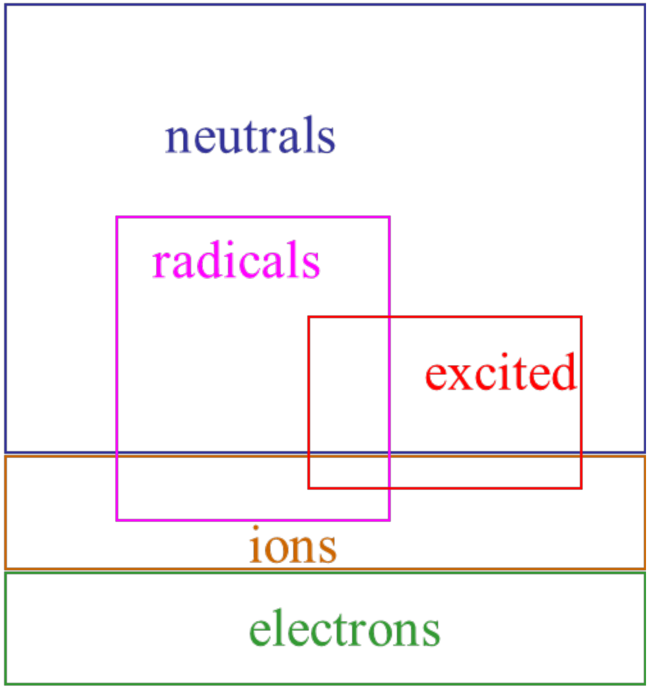
Example: Density of active species in a nitrogen discharge

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	$10^{10} – 10^{11}\ cm^{-3}$

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

1 eV ↔ 11 605 K

1 Torr = 133.32 Pa



neutrals

radicals

excited

ions

electrons

Hybrid (combined) processes:

Ion plating

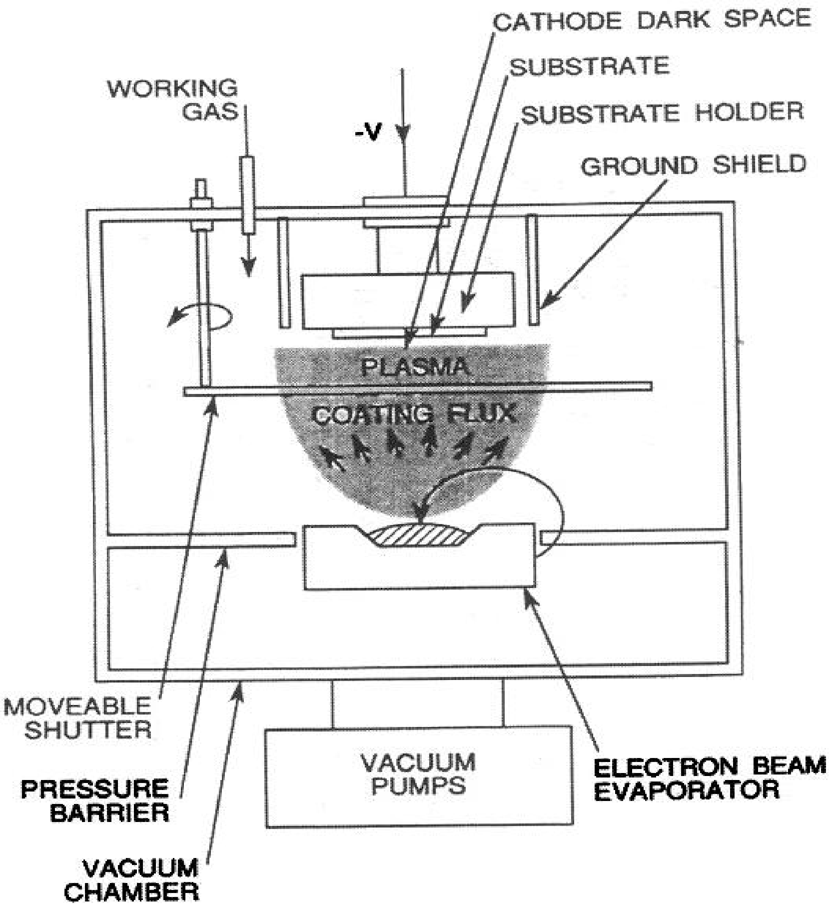


Figure 5-20 Ion plating system. (From Ref. 43.)

Activated reactive evaporation - ARE

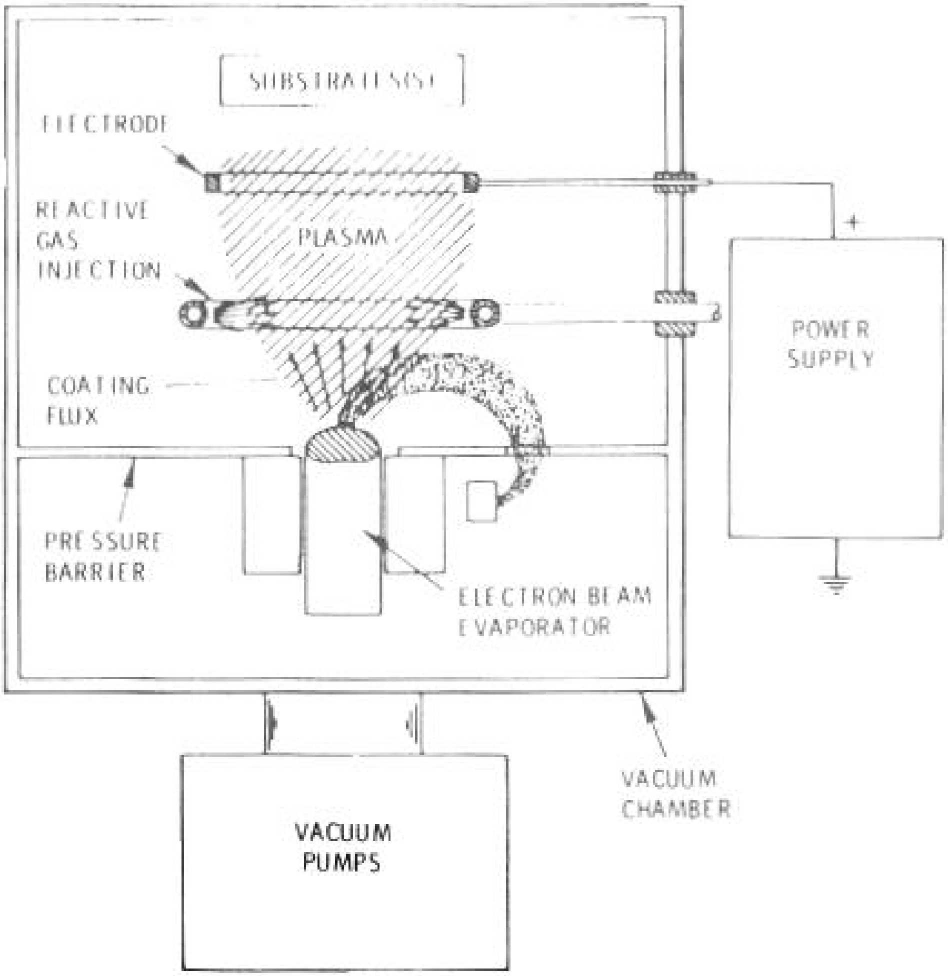


Figure 2.14. Schematic illustration of the activated reactive evaporation (ARE) process (see Ref. 49).

Ion sources – Kaufman type

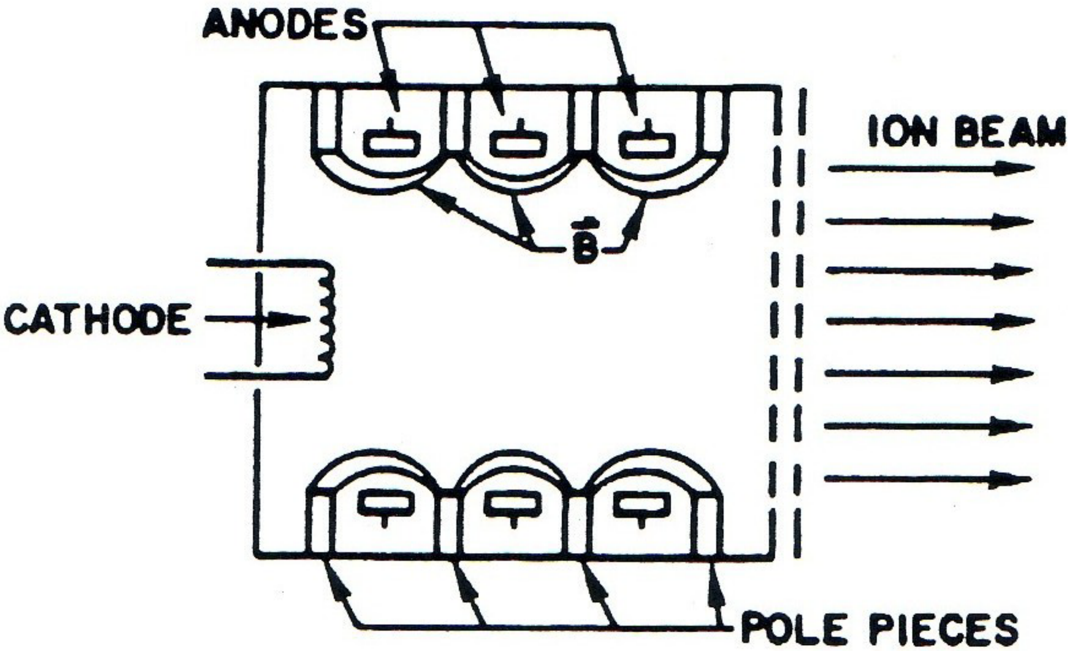
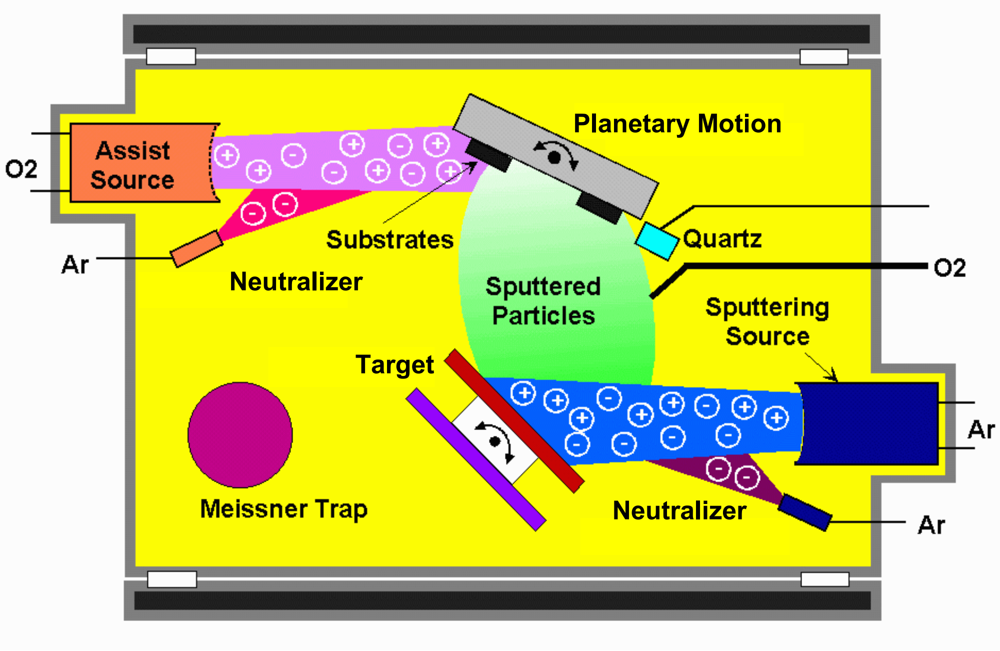


Figure E3.0.17. Kaufman-type ion source with multipole anode design. (After [73].)

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)



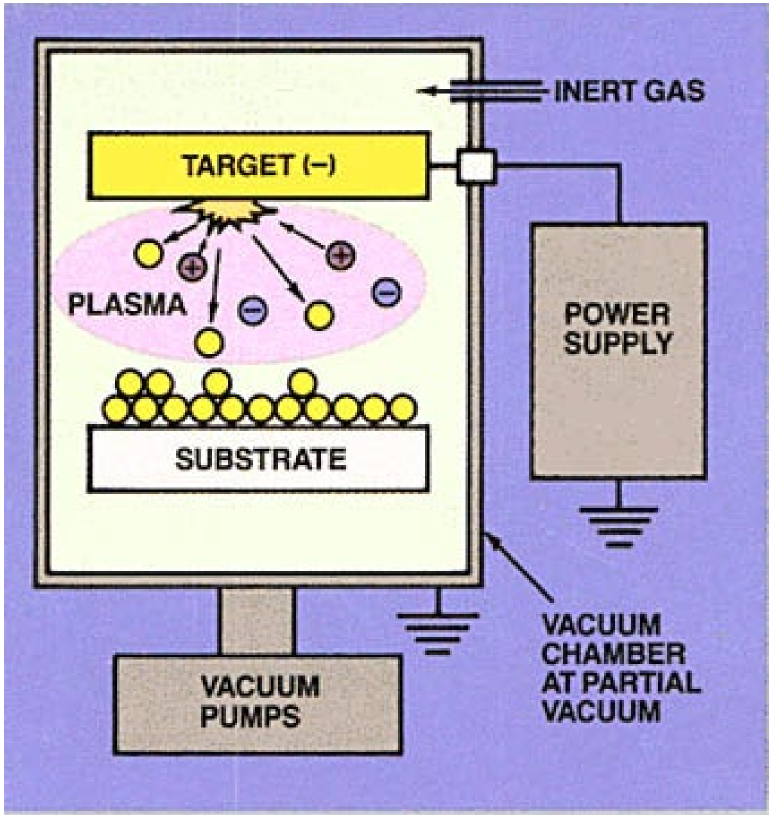
DIBS from Veeco at LaRFIS, Polytechnique

- 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



Sputtering Vacuum Deposition Process

Magnetron sputtering

a) Planar magnetron

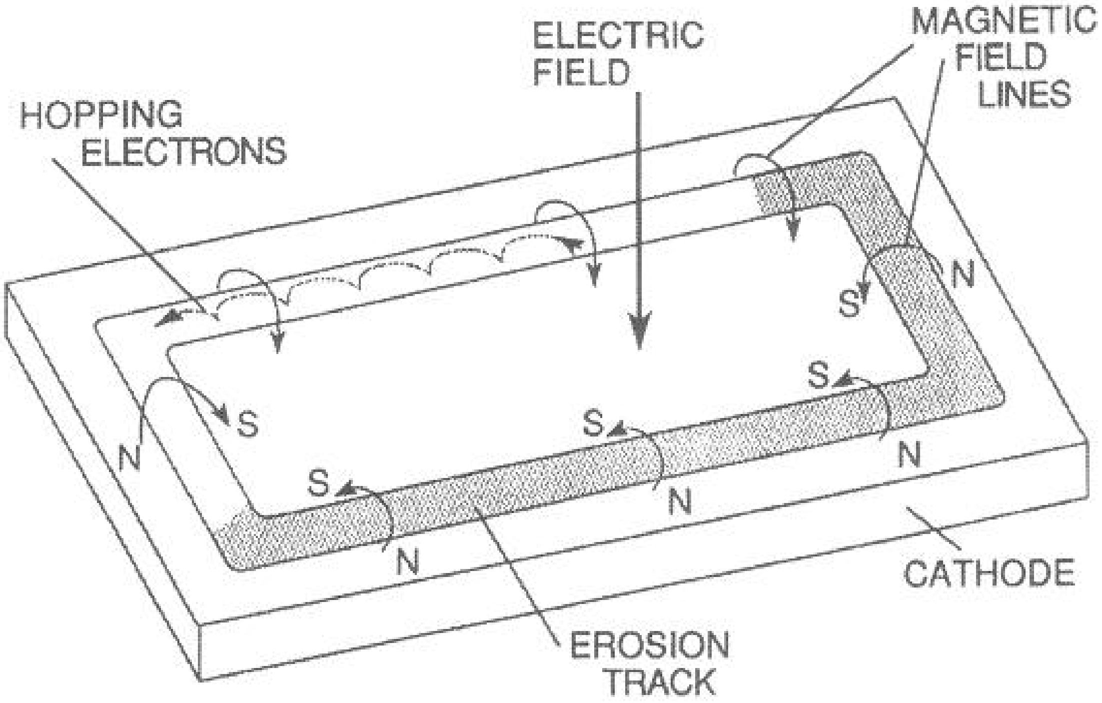


Figure 5-8 Applied fields and electron motion in the planar magnetron.

b) Cylindrical magnetron

c) Sputtering « gun »

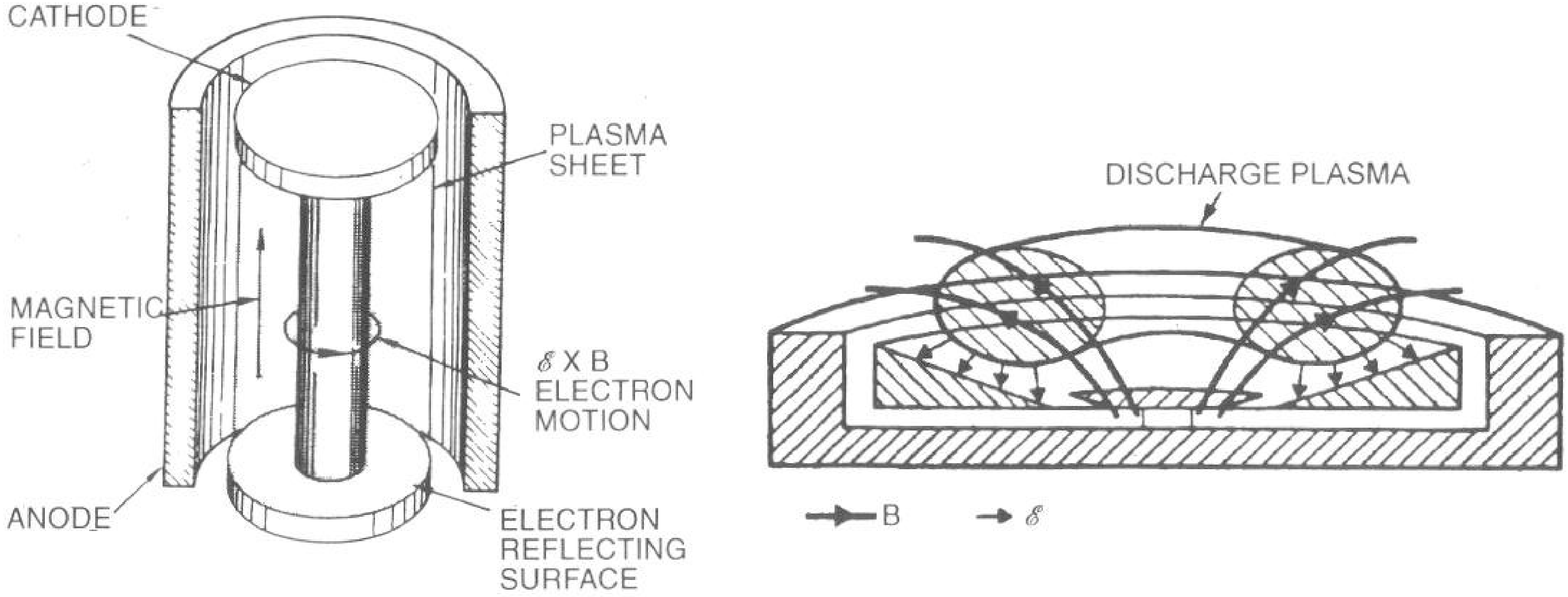


Figure 5-9 Nonplanar magnetron sputtering configurations. (Left) Cylindrical-post magnetron geometry. (From J. A. Thornton and A. S. Penfold, in J. L. Vossen and W. Kern, eds., *Thin Film Processes*. Academic Press, New York, 1978. Reprinted with the permission of Academic Press and A. S. Penfold.) (Right)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

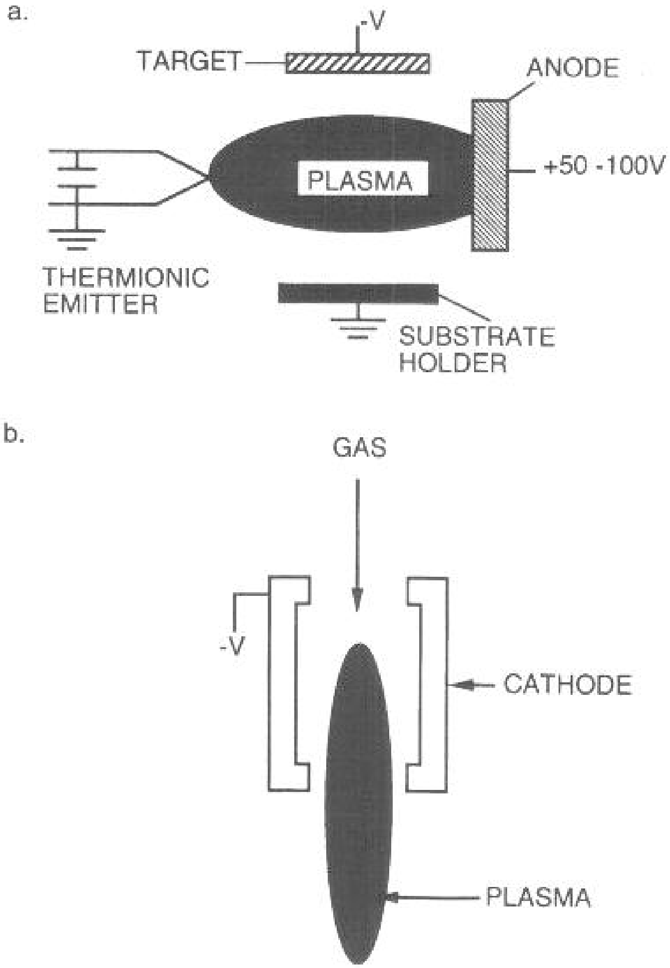
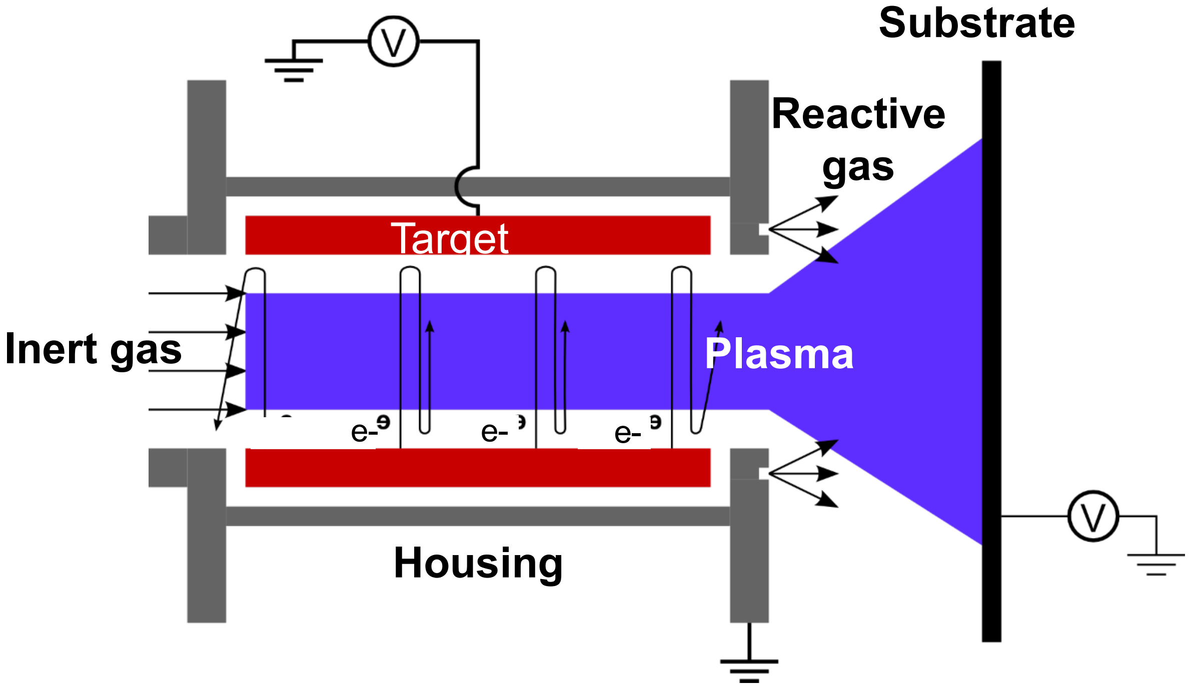
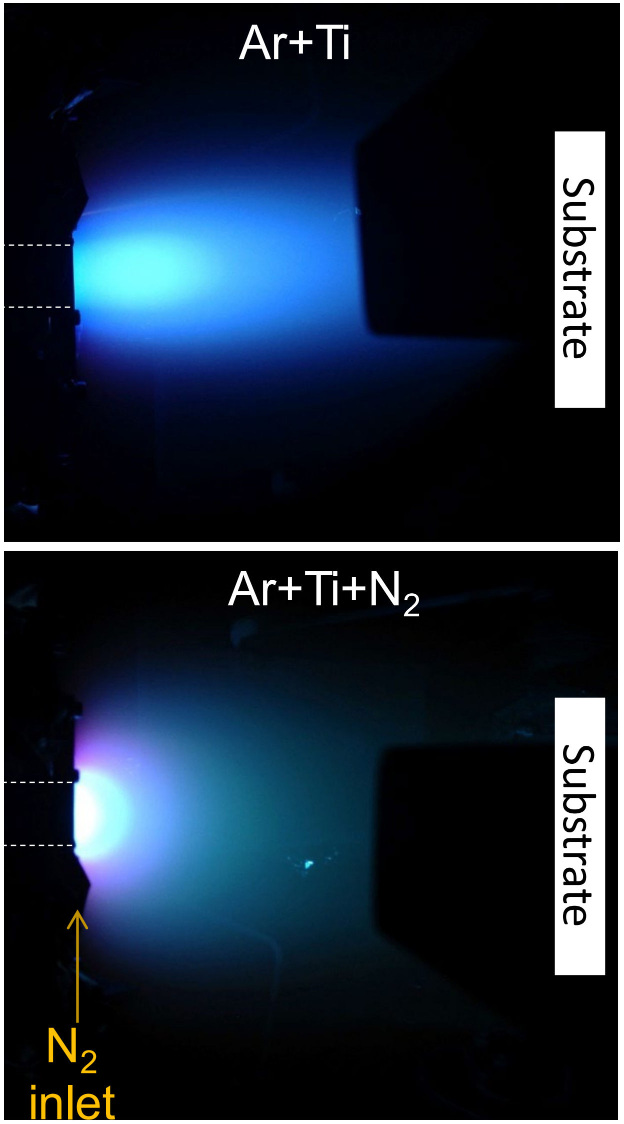


Figure 5-3 (a) Triode sputtering configuration utilizing a thermionic electron emitter. A magnetic field may be applied along the emitter–anode axis. (After L. I. Maissel in *Handbook of Thin Film Technology*, L. I. Maissel and R. Glang, eds., McGraw-Hill, New York, 1970.) (b) Hollow cathode source.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

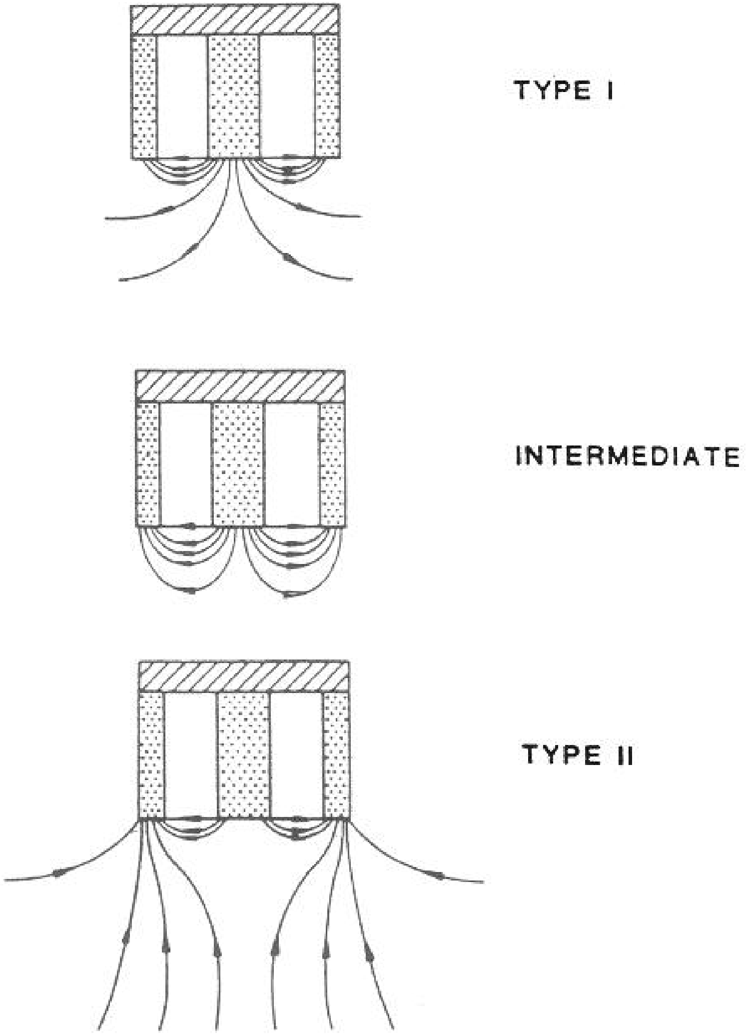


Figure 5-10 Planar magnetron configurations. (Top) Type-I (unbalanced). (Middle) Intermediate (balanced). (Bottom) Type-II (unbalanced). (From B. Window and N. Savvides, *J. Vac. Sci. Technol.* **A4**, 196, (1986). Reprinted with the permission of Dr. N. Savvides.)

Dual magnetron systems

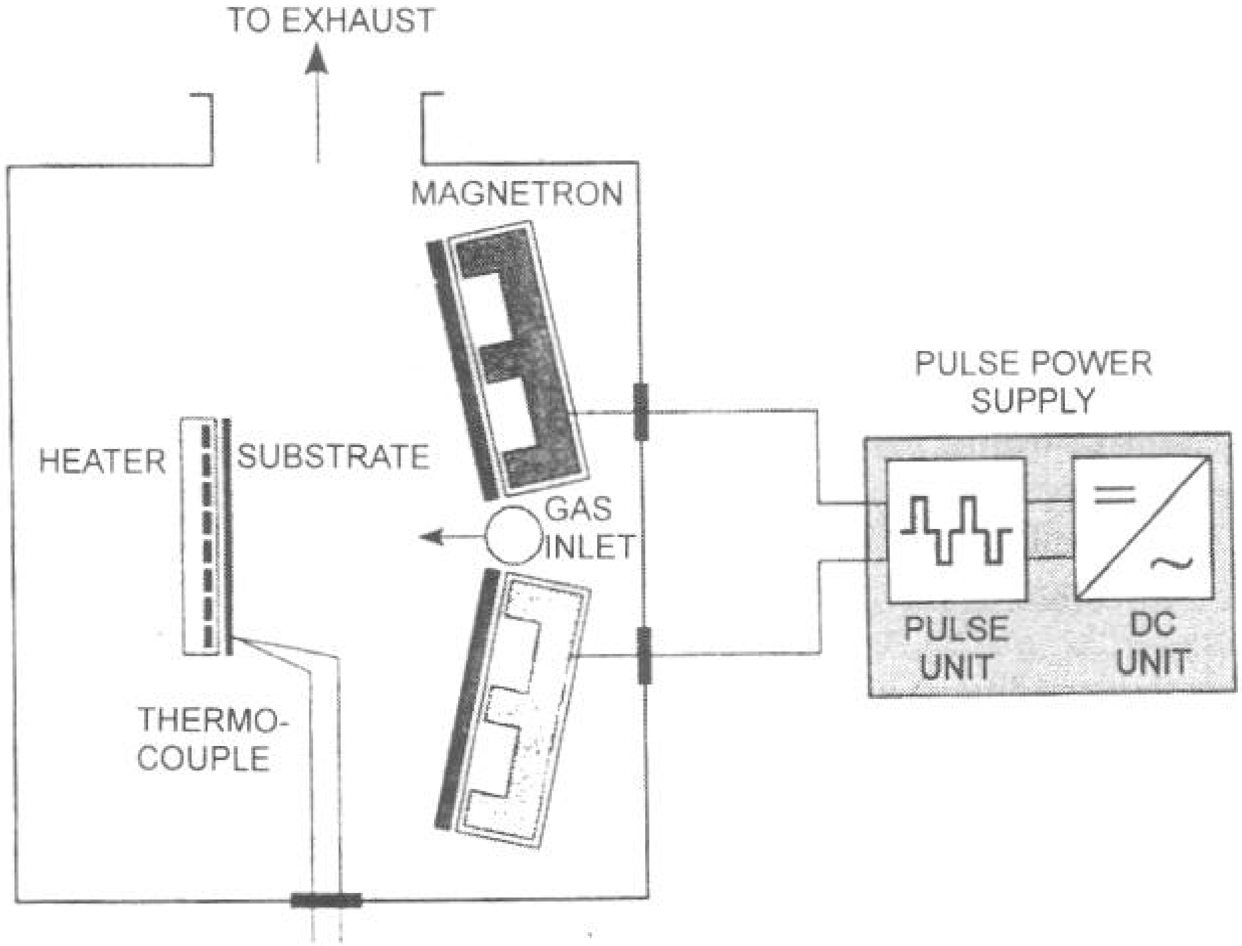


Figure 5-11 Arrangement for reactive pulsed-magnetron sputtering from dual Al targets. (From O. Zywitzki and G. Hoetzsch, International Conference on Metallurgical Coatings and Thin Films, San Diego, April 22–26, 1996). Reprinted with permission of the authors.

Cathodic arc deposition

(Arc evaporation)

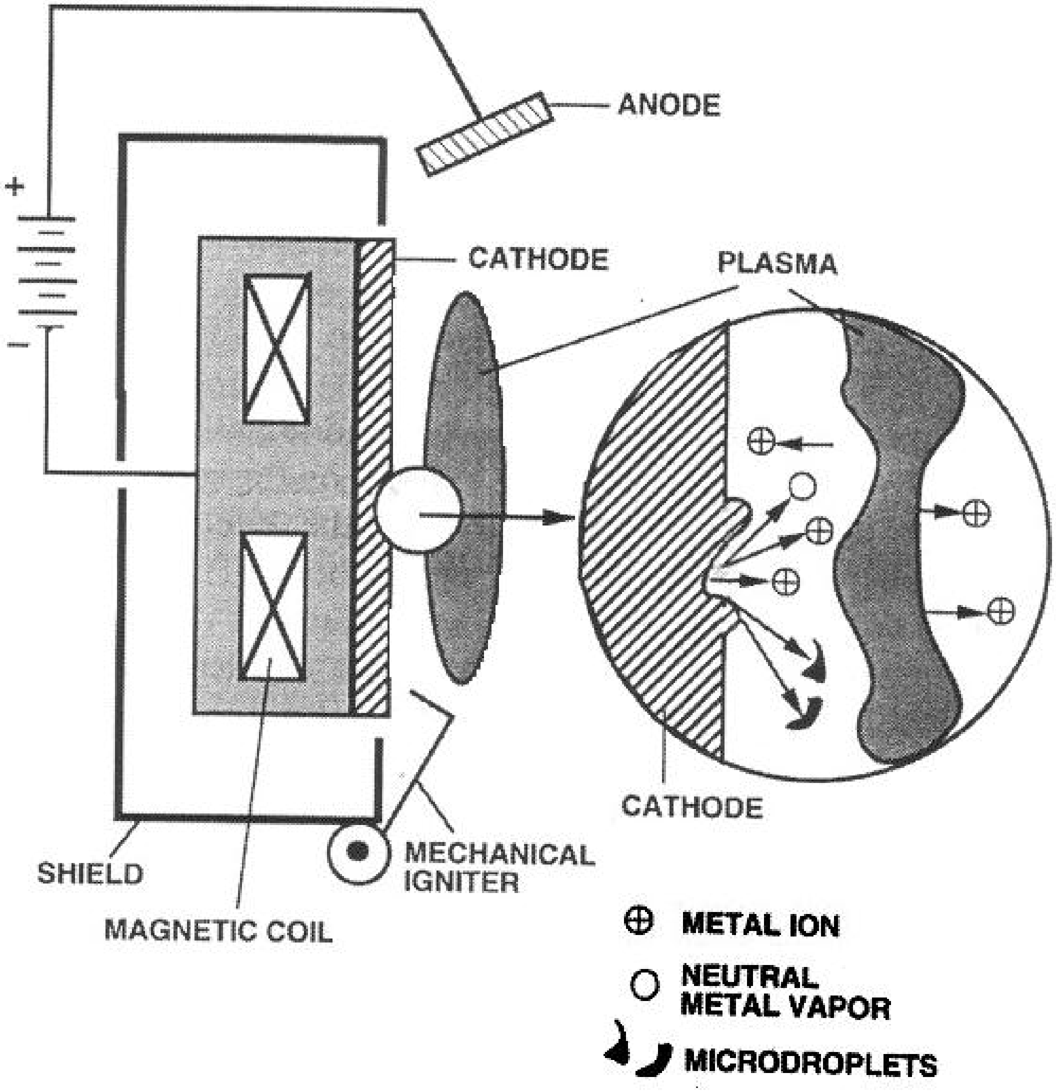
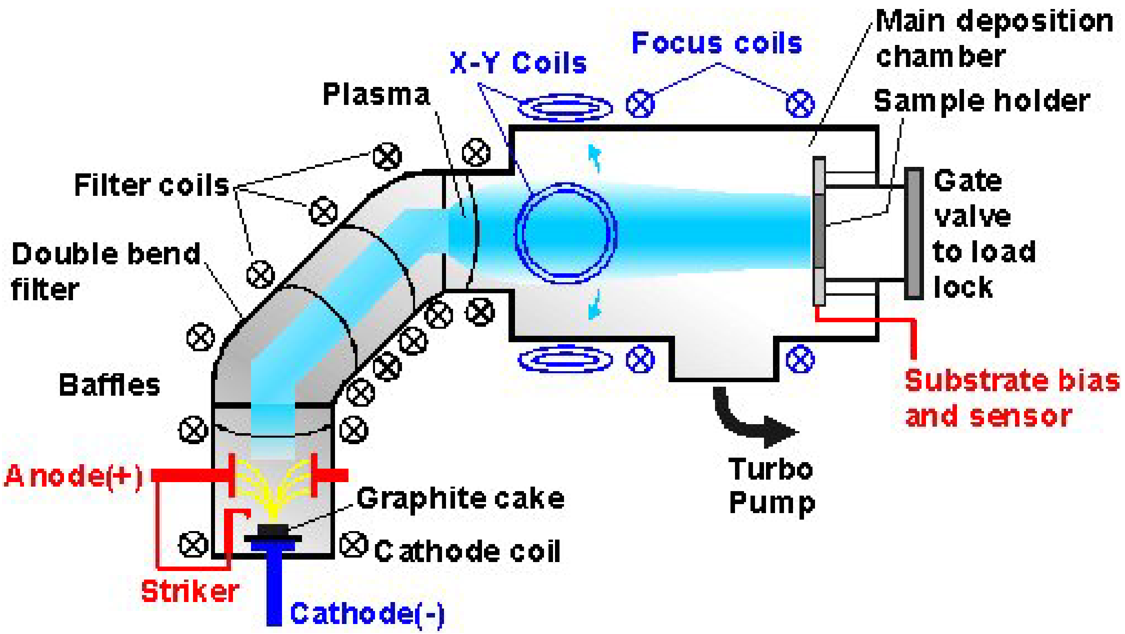


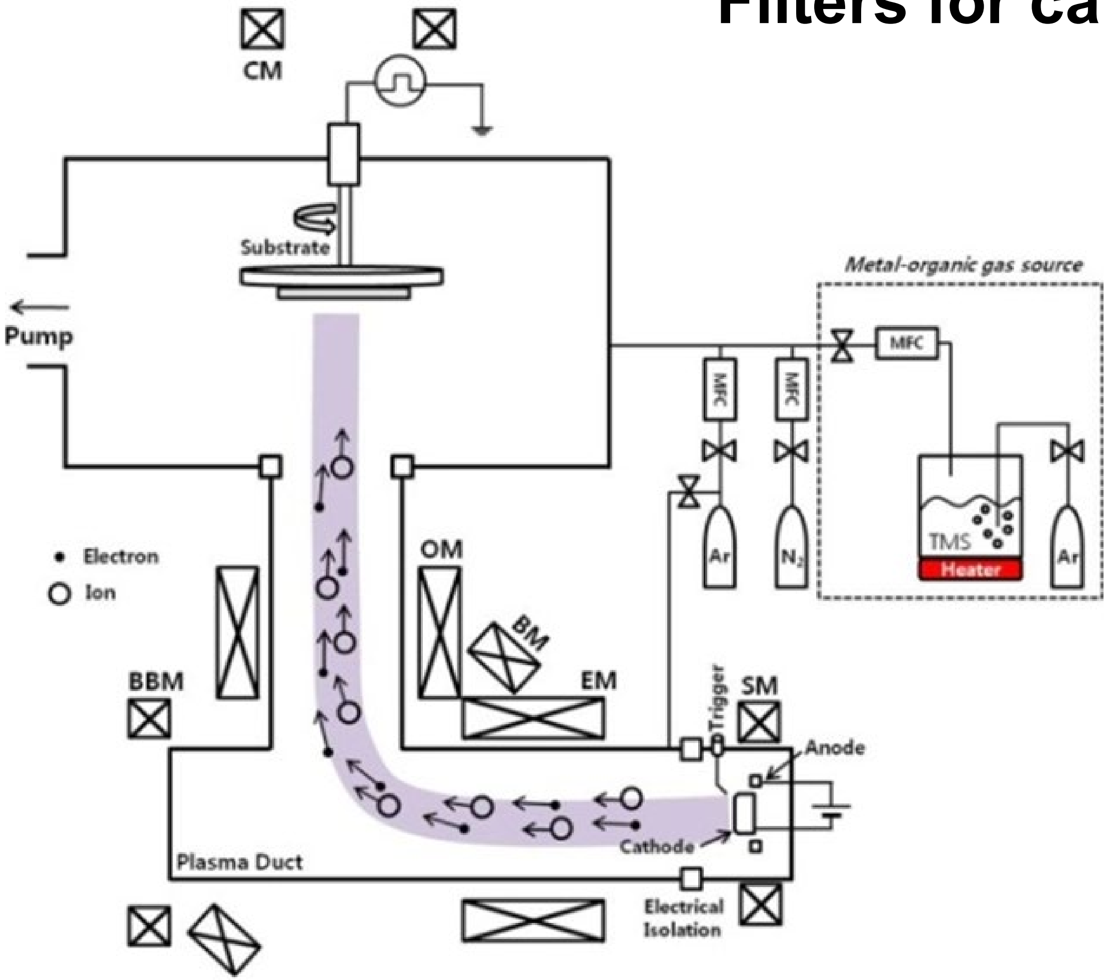
Figure 5-23 Cross section of cathodic-arc deposition system with a model of activity at a cathode spot. (From Ref. 48.)

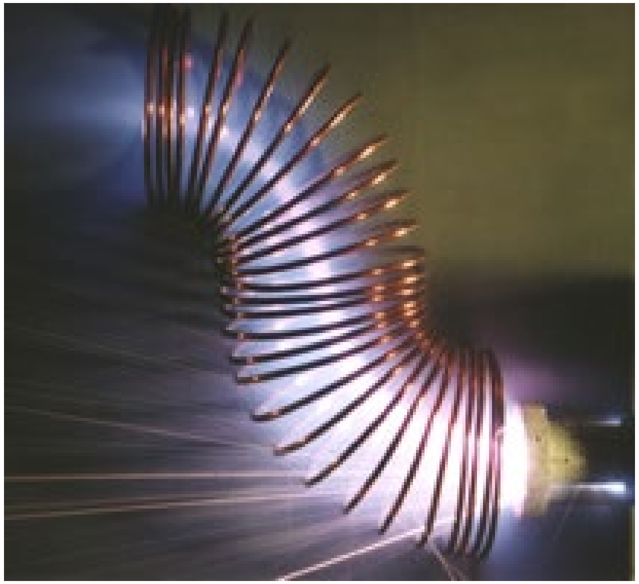
Filtered cathodic arc deposition



- 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

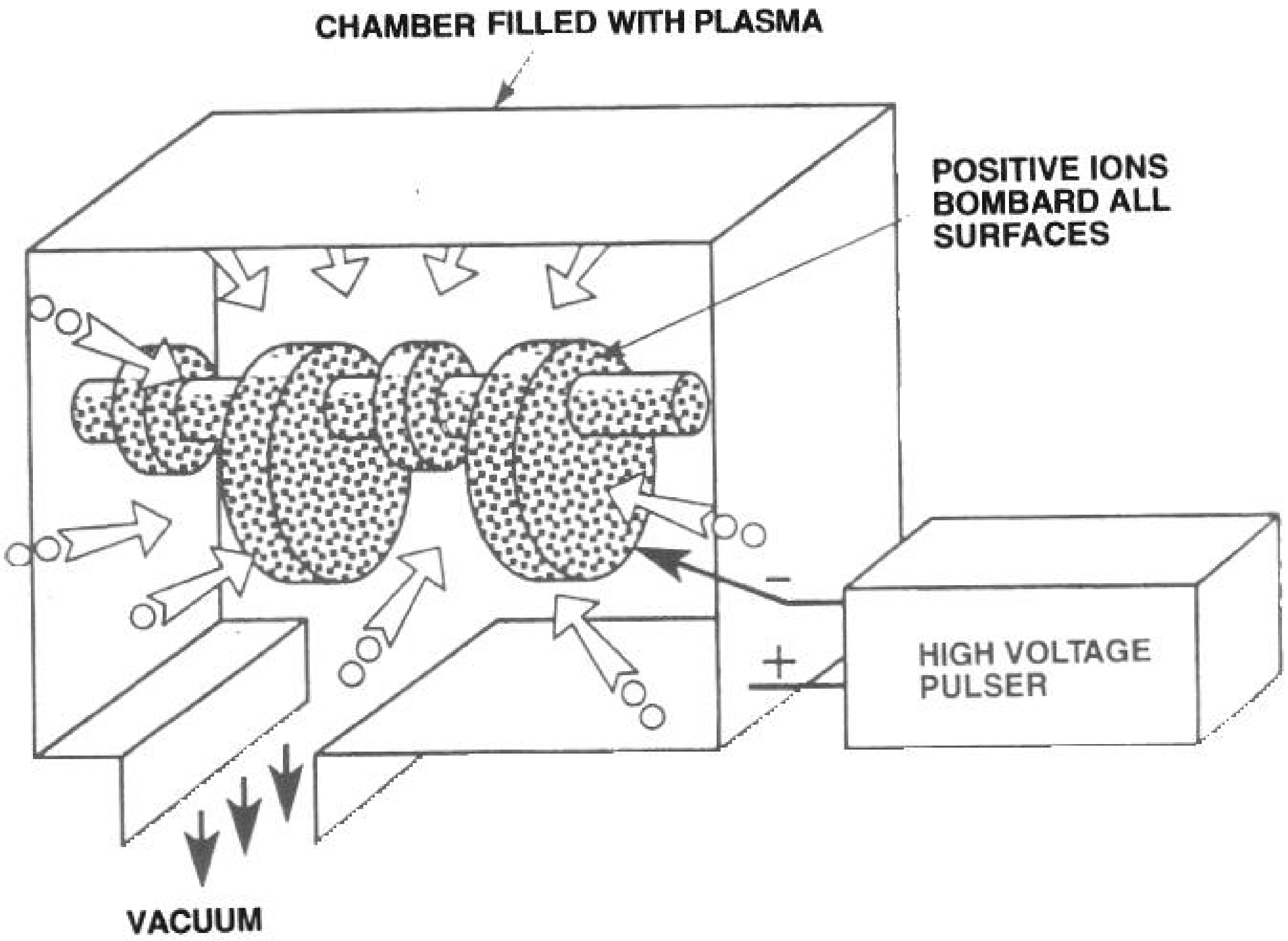


Figure 5-26 Illustration of the PIII process for automotive crankshafts. Because the plasma sheath surrounds the shaft, all of its surfaces are simultaneously ion bombarded without beam aiming or target manipulation. (From J. V. Mantese, I. G. Brown, N. W. Cheung, and G. A. Collins, *MRS Bulletin* **21**(8),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

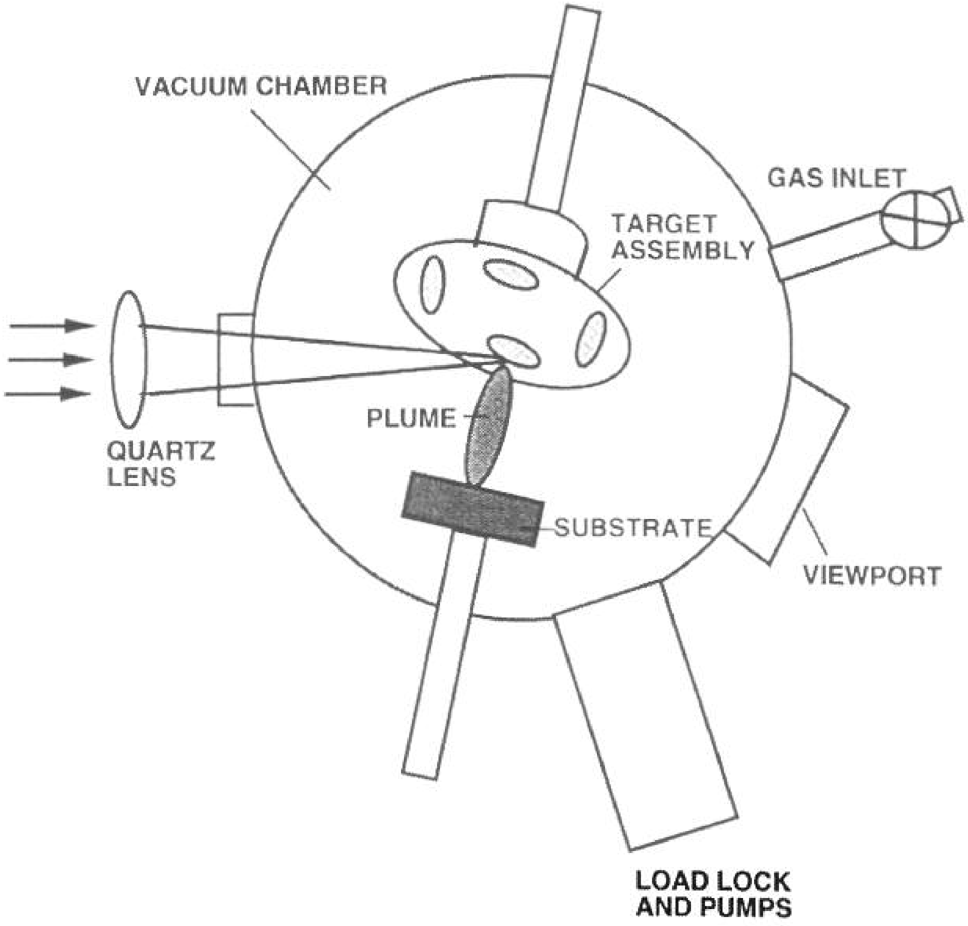


Figure 3-16 Schematic of PLD system for the deposition of metal oxide films. (From R. Ramesh, O. Auciello, V. G. Keramidas, and R. Dat in *Science and Technology of Electroceramic Thin Films*, O. Auciello and R. Waser, eds. Kluwer, Dordrecht, The Netherlands, 1995. Reprinted with the permission of the 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	Reactive evaporation	Chemical vapor deposition (thermal CVD)
• Joule effect		Plasma-Enhanced CVD (PECVD)
• Electron beam		
Sputtering	Reactive sputtering	Laser Assisted CVD (Laser CVD)
• Magnetron	Ion-assisted deposition	Atomic Layer Deposition (ALD)
• Ion beam		<u>New trends:</u>
	(Plasma Immersion Ion Implantation –PIII)	- Atmospheric pressure CVD
Molecular beam epitaxy	Surface cleaning	- Ion Beam Assisted CVD
Pulsed laser deposition (PLD)	Surface functionalization	- Hybrid methods:
	(nitriding, carburizing, boriding, … Implantation	a) PVD/CVD/PECVD b) Duplex – Thin-on-Thick
	Patterning, …)	

Thermal CVD Process

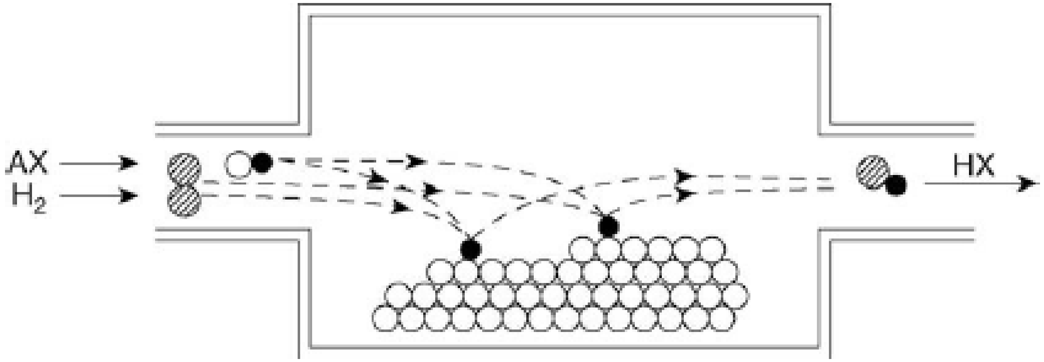


Figure 7.1: The principle of CVD.

Three step reaction:
- Initiation
- Propagation
- Termination

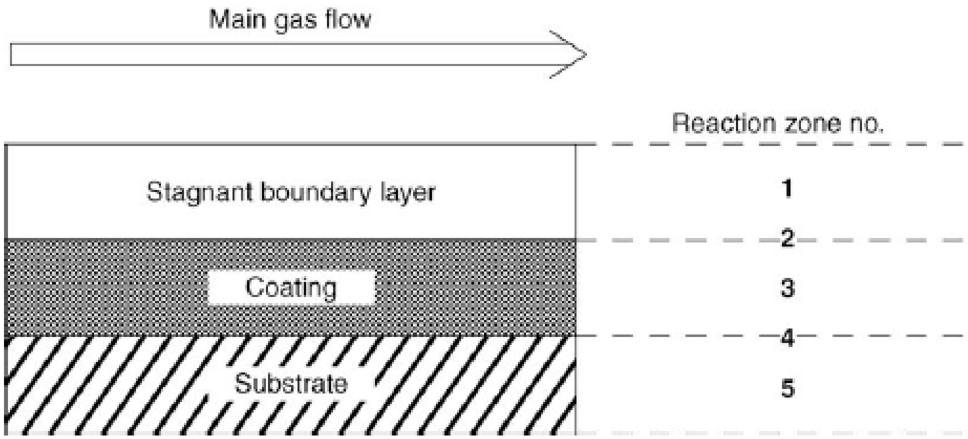


Figure 7.2: Important reaction zones in CVD.

Rate-limiting steps during CVD

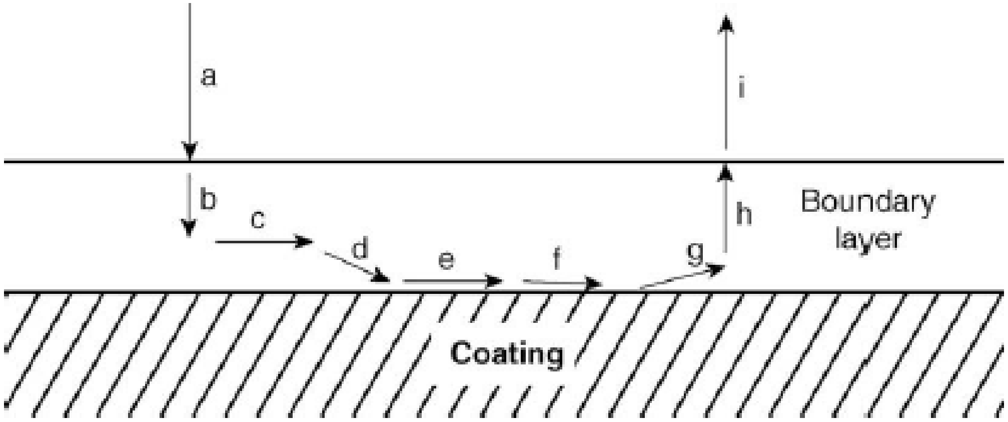


Figure 7.20: The various steps in a CVD process.

(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

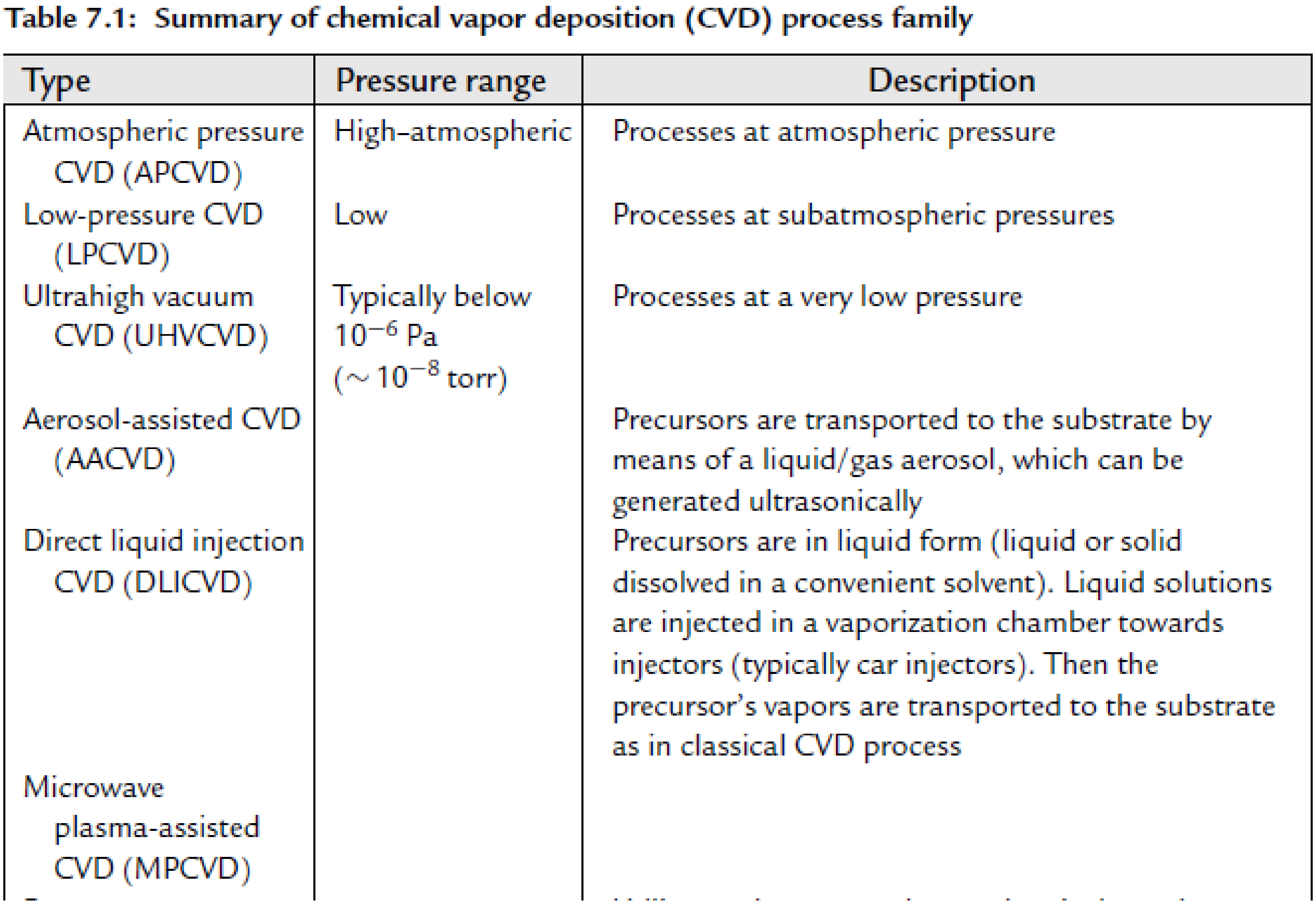
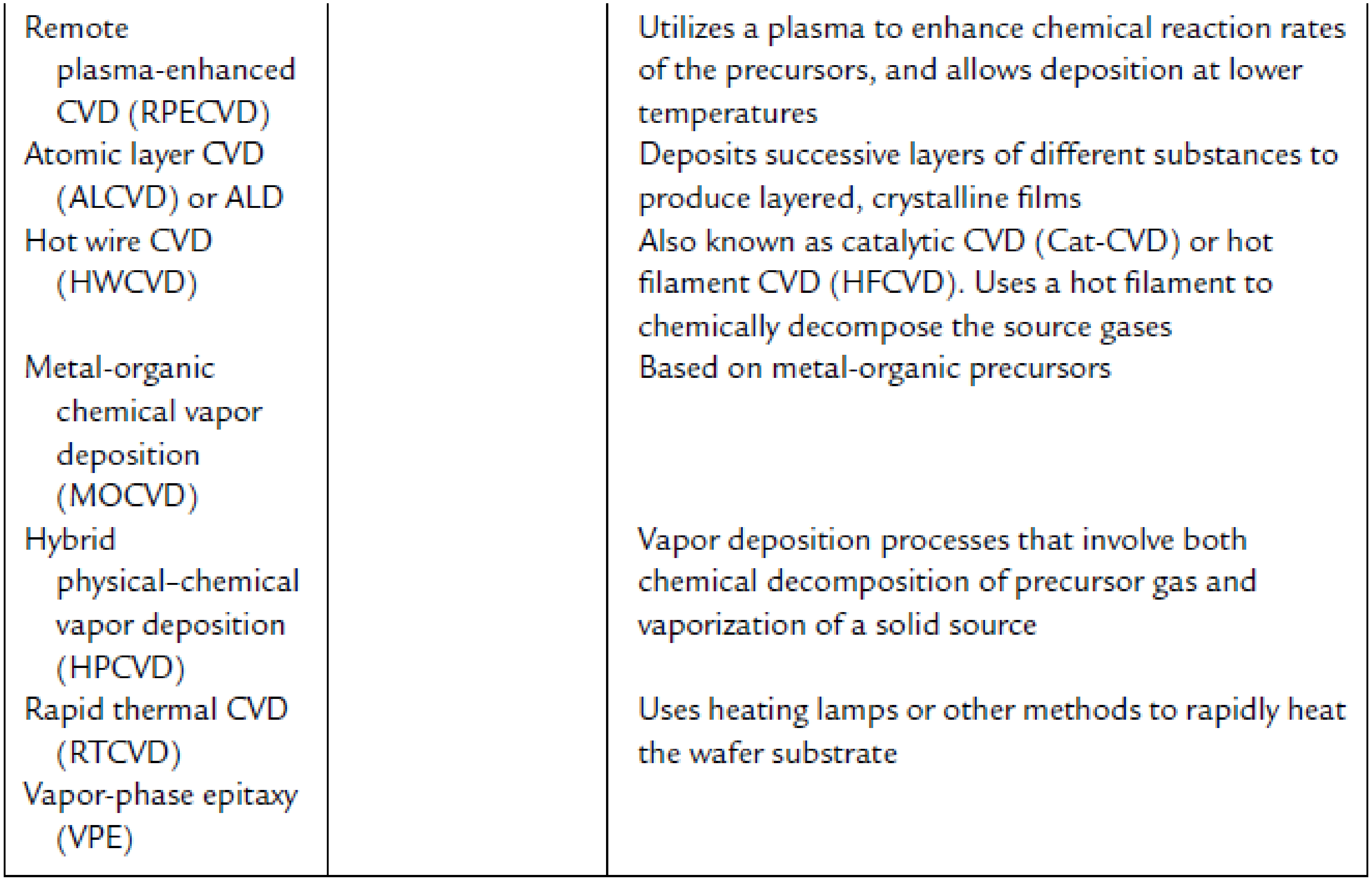


Table 7.1: Summary of chemical vapor deposition (CVD) process family

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)		

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

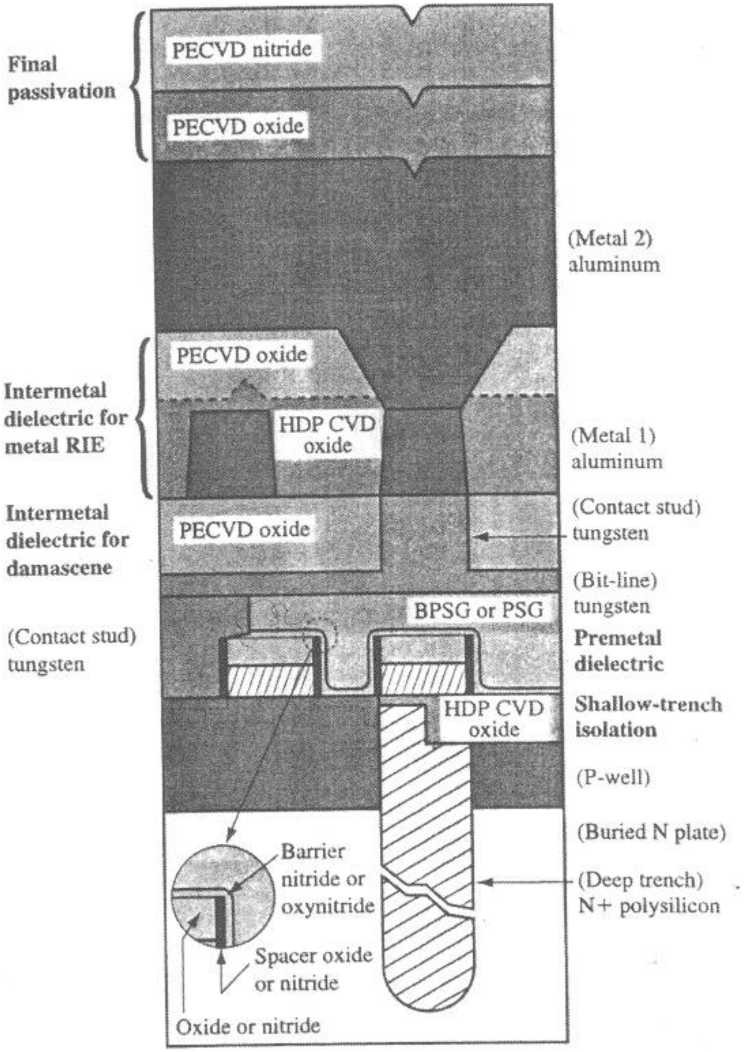


Figure 6-21 Schematic drawing of a three-level DRAM cell illustrating actual and potential (bold font) plasma CVD applications. (From Ref. 48. Copyright © 1999 by IBM Corp. Reprinted with permission.)

Structure of a MOS transistor

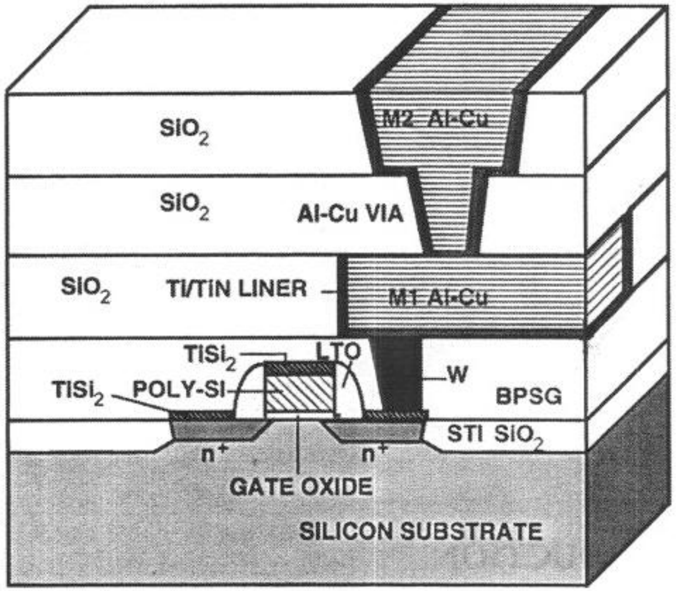


Figure 6-1 Schematic cross-sectional view of an MOS transistor structure with multilevel metallization scheme. Film materials deposited by CVD are indicated in the text. *Note:* LTO = low temperature oxide, BPSG = borophospho-silicate glass, STI = silicon trench insulator. After K. P. Rodbell, IBM, T.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

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

Schematics of a CVD System

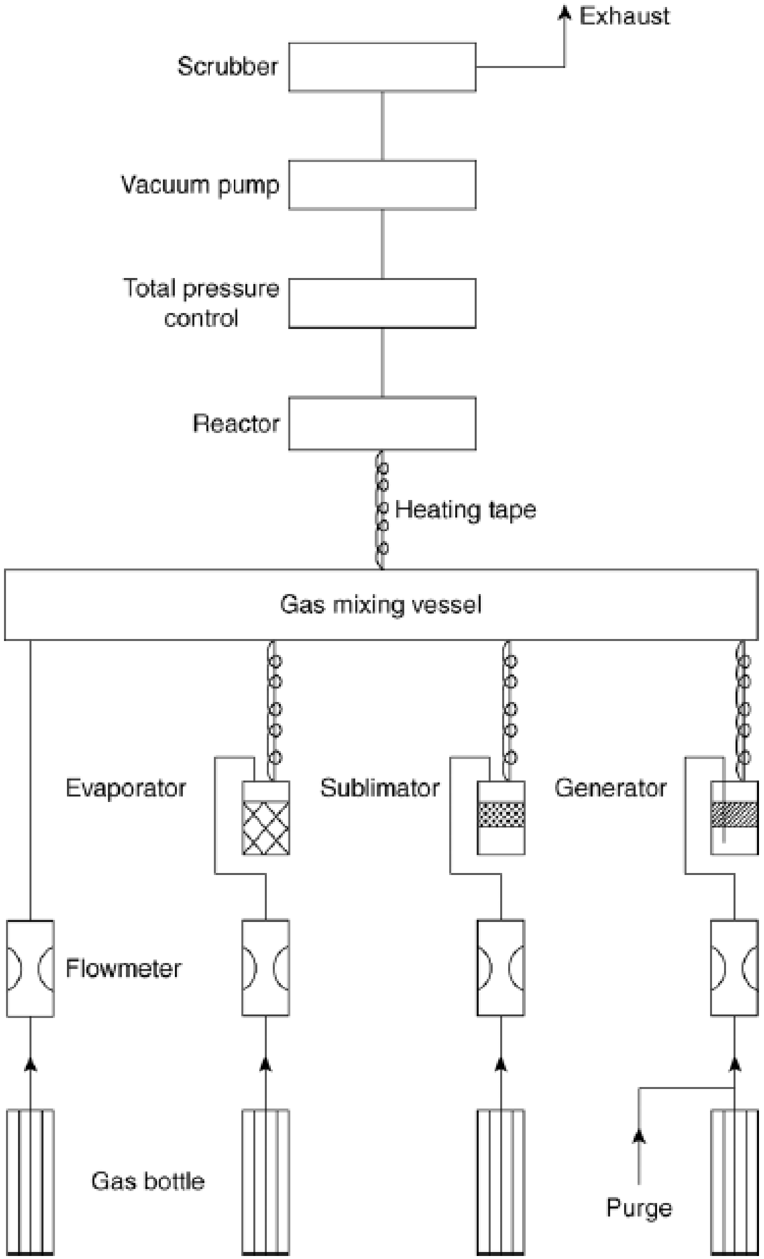


Figure 7.6: Sketch of a CVD system.

Types of reactors: hot and cold walls

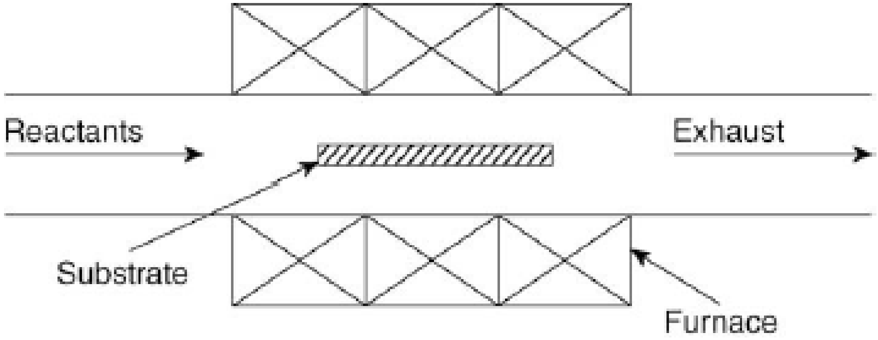


Figure 7.7: Hot wall CVD reactor.

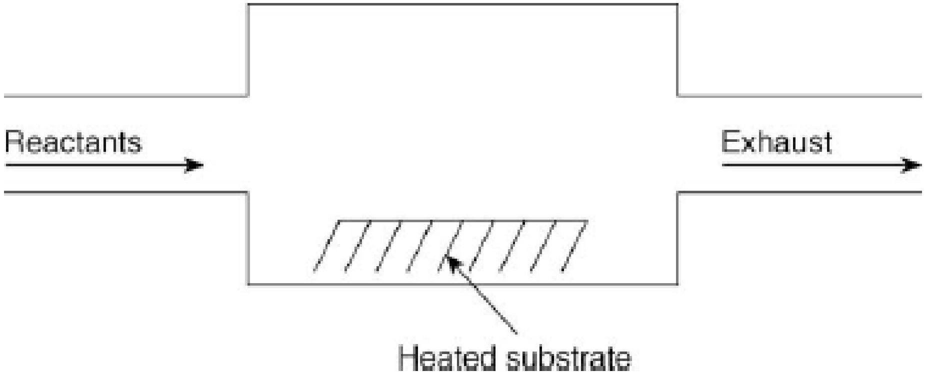


Figure 7.8: Cold wall CVD reactor.

Reactor configurations

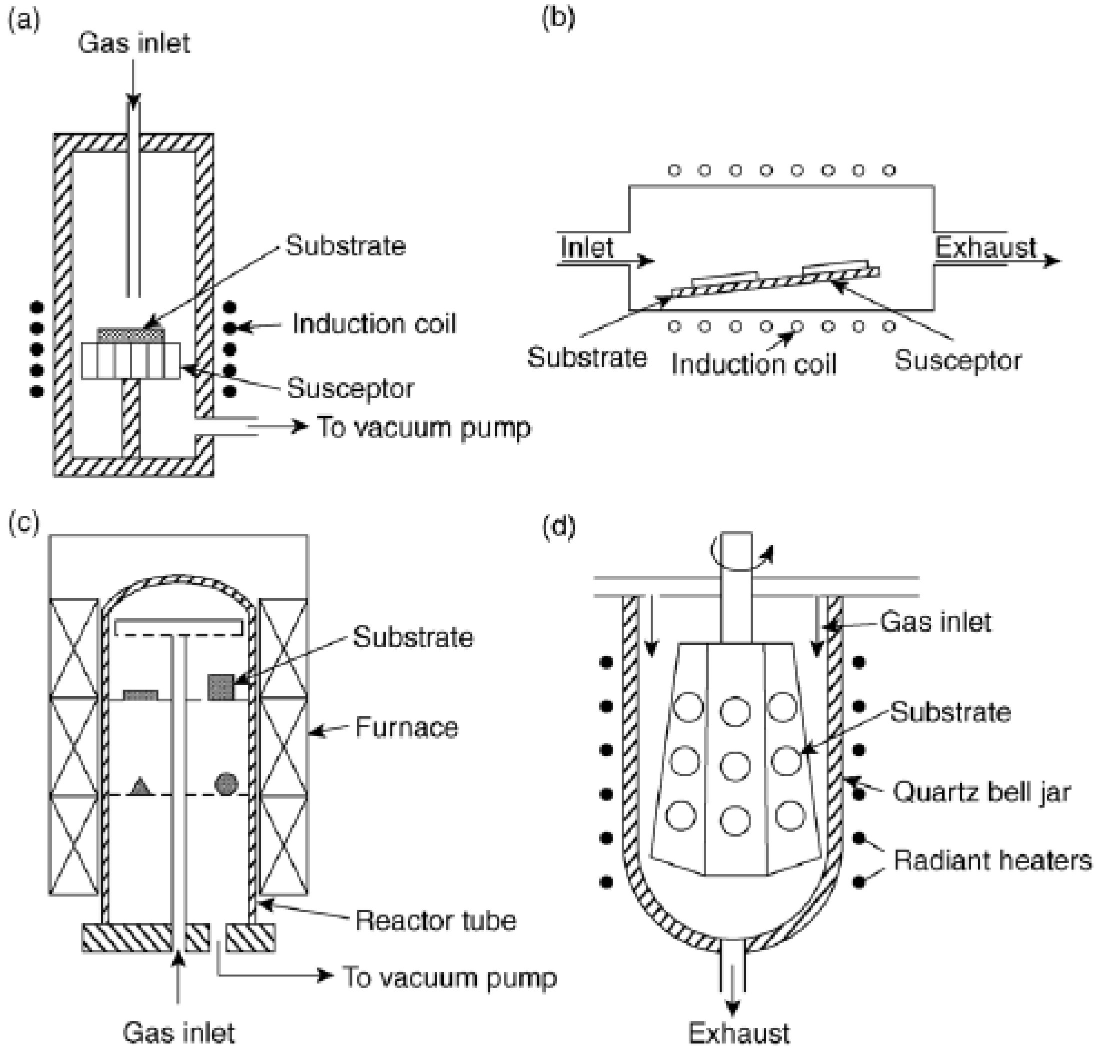


Figure 7.9: Examples of some CVD reactors: (a, b) RF heated cold wall reactors; (c) vertical hot wall reactor; (d) barrel reactor.

Gas flow patterns

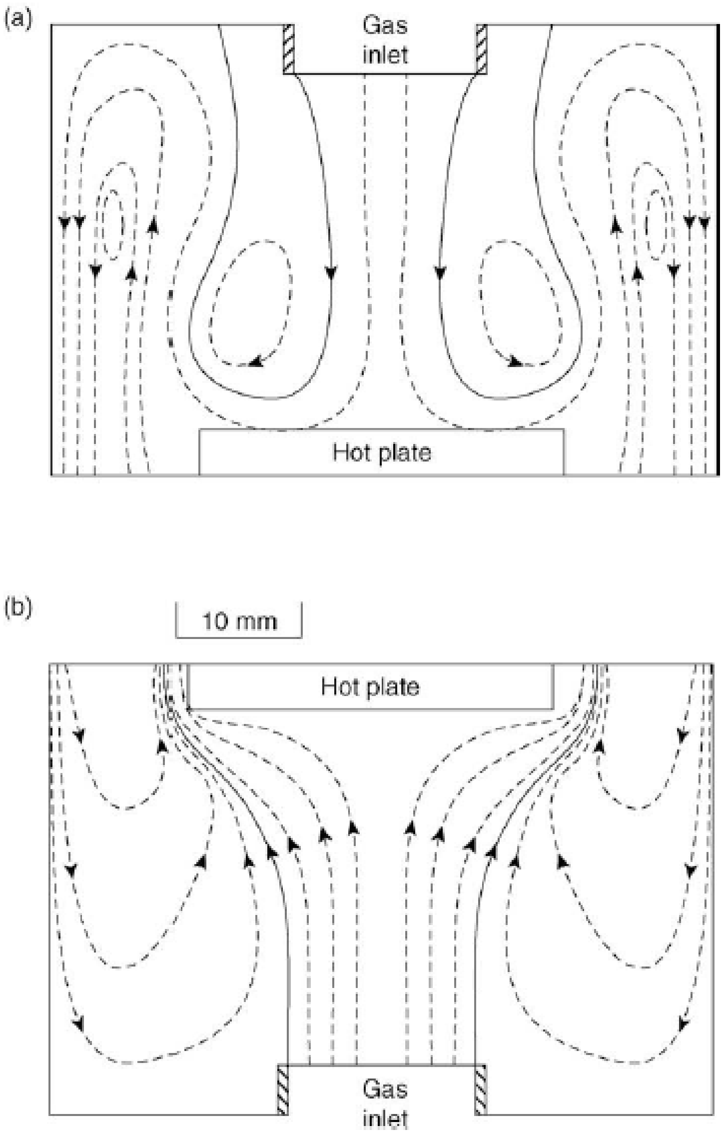


Figure 7.12: Gas flow pattern in a cold wall reactor, where the forced and buoyance-driven convection (a) interact, and (b) counteract, substrate temperature 900 K, Re = 50 [35].

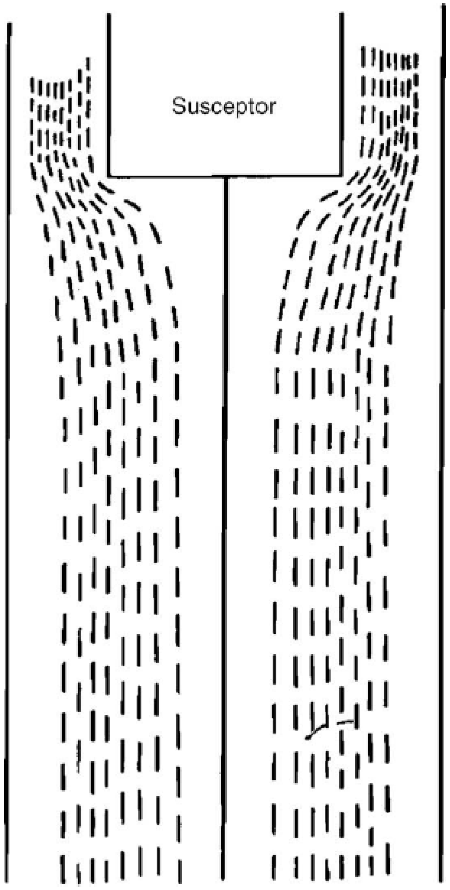


Figure 7.13: Gas flow pattern in a cold wall reactor with geometry different than that sh
Figure 12 [36].

Control of the CVD film microstructure

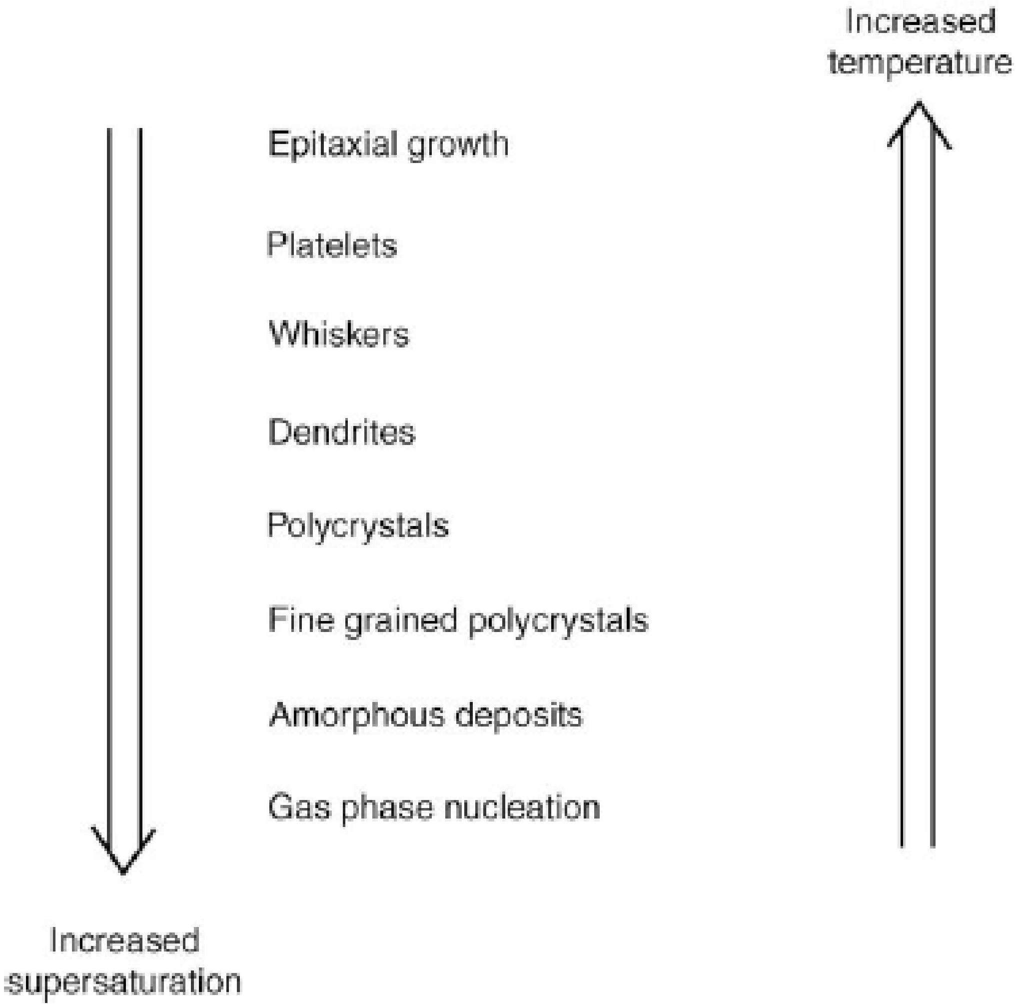


Figure 7.31: Microstructure sequence of CVD materials [55].

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

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

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

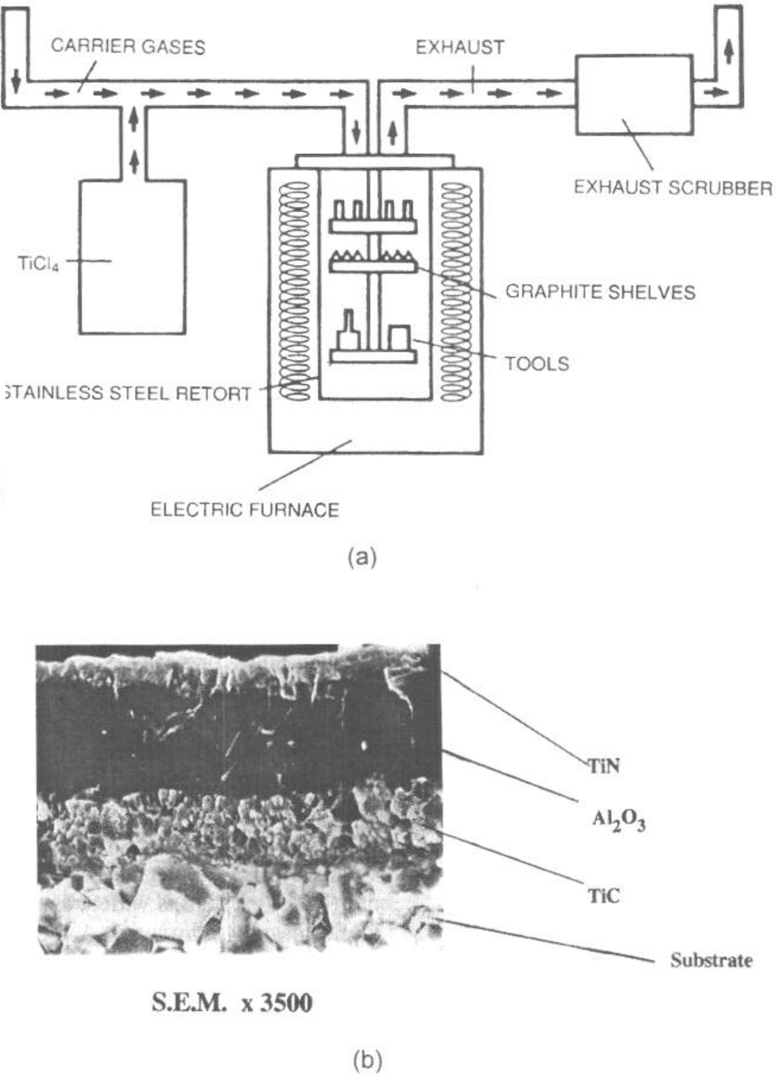
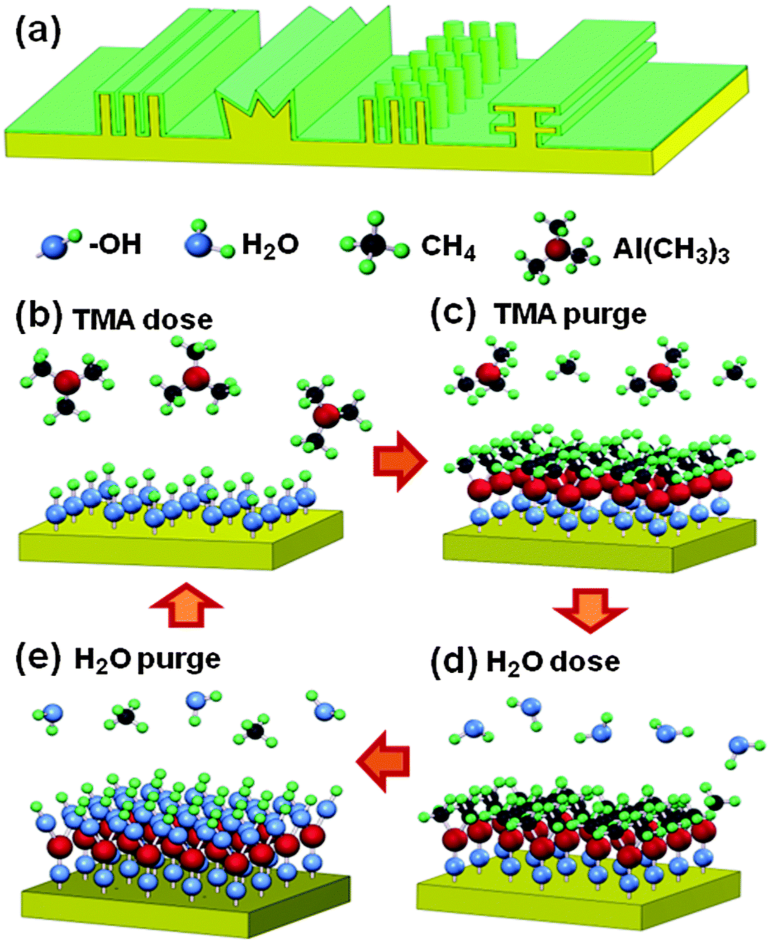


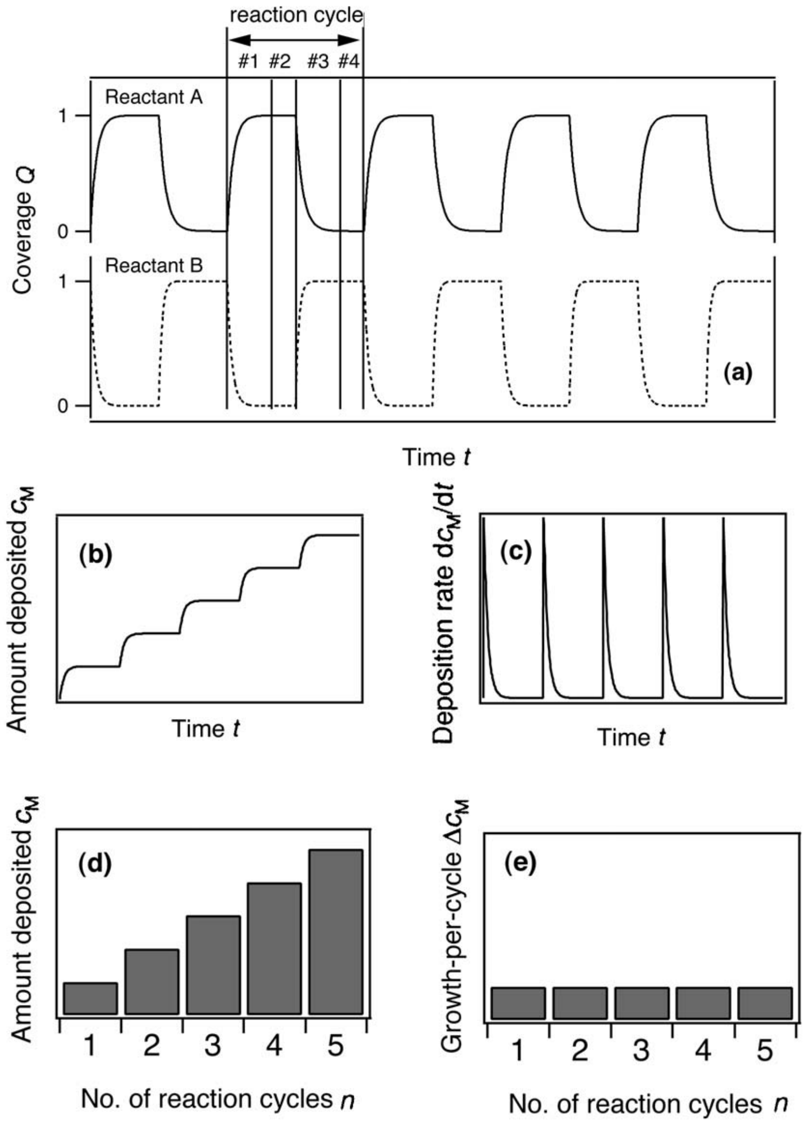
Figure 6-16 Schematic view of a commercial CVD reactor for deposition of TiC, TiN, and Al_2O_3 on carbide cutting tools. (Courtesy of A. Gates, Multi-Arc Scientific Coatings Inc.) (b) SEM image of CVD multilayer coating for cutting tool inserts. Carbide substrate/TiC/Al_2O_3/TiN (3500 ×). Courtesy of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

ALD principles

Deposition of Al_2O_3



T. Wang et al., Chem. Soc. Rev., 2014, 43, 7469-7484
http://dx.doi.org/10.1039/C3CS60370A



Riikka L. Puurunen, J. Appl. Phys. 97, 121301 (2005)

ALD of TiN

**See also:
Atomic Layer
Etching - ALE**

Challenges:

a) Can one apply CVD at low temperature?

b) Can one better control the microstructure?

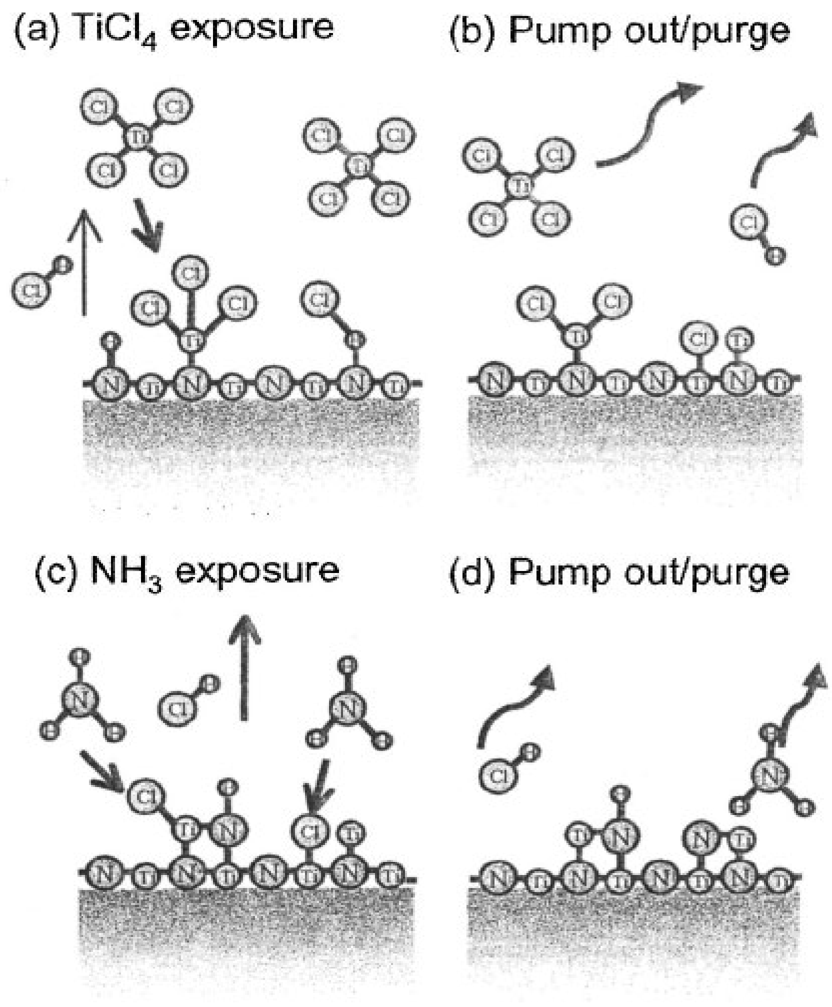
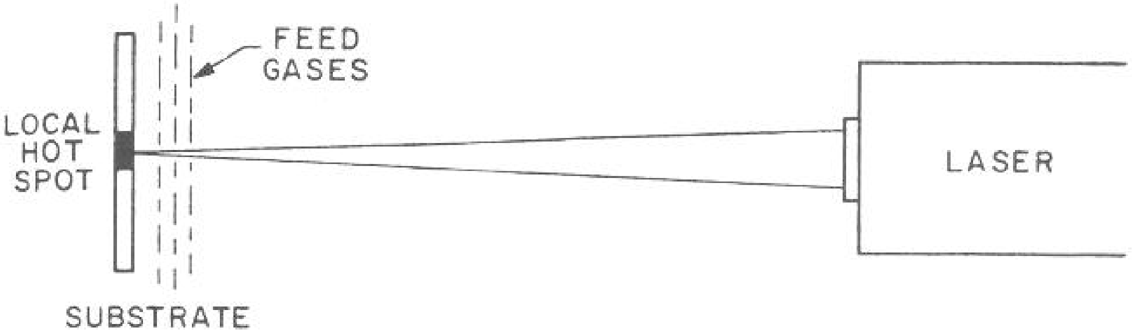
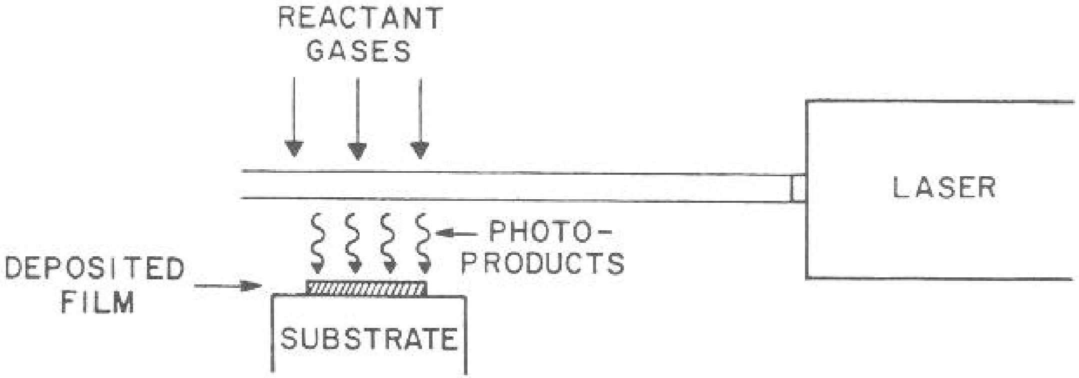


FIG. 2. Schematic representation of each process step for TiN ALD using $TiCl_4$ and NH_3 precursors. (a) $TiCl_4$ exposure, (b) pump out/purge, (c) NH_3 exposure, and (4) pump out/purge step.

Laser enhanced CVD - LECVD



PYROLYSIS



PHOTOLYSIS

Figure 6-17 (a) Pyrolytic and (b) photolytic laser-induced chemical-vapor deposition of films (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

Examples of applications of CVD films also PVD)

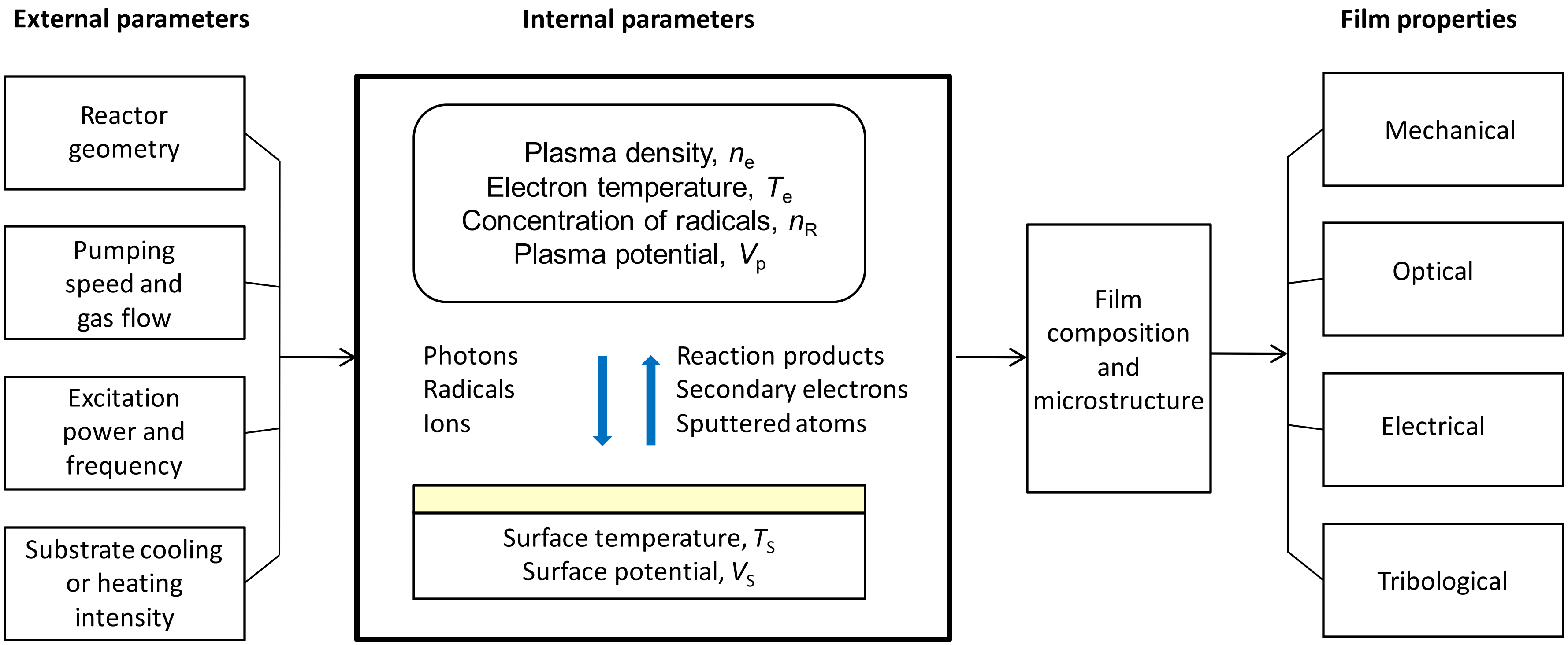
- ***Microelectronics*** industries use CVD for growth of epitaxial layers (vapor-phase epitaxy (VPE)) and for making films serving as dielectrics (low and high *k*), conductors, passivation layers, diffusion barriers, oxidation barriers, etc.
- ***Semiconductor lasers*** of GaAs/(Ga,Al)As and InP/(In,Ga)As. 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 …

Plasma system and process control



External parameters

Reactor geometry

Pumping speed and gas flow

Excitation power and frequency

Substrate cooling or heating intensity

Internal parameters

Plasma density, n_e
Electron temperature, T_e
Concentration of radicals, n_R
Plasma potential, V_p

Photons
Radicals
Ions

Reaction products
Secondary electrons
Sputtered atoms

Surface temperature, T_S
Surface potential, V_S

Film composition and microstructure

Film properties

Mechanical

Optical

Electrical

Tribological

Today:

Plasma-based processes and deposition approaches

Plasma-based techniques: effect of frequency - DC, RF, MW

Atmospheric plasma techniques: Corona, APGD, Fluidized bed CVD

L. Martinu et al., Chapter 9 in “*Handbook of Thin Film Process Technology*”, P.M. Martin, ed., Elsevier, 2010.

Efficient operation of low pressure nonequilibrium plasma

Types of discharges according to the excitation frequency

- Mouvement in an alternating field: $m_e\, dx^2/dt^2 = -q\, \mathcal{E}_o \sin \omega t$

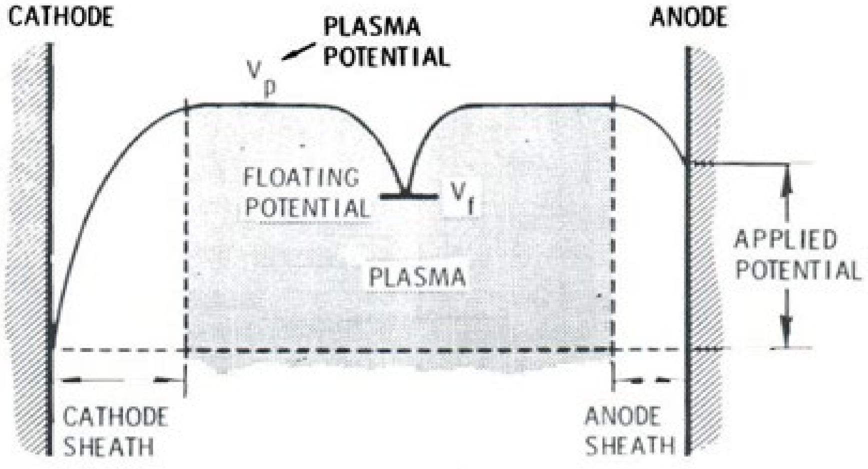
- Maximum displacement: $x_0 = q\mathscr{E}_0/m_e\omega^2$

- Maximum energy: $E_0 = (q\mathscr{E}_0)^2/2m_e\omega^2$

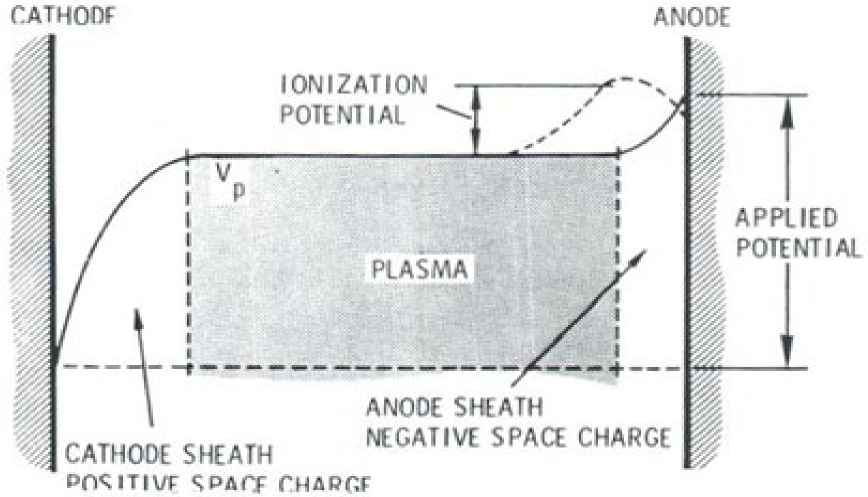
<u>Critical discharge frequencies:</u>

- **DC and alternative discharge** : $f < f_{ci} = (1/\pi)\,(q^2 n_e/m_i \varepsilon_o)^{1/2}$
- **Mobility-controlled discharge**: $f_{ci} < f < f_{ce} = (1/\pi)\,(q^2 n_e/m_e \varepsilon_o)^{1/2}$
  (Radiofrequency – RF, e.g., 13.56 MHz)
- **Discharge controlled by ambipolar diffusion:** $f > f_{ce}$
  (Microwaves – MW, e.g., 2.45 GHz)

Distribution of the potentials in the plasma



A. LARGE ANODE



B. SMALL ANODE

Figure 2.8. Schematic illustration of sheaths that form between a plasma discharge and the surrounding apparatus walls for systems having *(A)* a large anode and *(B)* a small anode.

Potentials in the plasma and in the sheath

Surface potential (of the sheath): $V_s = V_p - V_f$

- n^* - nb. of electrons that cross the sheath
- V_p – plasma potential
- V_f – floating potential (5-30 V)
- d_s – sheath thickness
- potential barrier : $q\,(V_p - V_f)$

$$\frac{n_e^*}{n_e} = \exp - \frac{q(V_p - V_f)}{k_B T_e}$$

$$V_p - V_f = k_B T_e / 2q \ln(m_i / 2.3 m_e)$$

Ion current across the sheath:

Child-Langmuir equation

Colision-less sheath (limited by the space charge):

$$j = \frac{4\mathscr{E}_0}{9d_s^2} \cdot \left(\frac{2q}{m}\right)^{1/2} V^{3/2}$$

Collisional sheath (limited by the mobility):

$$j = \frac{9\mathscr{E}_0}{8d_s^3} \cdot V^2$$

Sheath characteristics

Debye length: $\lambda_D \sim 100\ \mu m$

$d_s \sim [q(V_p - V_f) / k_B T_e]^a \lambda_D$

$2/3 < a < 3/4;\ d_s \sim 10\ \lambda_D$

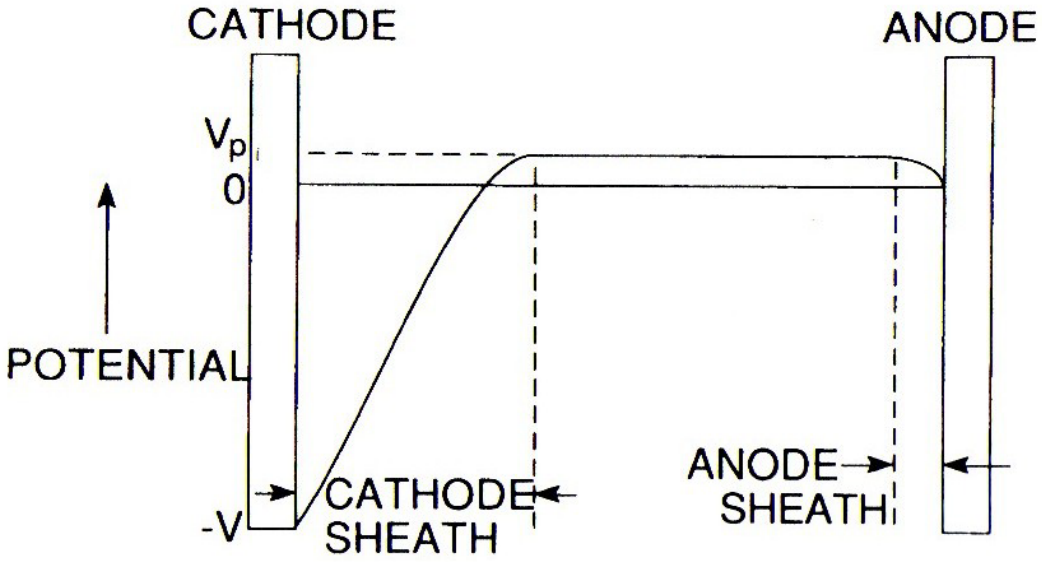


Figure 4-6 Voltage distribution across DC glow discharge. Note cathode sheath is wider tha
anode sheath.

Structure and properties of the sheath

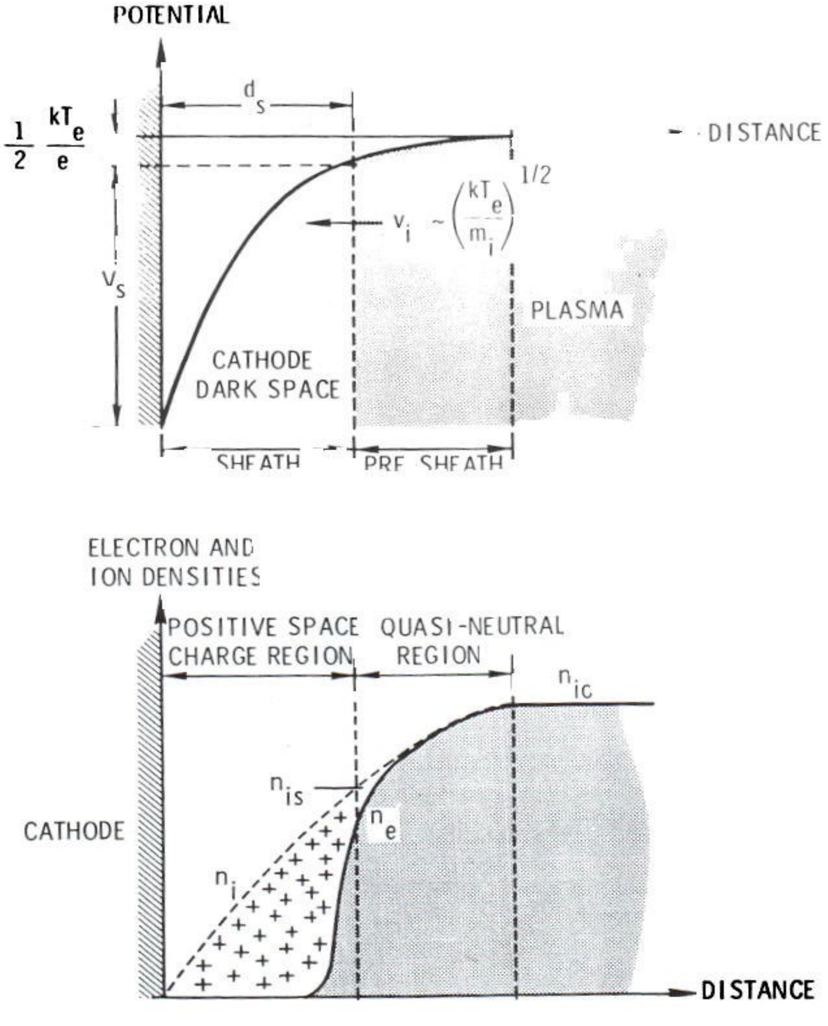


Figure 2.9. Schematic representation of the positive space-charge sheath that develops over a cathode (from Ref. 1).

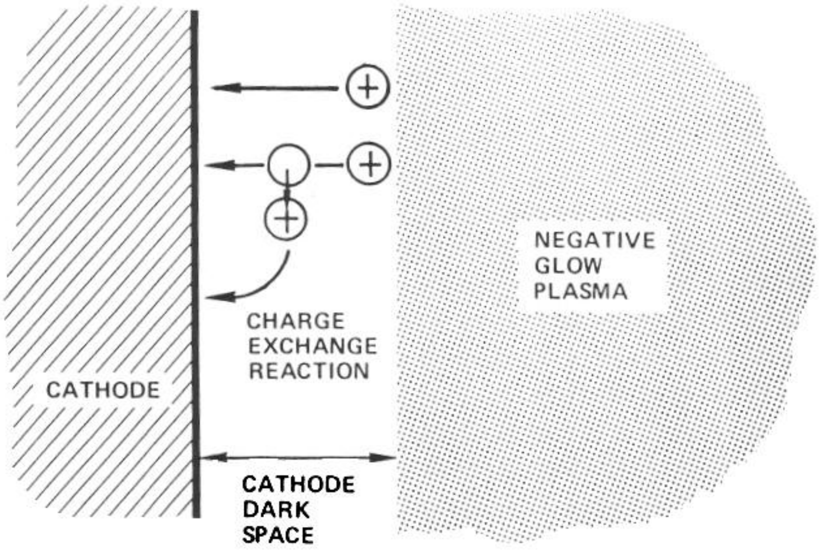


Figure 2.10. Schematic representation of charge exchange reactions in the cathode fall region of a glow discharge.

Plasma systems – reactor configuration

1. Components of an RF plasma system (13.56 MHz)

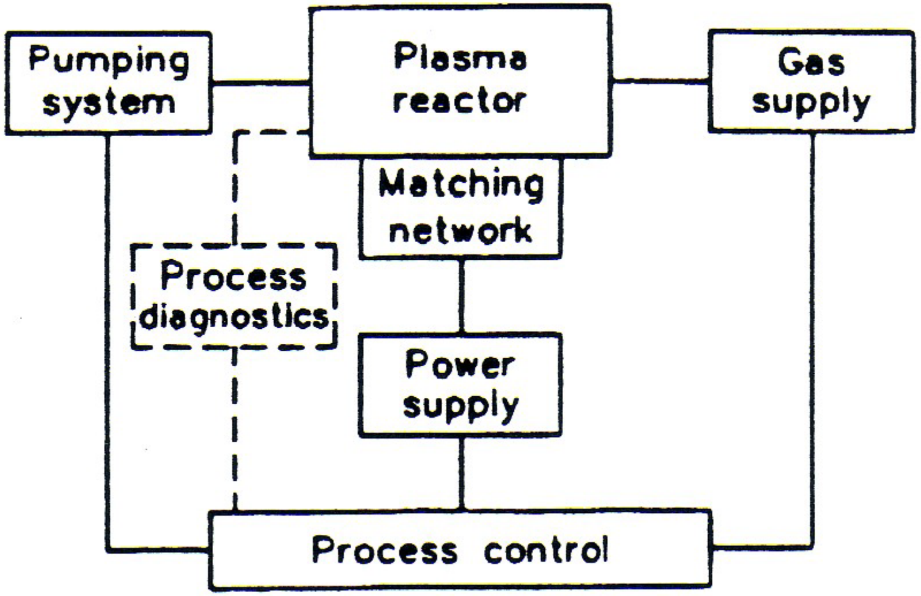


Figure E3.0.9. Modules which comprise a typical RF plasma equipment set-up.

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.

DC and RF systems (capacitive coupling)

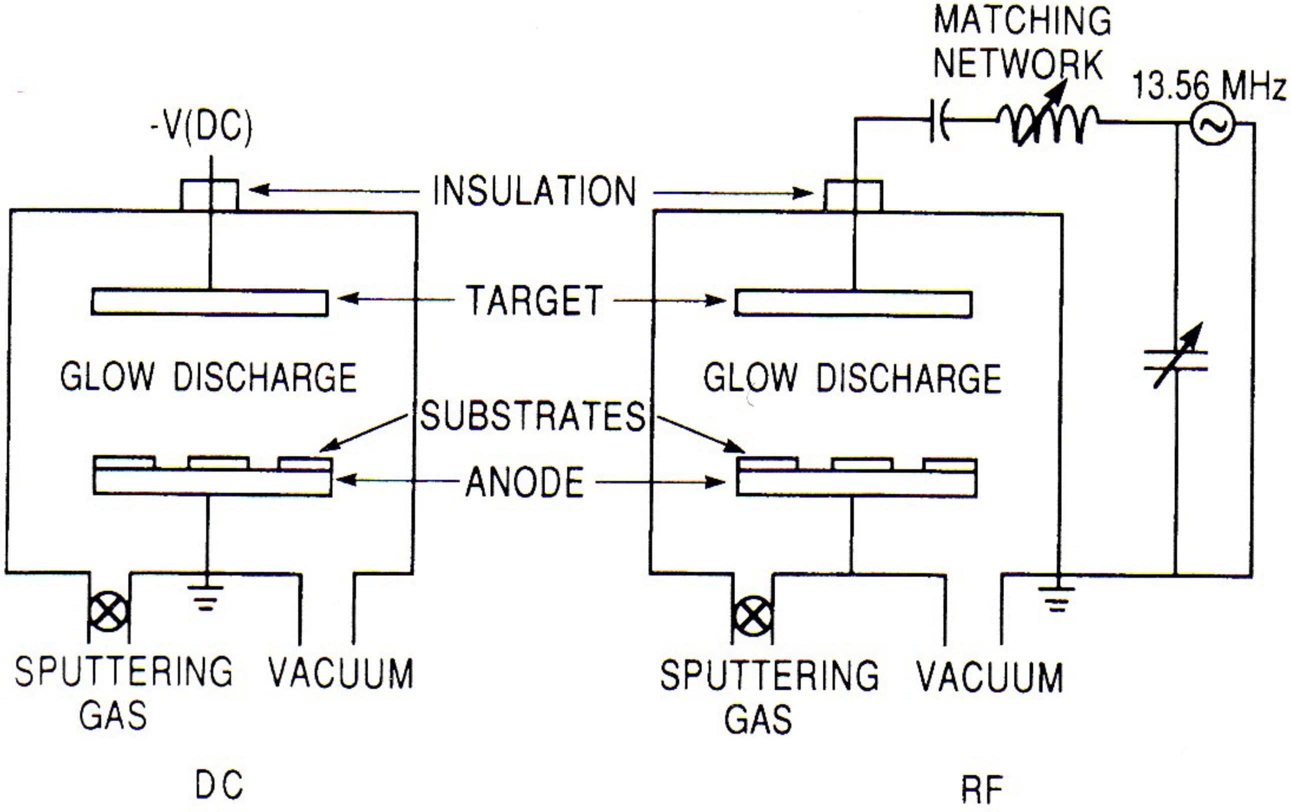
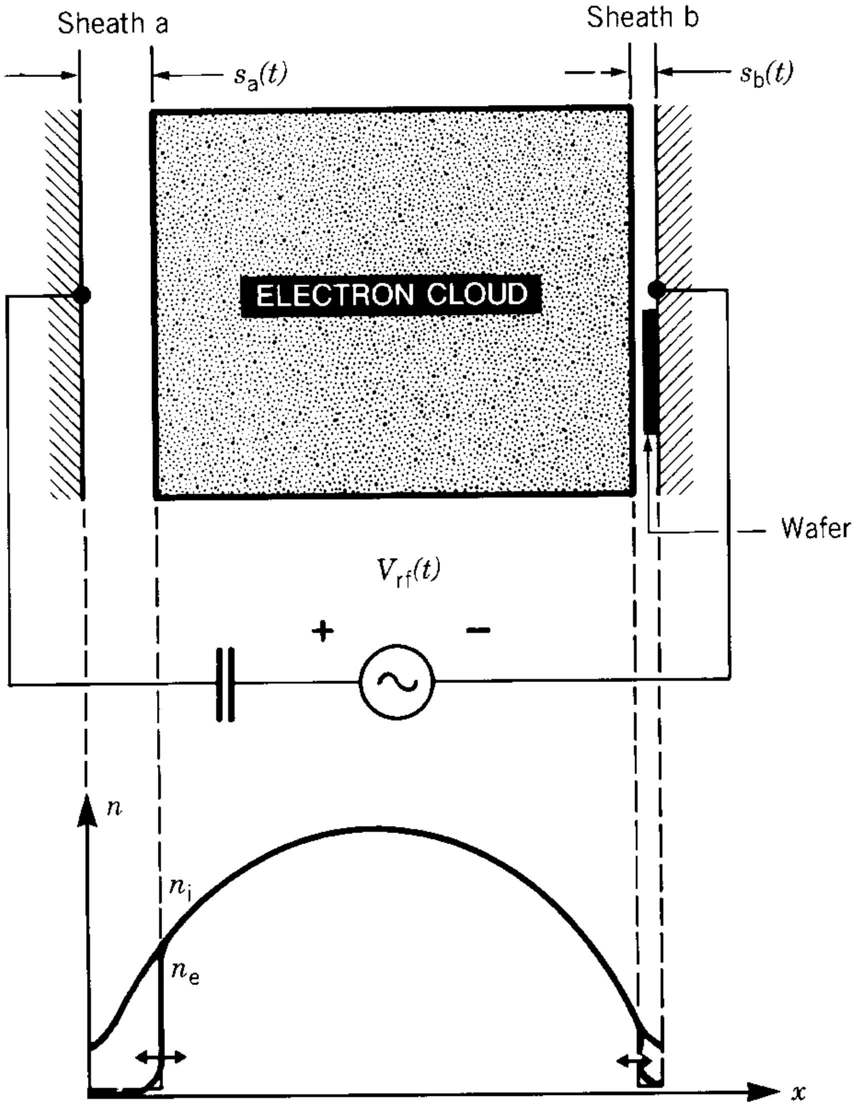
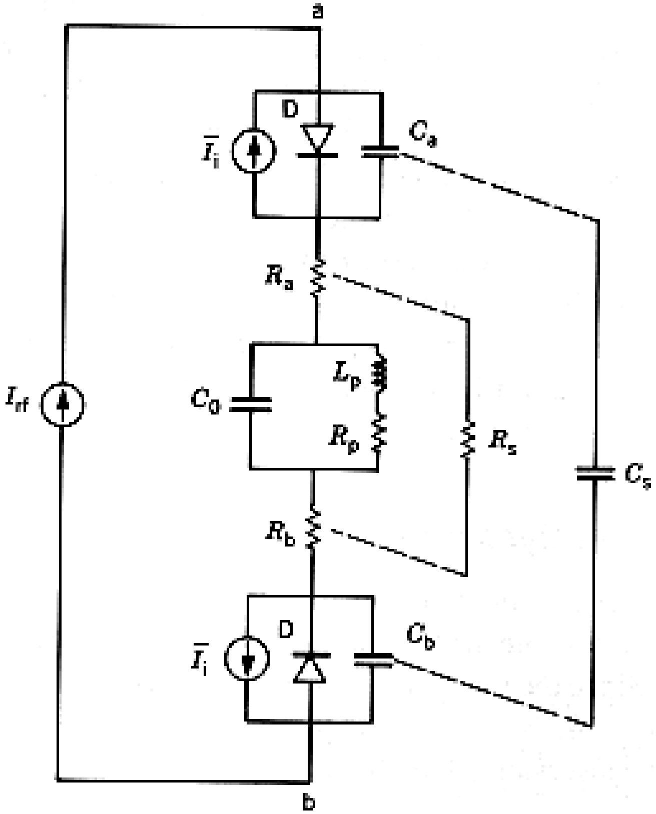


Figure 4-1 Schematics of simplified sputtering systems: (a) DC, (b) RF.

Physical model of an RF reactor





Sheath in an RF plasma: Capacitive coupling

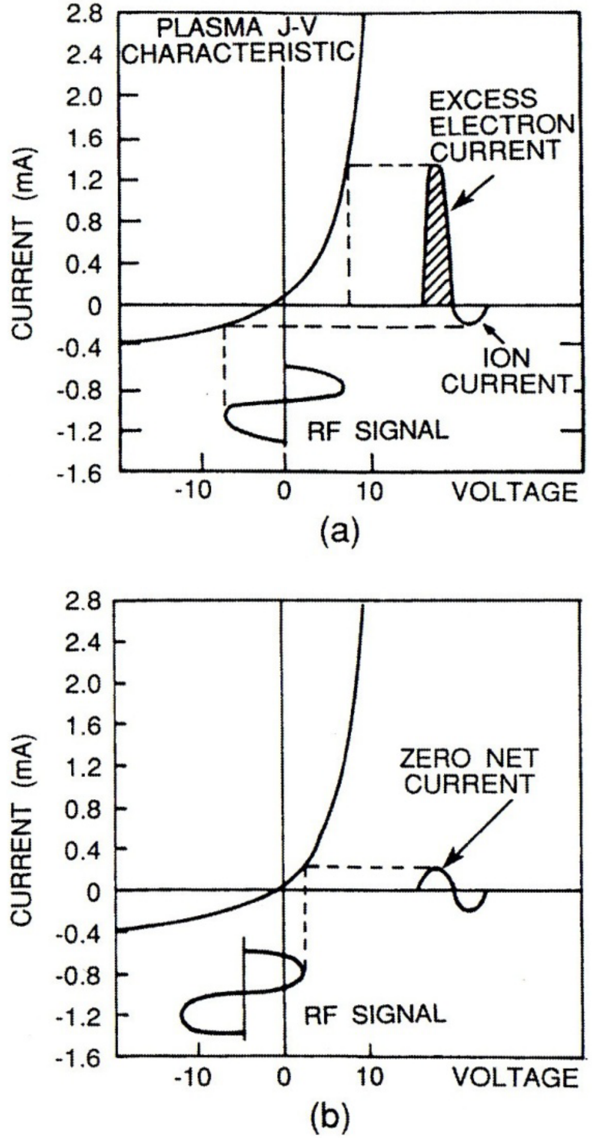
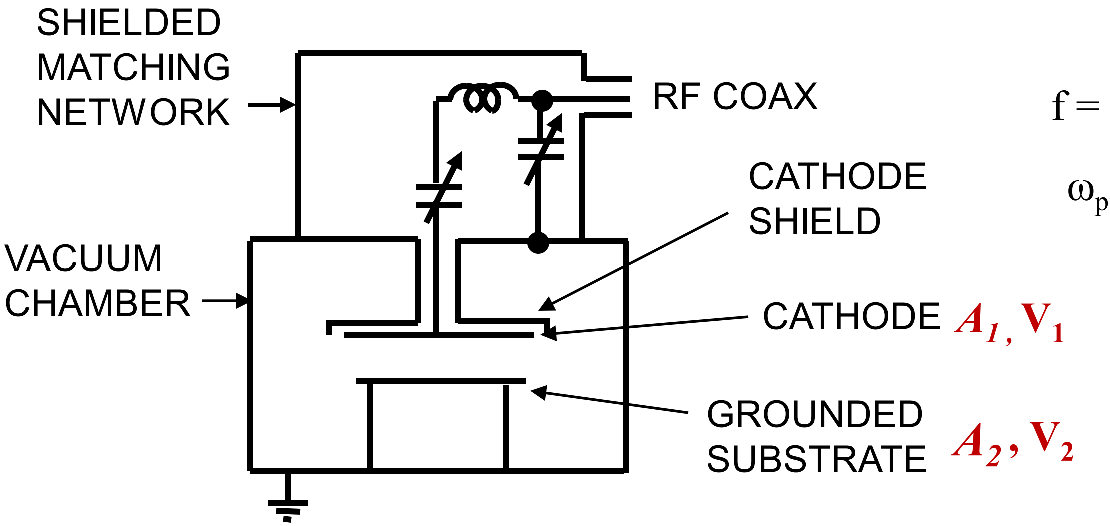


Figure 5-4 Formation of pulsating negative voltage on the capacitively coupled cathode in an RF discharge. (a) Net current/zero self-bias voltage. (b) Zero current/nonzero self-bias voltage. (From Ref. 3.)

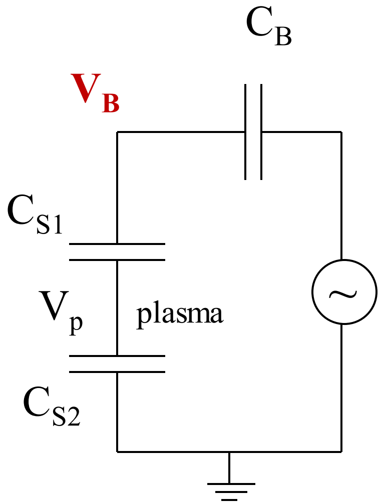
Capacitively coupled RF reactor



(After J. S. Logan in Handbook of Plasma Processing Technology)

$$f = 13.56\ \mathrm{MHz}$$

$$\omega_{pi} < 2\pi f < \omega_{pe}$$



$$V_1 / V_2 = (C_{S2} / C_{S1}) \qquad C = \frac{\varepsilon_0 A}{s(t)}$$

$$V_1 / V_2 = (A_2 / A_1)^K \qquad V_B = V_p\,(1 + (A_2 / A_1)^K)$$

where 1 < K < 4, usual experimental value for collisional sheaths is $K \approx 2.5$

Capacitively coupled RF reactors:

Electrode configurations

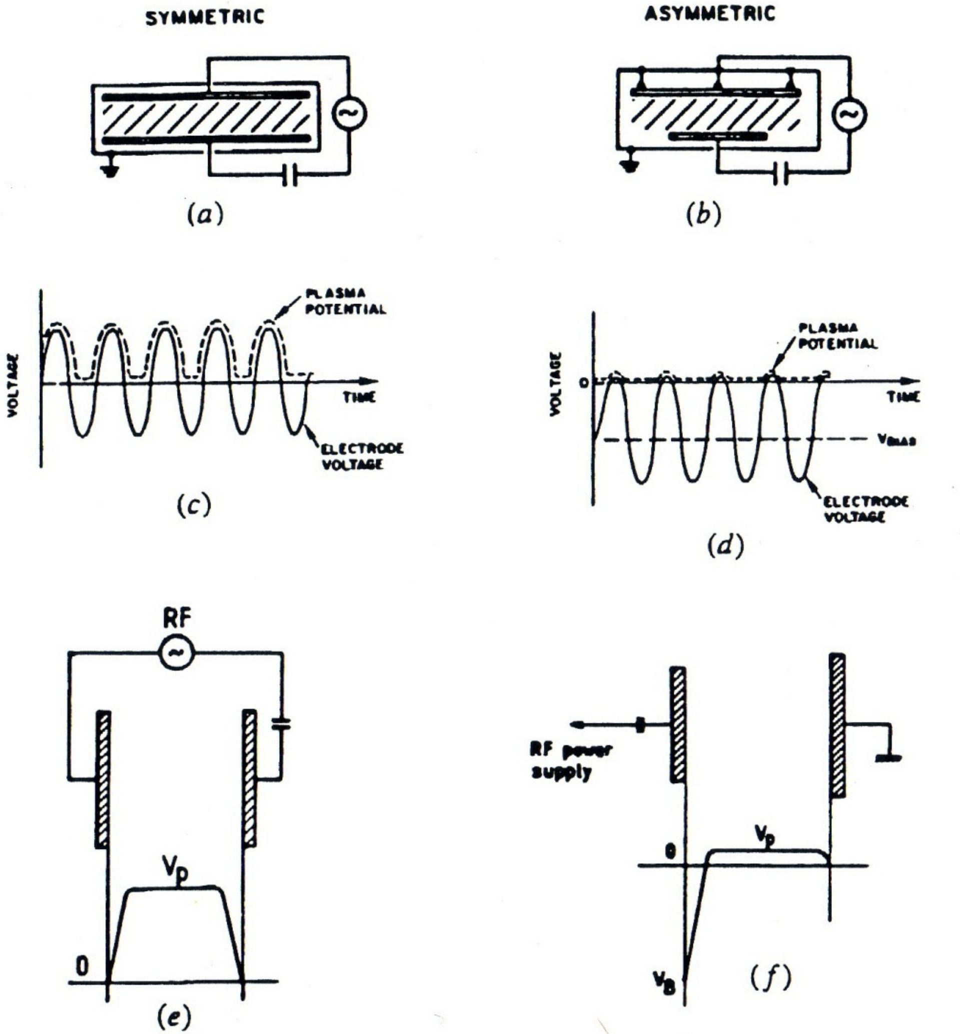
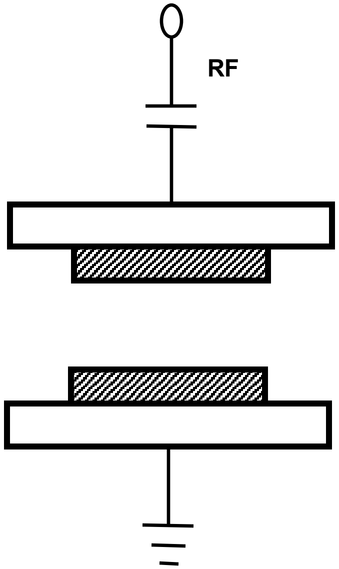


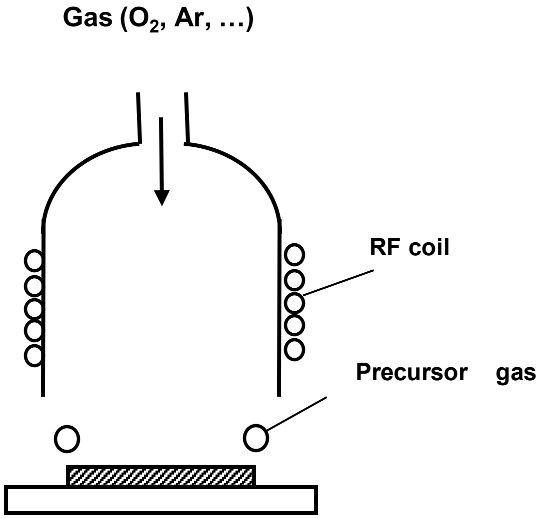
Figure E3.0.10. Comparison of symmetric and asymmetric RF plasma systems: (*a*) symmetric RF-powered electrodes of the same size, (*b*) an asymmetric discharge with a smaller, capacitively coupled RF electrode, and the remaining surface grounded; (*c*) electrode voltage and plasma potential vs time for the symmetric RF system; (*d*) powered electrode voltage and plasma potential for the asymmetric RF system. Time-average potential distribution between the electrodes in (*e*) symmetric, and (*f*) asymmetric RF plasma systems. ((*a*)–(*d*) 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.

High frequency (RF) coupling



Parallel plate RF system



Inductively coupled RF plasma

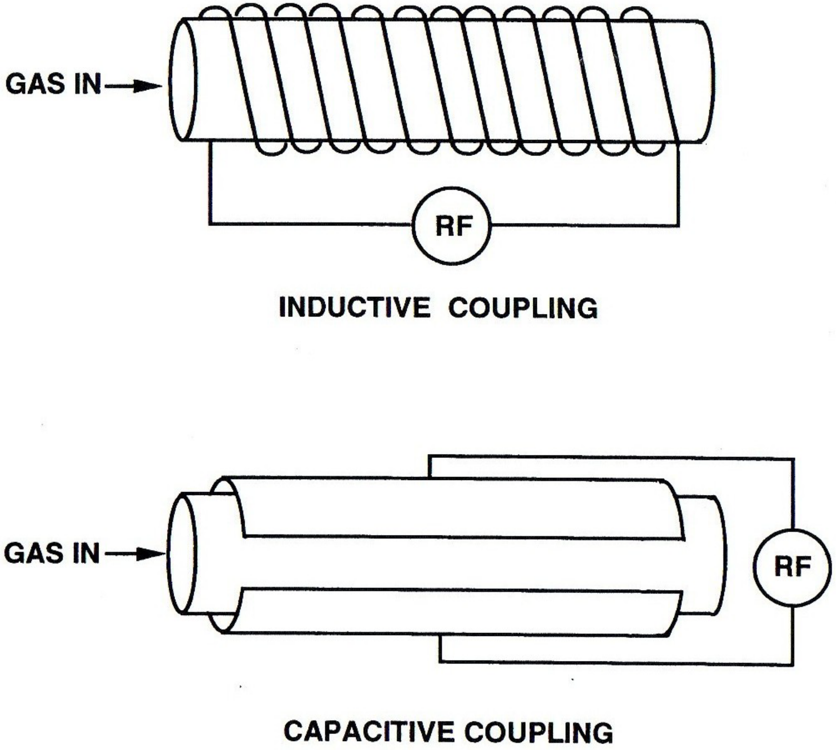


Figure 4-5 Inductively and capacitively coupled tubular RF plasma reactors.

Examples of RF plasma systems

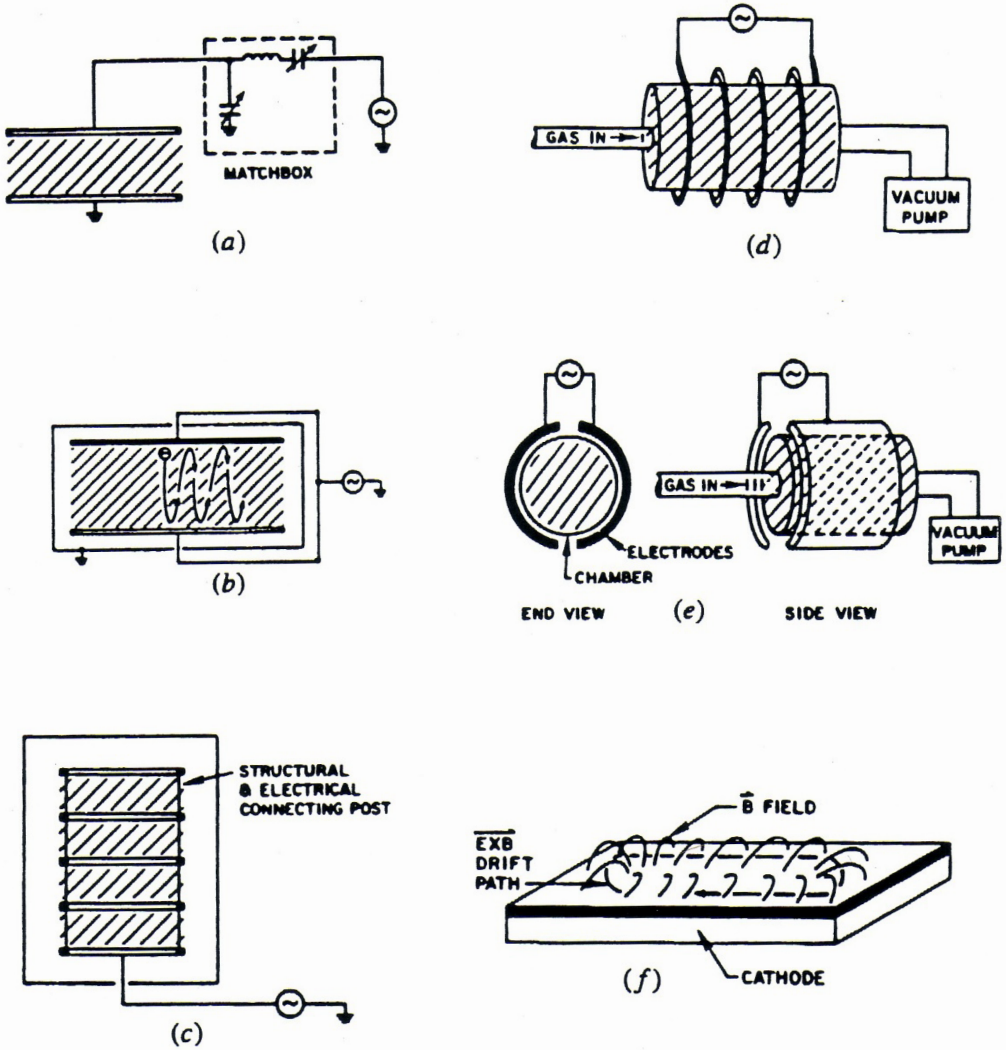


Figure E3.0.11. RF plasma sources: (*a*) typical diode system with an L-type matching unit; (*b*) hollow cathode configuration; (*c*) multiple-level hollow cathode configuration; (*d*) inductively coupled RF reactor–barrel system; (*e*) capacitively coupled RF barrel system; (*f*) rectangular planar magnetron. (After [73].)

Microwave plasma system (2.45 GHz)

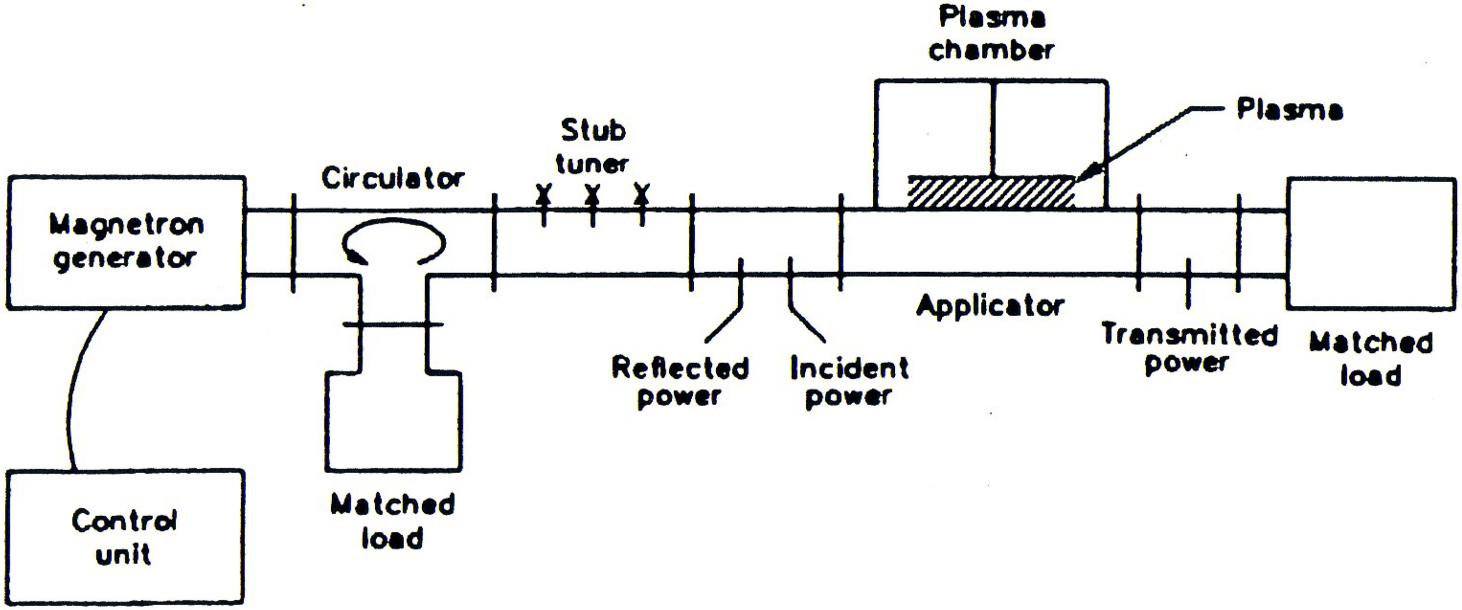


Figure E3.0.12. Modules which comprise a typical microwave plasma system.

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.

Microwave applicators

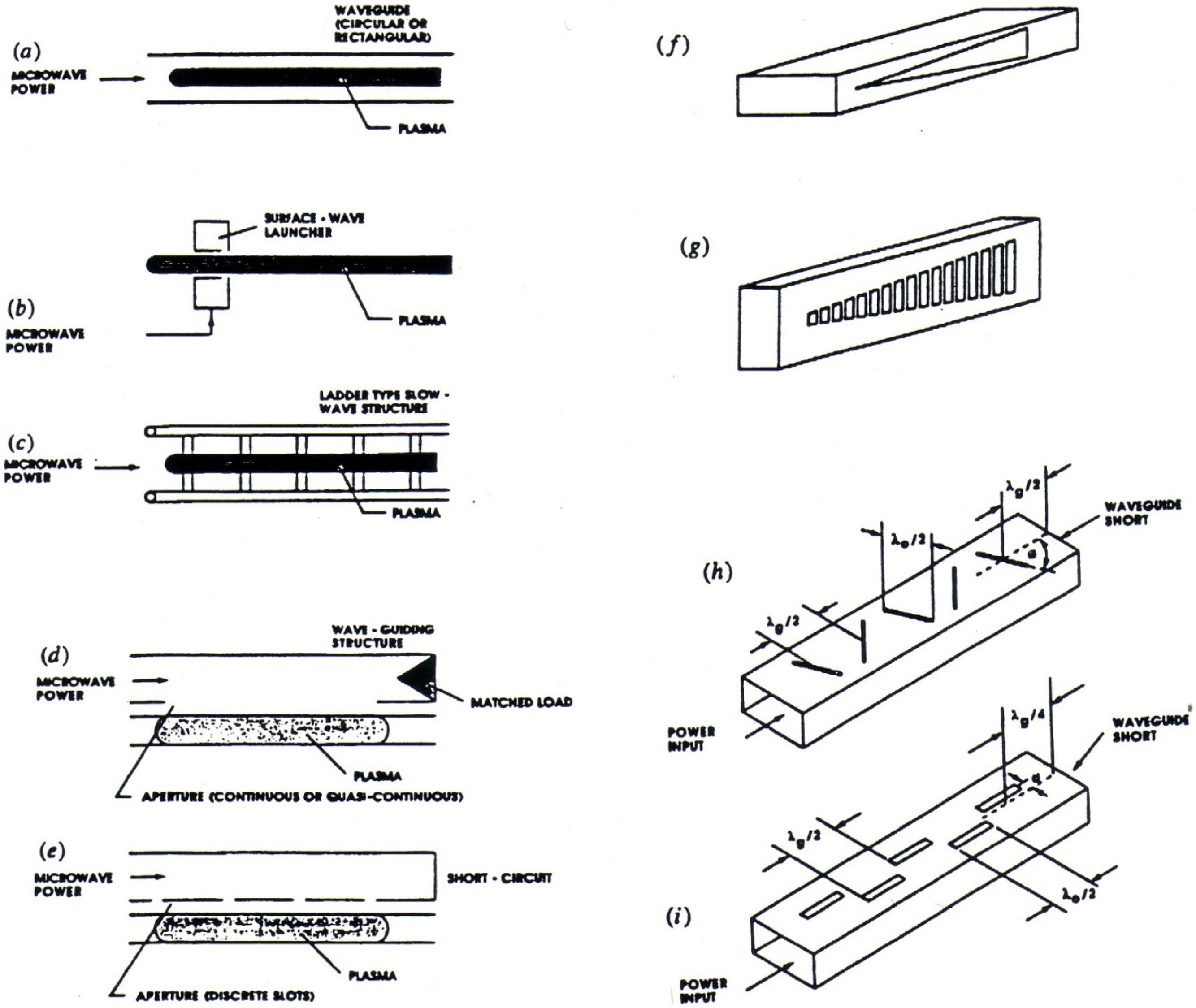
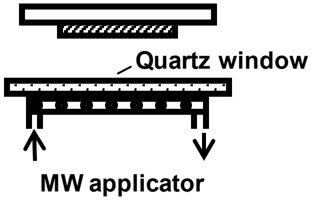
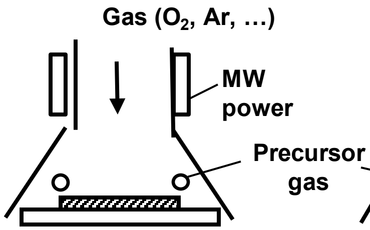


Figure E3.0.13. Long linear microwave plasma sources. Transmission line applicators: (*a*) waveguide containing a coaxially placed discharge tube; (*c*) ladder-type slow wave structure (see also figure E3.0.15); (*b*) surface-wave sustained plasma column. Antenna applicators: (*d*) travelling wave system; (*e*) standing wave system; (*f*) continuous leaky wave antenna; (*g*) quasi-continuous leaky wave antenna with apertures; standing-wave applicators (*h*) with centered, inclined series-slots and (*i*) with longitudinal shunt-slots. (After [82].)

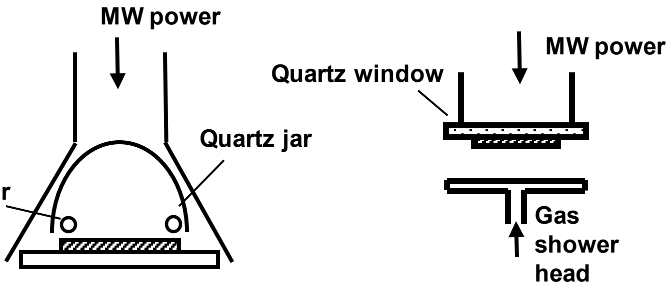
Microwave plasma – different ways of excitation



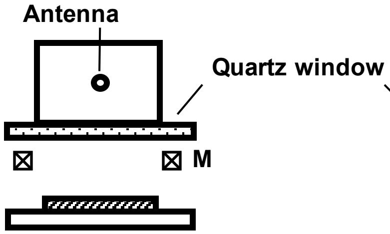
Slotted MW applicator



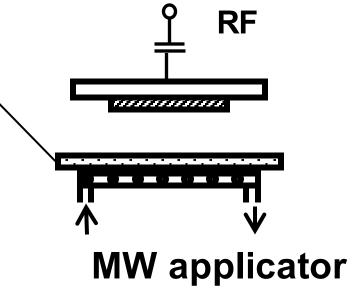
Surfatron



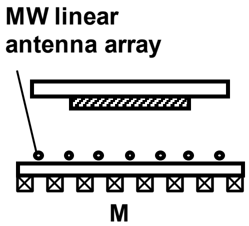
Direct MW coupling



Electron cyclotron Resonance: ECR



Dual MW/RF plasma



Distributed ECR: DECR

Post-discharge reactor - afterglow

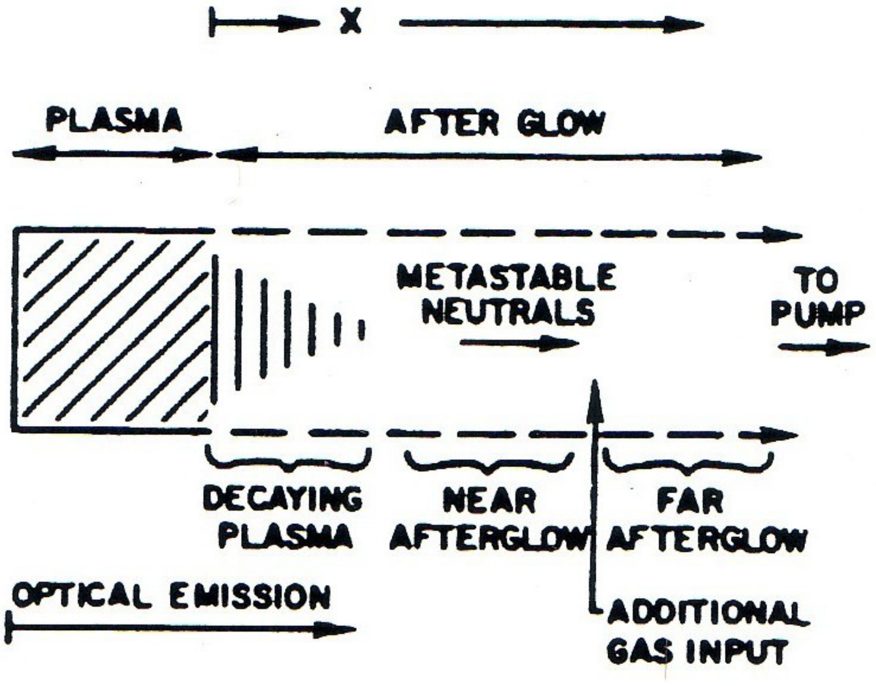
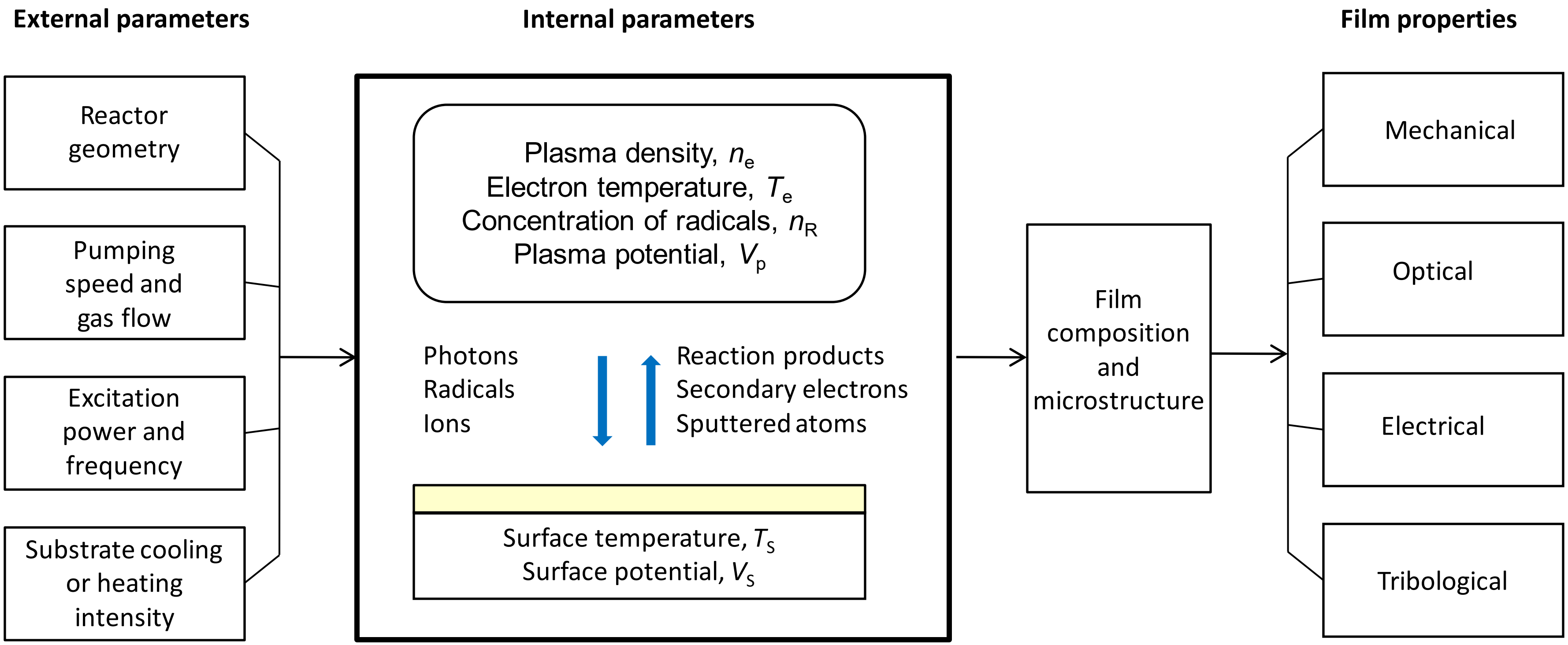


Figure E3.0.16. Regions in downstream (afterglow) plasma. (After [73].)

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.

Plasma system and process control



External parameters

Reactor geometry

Pumping speed and gas flow

Excitation power and frequency

Substrate cooling or heating intensity

Internal parameters

Plasma density, n_e
Electron temperature, T_e
Concentration of radicals, n_R
Plasma potential, V_p

Photons
Radicals
Ions

Reaction products
Secondary electrons
Sputtered atoms

Surface temperature, T_S
Surface potential, V_S

Film composition and microstructure

Film properties

Mechanical

Optical

Electrical

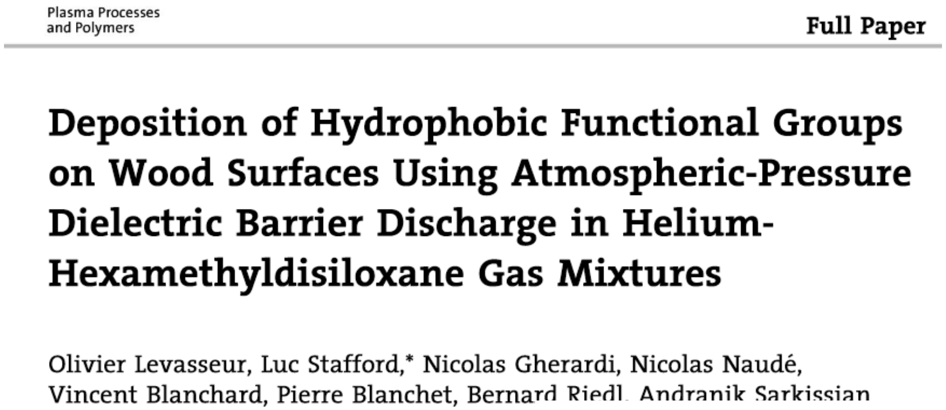
Tribological

Today:

Plasma-based processes and deposition approaches
Plasma-based film fabrication techniques: DC, RF, MW
Atmospheric plasma techniques: Corona, APGD, Fluidized bed CVD

L. Martinu et al., Chapter 9 in “*Handbook of Thin Film Process Technology*”, P.M. Martin, ed., Elsevier, 2010.

Hydrophobic treatment of wood



Plasma Processes and Polymers

Full Paper

Deposition of Hydrophobic Functional Groups on Wood Surfaces Using Atmospheric-Pressure Dielectric Barrier Discharge in Helium-Hexamethyldisiloxane Gas Mixtures

Olivier Levasseur, Luc Stafford,* Nicolas Gherardi, Nicolas Naudé, Vincent Blanchard, Pierre Blanchet, Bernard Riedl, Andranik Sarkissian

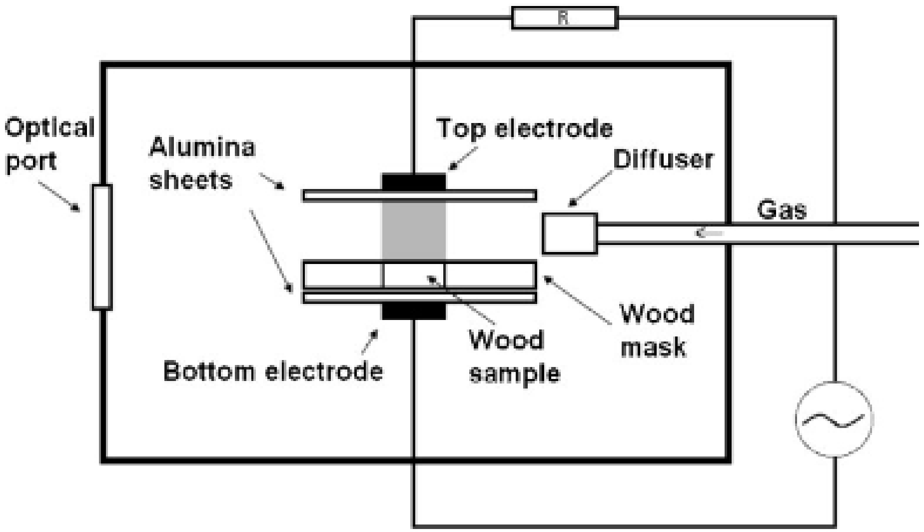


Figure 1. Schematic of the atmospheric-pressure DBD used for the growth of functional coatings on wood surfaces.

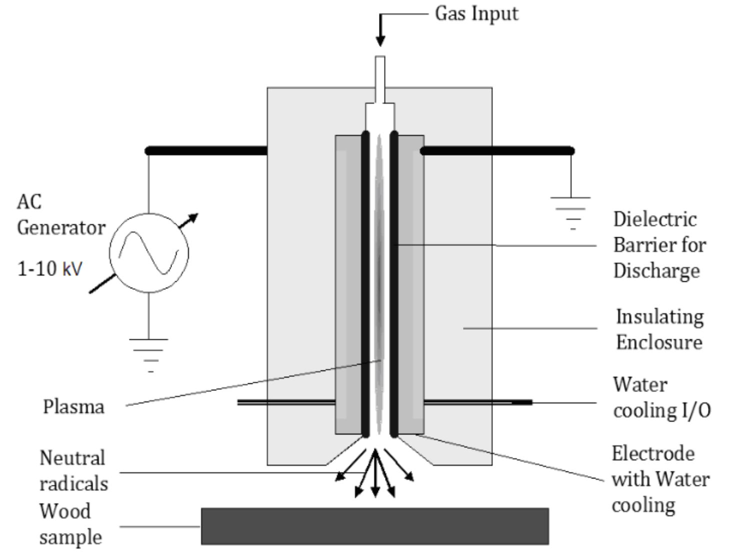
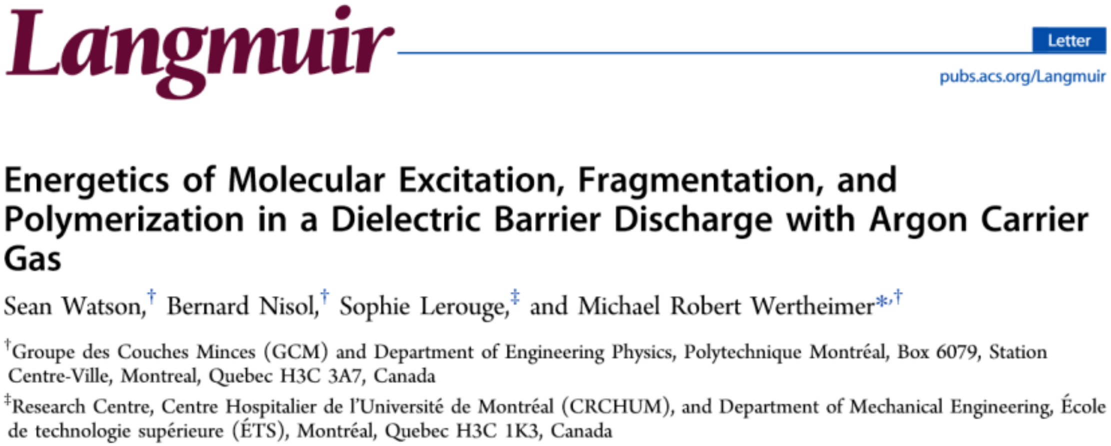


Fig. 1. Schematics of the flowing DBD apparatus used in this work - wood samples are moved on a conveyer along the plasma jet

Reidl *et al.* (2013). "Wood surface & plasma," ***Lignocellulose*** 2(1), 292-306. 295

AP Plasma Polymerization with Inert Carrier Gas



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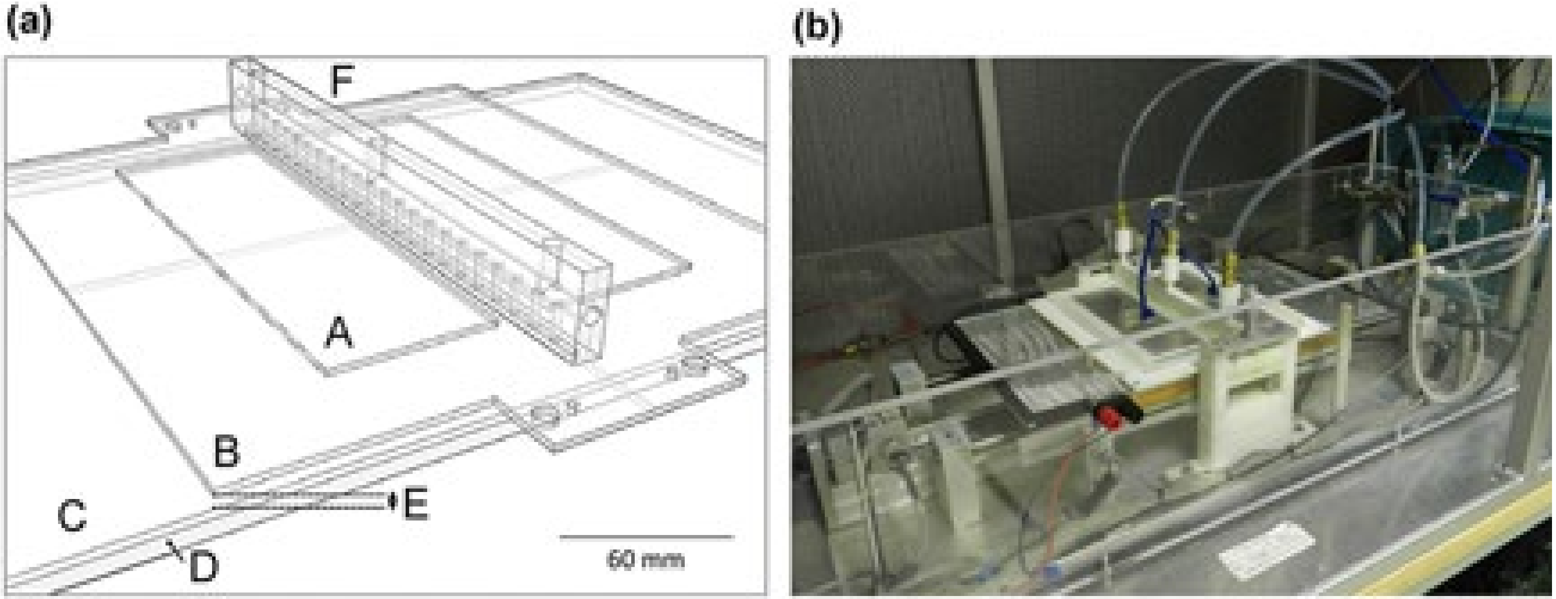
Energetics of Molecular Excitation, Fragmentation, and Polymerization in a Dielectric Barrier Discharge with Argon Carrier Gas

Sean Watson,[†] Bernard Nisol,[†] Sophie Lerouge,[‡] and Michael Robert Wertheimer*,[†]

[†]Groupe des Couches Minces (GCM) and Department of Engineering Physics, Polytechnique Montréal, Box 6079, Station Centre-Ville, Montreal, Quebec H3C 3A7, Canada

[‡]Research Centre, Centre Hospitalier de l'Université de Montréal (CRCHUM), and Department of Mechanical Engineering, École de technologie supérieure (ÉTS), Montréal, Quebec H3C 1K3, Canada



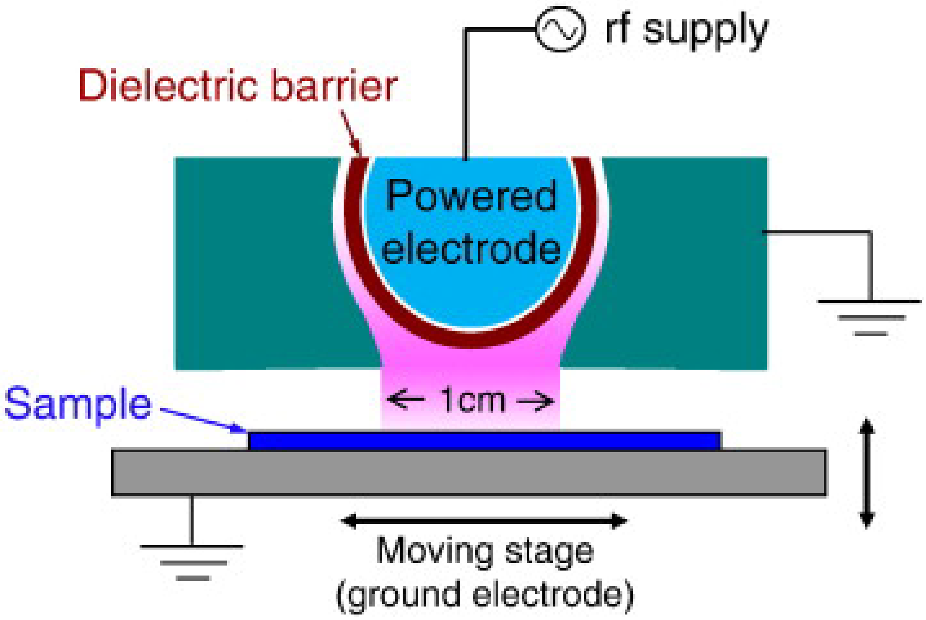
Plasma jet surface treatment

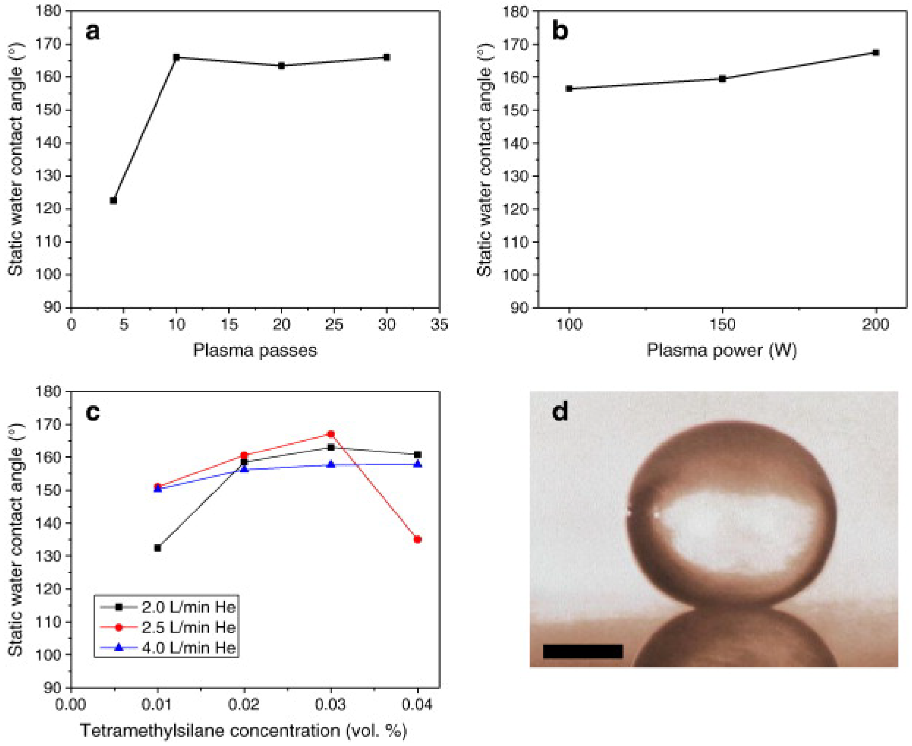
For example: Prof. T. Gervais (Poly): Surface modification for microfluidics (commercial system)

AP plasma deposition

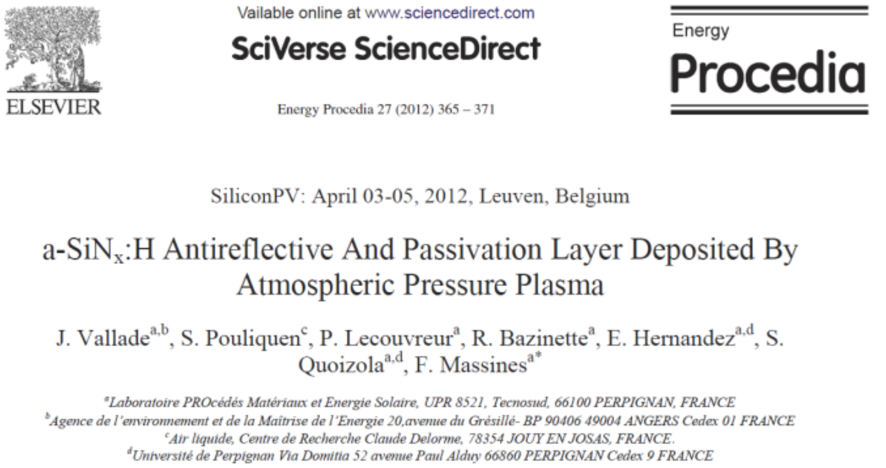
Atmospheric rf plasma deposition of superhydrophobic coatings using tetramethylsilane precursor

D.J. Marchand et al, The Pennsylvania State University,
Surface and Coatings Technology 2013





AP plasma deposition



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Energy Procedia 27 (2012) 365 – 371

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SiliconPV: April 03-05, 2012, Leuven, Belgium

a-SiN$_x$:H Antireflective And Passivation Layer Deposited By Atmospheric Pressure Plasma

J. Vallade[a,b], S. Pouliquen[c], P. Lecouvreur[a], R. Bazinette[a], E. Hernandez[a,d], S. Quoizola[a,d], F. Massines[a*]

[a]Laboratoire PROcédés Matériaux et Energie Solaire, UPR 8521, Tecnosud, 66100 PERPIGNAN, FRANCE
[b]Agence de l'environnement et de la Maîtrise de l'Energie 20,avenue du Grésillé- BP 90406 49004 ANGERS Cedex 01 FRANCE
[c]Air liquide, Centre de Recherche Claude Delorme, 78354 JOUY EN JOSAS, FRANCE.
[d]Université de Perpignan Via Domitia 52 avenue Paul Alduy 66860 PERPIGNAN Cedex 9 FRANCE

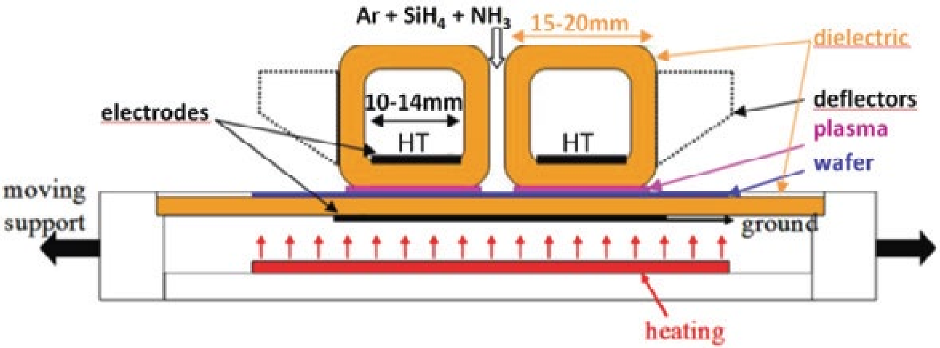


Fig. 1. Schema of the AP-PECVD experimental setup: a laminar gas blade of 5cm length is injected between the two plasma zones having the same length

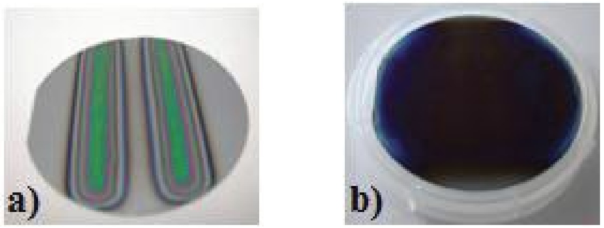


Fig. 2. Pictures of a-SiNx:H coating made in a) static mode: coatings are an image of the plasma zones, b) dynamic mode: the sample displacement allows to uniformly coat the entire surface.

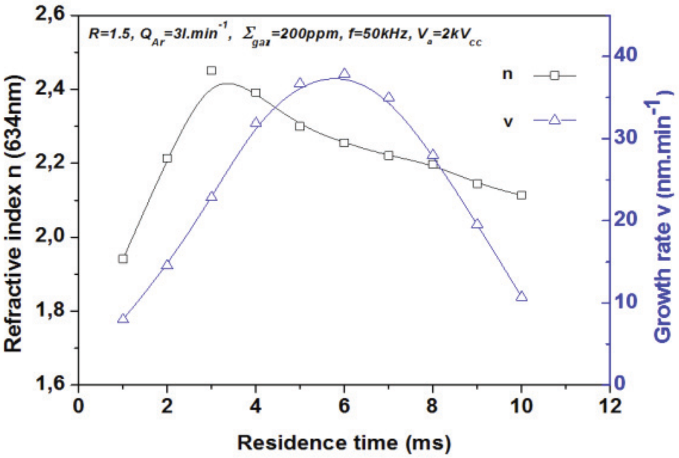


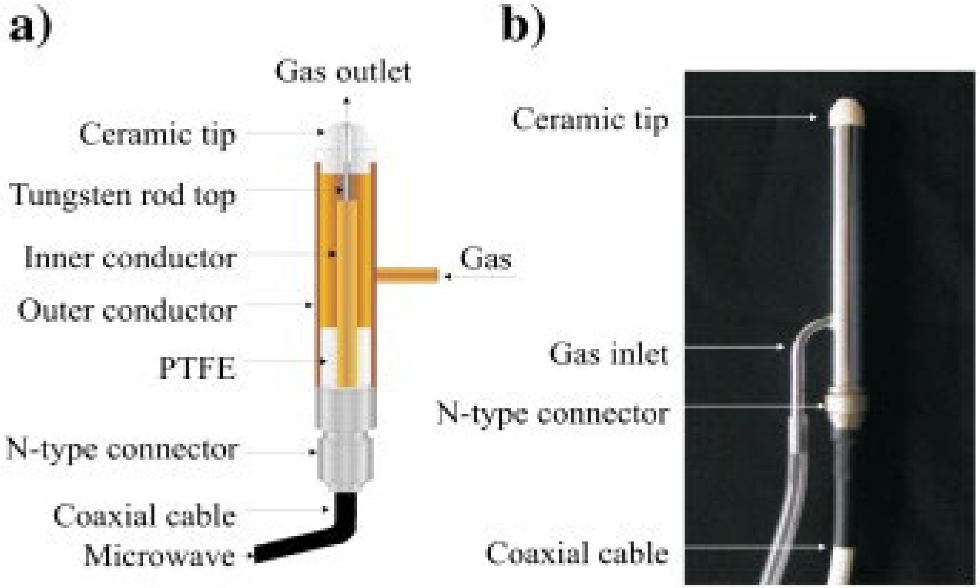
Fig. 7. Evolution of the refractive index and growth rate as a function of the gas residence time determined from the position on the film and the mean gas velocity.

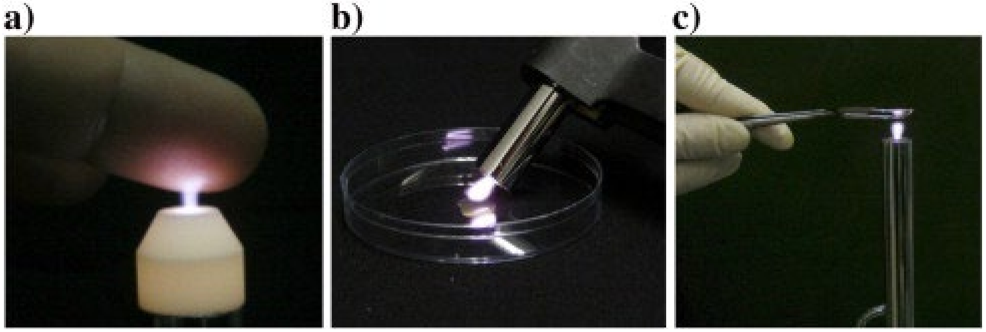
AP microwave microplasma

Atmospheric pressure microwave microplasma microorganism deactivation

D. Czylkowski et al, Polish Academy of Sciences, Gdańsk, Poland

Surface and Coatings Technology 2013

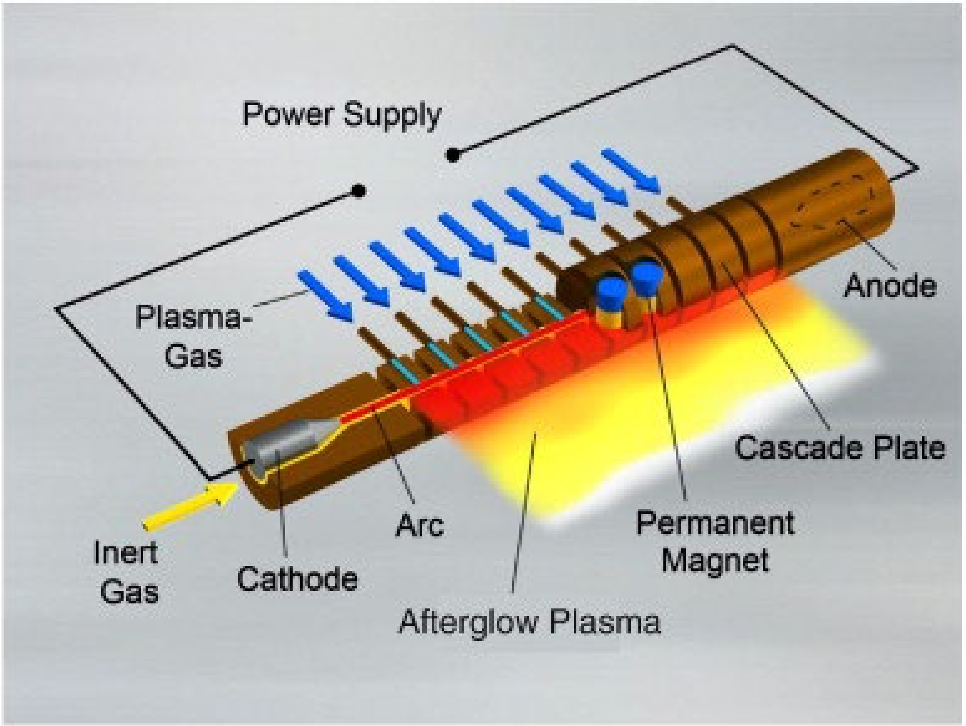




AP plasma arcs

AP PECVD using a linearly extended DC arc for adhesion promotion

L. Kotte et al, Fraunhofer IWS, Dresden, Germany, Surface and Coatings Technology 2013



Linearly extended DC arc

AP direct liquid injection CVD

Surface & Coatings Technology 204 (2009) 887–892

Contents lists available at ScienceDirect

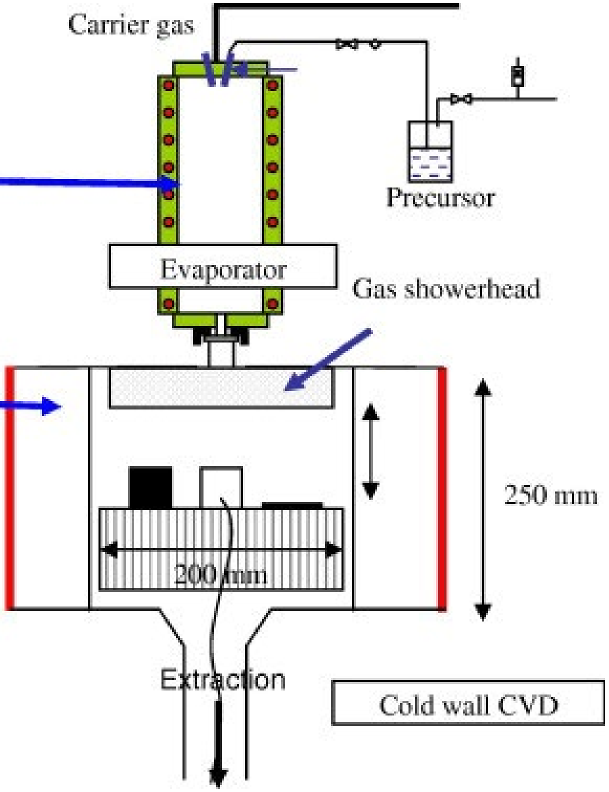
Surface & Coatings Technology

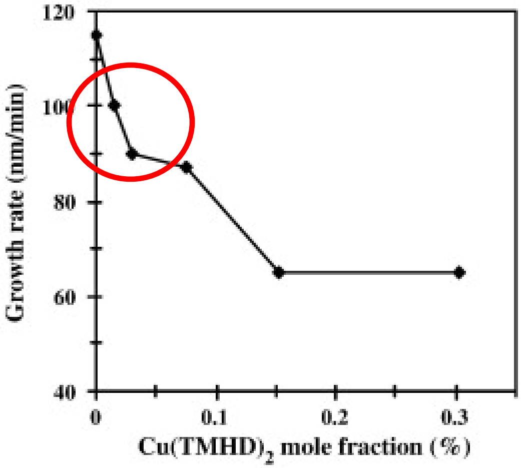
journal homepage: www.elsevier.com/locate/surfcoat

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

J. Mungkalasiri [a,b], L. Bedel [b], F. Emieux [b], J. Doré [c], F.N.R. Renaud [c], F. Maury [a,*]

[a] CIRIMAT, CNRS/INPT/UPS, ENSIACET, 118 Route de Narbonne, 31077 Toulouse cedex 4, France
[b] LTS/DTNM, CEA Grenoble, 17 rue des martyrs, 38054 Grenoble, France
[c] Nosoco.Tech®, Université Lyon 1, EA 3090, Lyon, France





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

Fluidized bed materials processing at AP

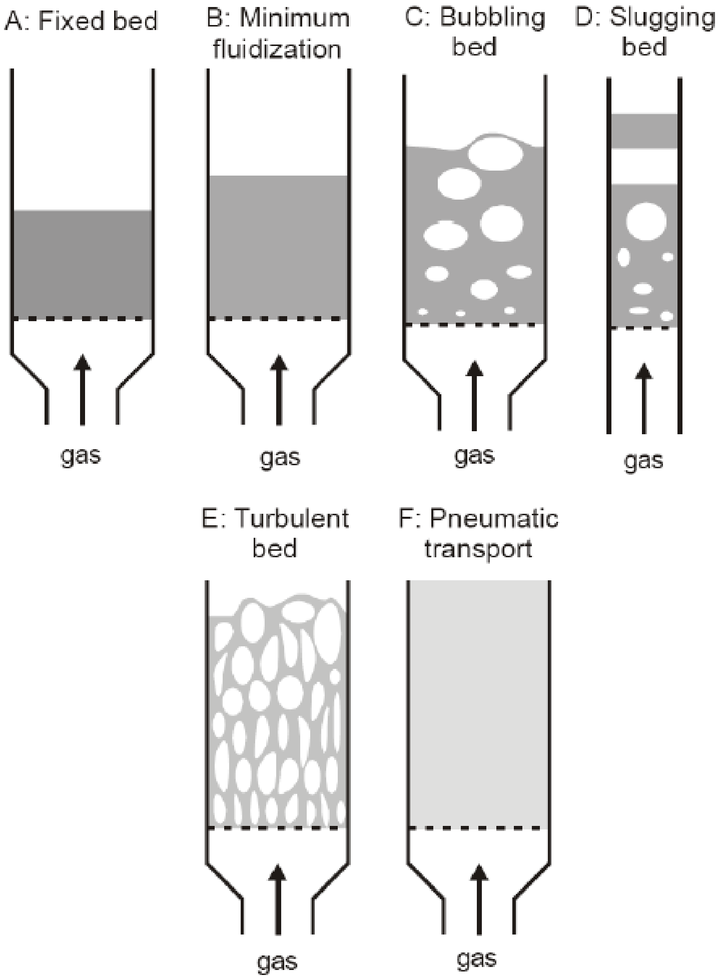
Fluidization regimes

Solids → like a fluid by blowing gas or liquid upwards

Commercial operation

Physical operations

Chemical operations



Kunii D. and Levenspiel O., Fluidization Engineering, second edition, Butterworth-Heinemann, Stoneham, 1991.

Assisting Method to Smoothen Fine Particles

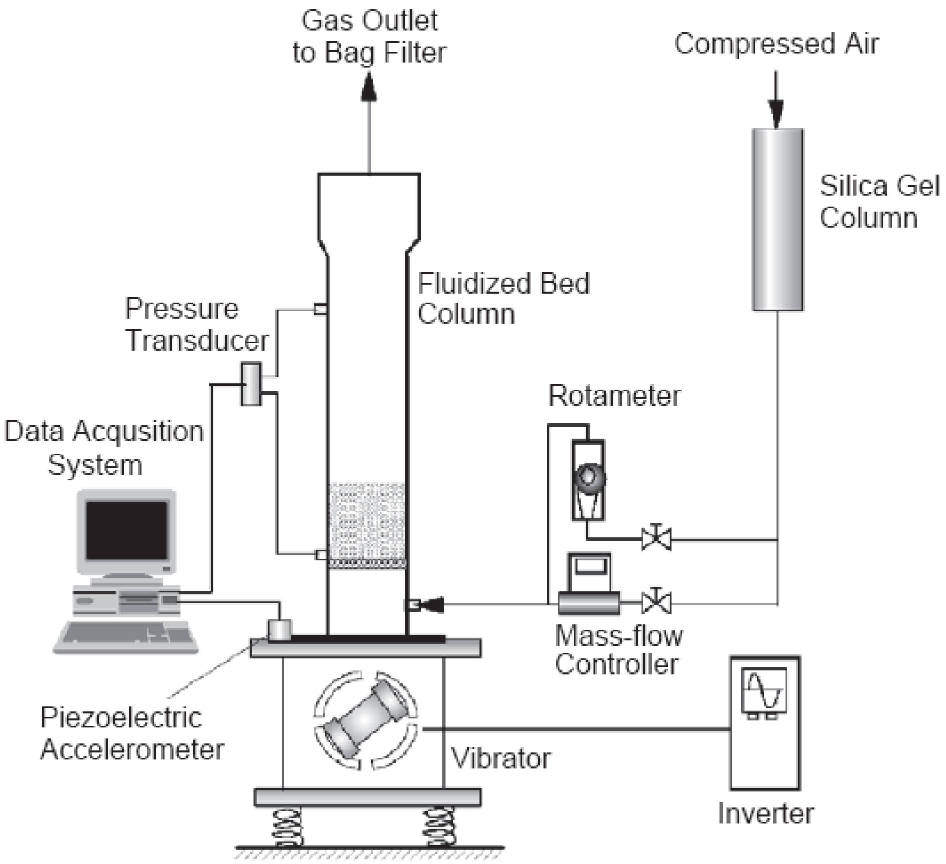
Fluidization: Mechanical Vibration

- Vibration strength

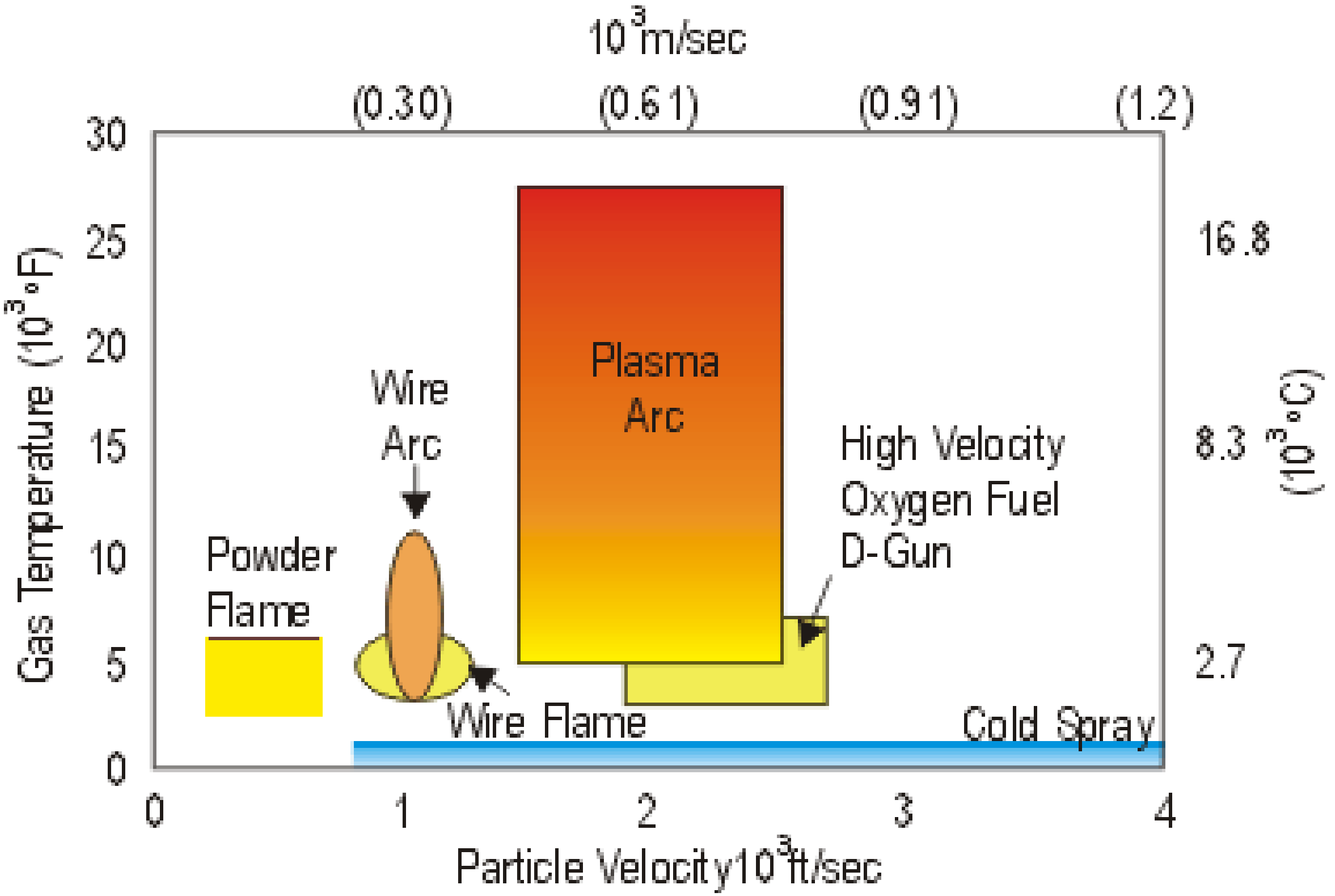
$$\Lambda = A\,(2\pi f)^2 / g$$

where A and f are the **amplitude** and the **frequency** of vibration, respectively

Xu, et al, Powder Technology, 2006. **161**(2): p. 135-144.



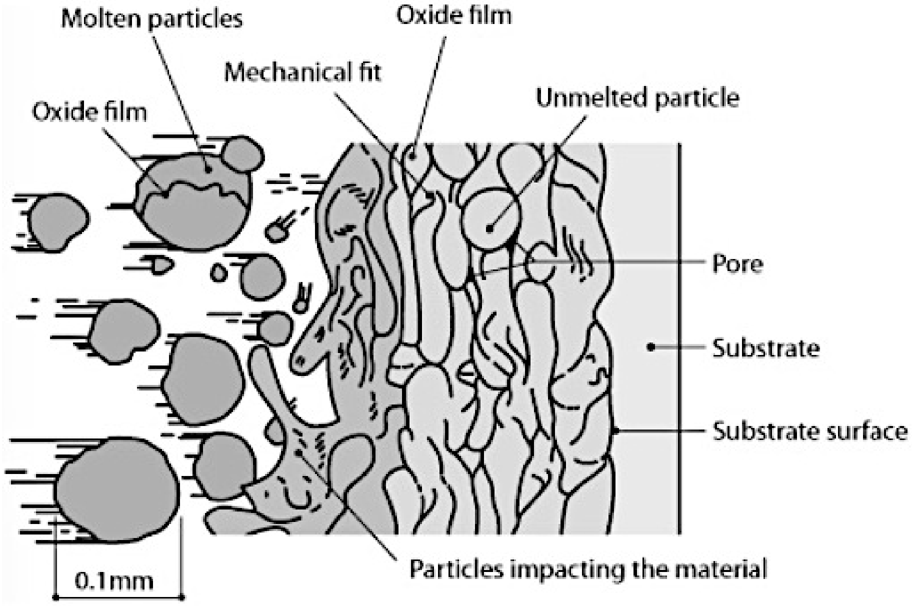
Atmospheric pressure thermal spray techniques: Thick coatings



Thermal spray deposition

Material is heated, accelerated and deposited

<u>Multipass deposition:</u>
Particles (heated or fused),
splats, oxides, pores



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<u>Two main processes:</u>
Plasma (electric)
Combustion (flame)

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 and process optimization
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**

Project #1: Techniques for the fabrication of nanostructured films and coatings

Mohamed Ammari – HiPIMS (High Plasma Impulse Magnetron Sputtering)
Veronika Cervenkova - Atomic layer deposition (ALD)
Emilien Martel – HVOF
Alexandre Lussier – DIBS
Gabriel Juteau - OMBE
Thomas Lapointe – Supersonic MBE
Luc Montpetit - …
Alexandre Fall - …
Arghavan Yazdanpanah Ardakani - PECVD
Alexandre Pinel – ….
Izacard Bastien – Cold spray

Etienne Tremblay-Nathan Sasseville – PIII
Alexandre Gamache-Thomas Sicotte – PLD
Alexandre Carrière-Yusef Ben Mami – Langmuir-Blodgett