



Thin Film Deposition by Sputtering and PVD

Essential Step of Modern
High Technology

Overview of Deposition Methods

	Physical Vapor Deposition (PVD)			Chemical Vapor Deposition
	Evaporation	Sputtering	Pulsed Laser Deposition	CVD, MOCVD, PECVD, ...
Production of species	Thermal energy	Momentum transfer	Thermal energy+	Chemical reaction
Deposition rate	High, 10 $\text{k}\text{\AA}/\text{s}$	Low	Moderate	Moderate, 2.5 $\text{k}\text{\AA}/\text{s}$
Species	Atoms & ions	Atoms & ions	Atoms, ions & clusters	molecules \rightarrow atoms
Energy of species	Low, 0.1-0.5 eV	High, 1-10 eV	Low to high	Low, high for PECVD
Complex objects	Shadowing	Non-uniform thickness	Shadowing, non-uniform	Good coverage
Scalability to large wafers	yes	yes	no	yes

Fundamentals of Film Deposition



■ Gas Kinetics

Have a good vacuum !

$$\lambda = \frac{1}{\sqrt{2\pi}nd^2} = \frac{k_B T}{\sqrt{2\pi}Pd^2},$$

d : molecular diameter,

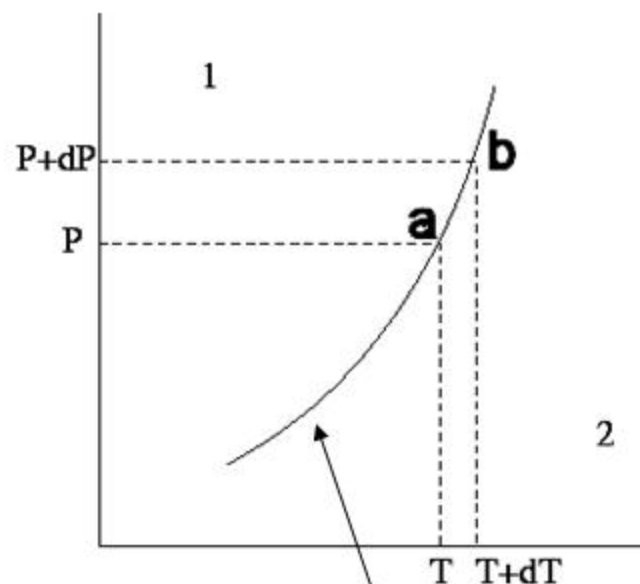
n : concentration of the gas,

P : pressure, T : temperature

$P(\text{mbar})$	$\lambda \text{ (cm)}$	Collisions (1/s)	Impinging flux (1/cm ² s)	Monolayer /s
1	$7 \cdot 10^{-3}$	$7 \cdot 10^6$	$3 \cdot 10^{20}$	$3 \cdot 10^5$
10^{-3}	$7 \cdot 10^0$	$7 \cdot 10^3$	$3 \cdot 10^{17}$	$3 \cdot 10^2$
10^{-6}	$7 \cdot 10^3$	$7 \cdot 10^0$	$3 \cdot 10^{14}$	$3 \cdot 10^{-1}$
10^{-9}	$7 \cdot 10^6$	$7 \cdot 10^{-3}$	$3 \cdot 10^{11}$	$3 \cdot 10^{-4}$

Fundamentals of Film Deposition

■ Thermodynamics



$$g_1 = g_2$$

Thermodynamic Gibbs potential G ,

$$dG = -SdT + VdP$$

in equilibrium, $dg_{\text{Liquid}} = dg_{\text{Vapor}}(v, P)$;

$$-s_L dT + v_L dP = -s_V dT + v_V dP$$

$$\frac{dP}{dT} = \frac{s_V - s_L}{v_V - v_L} = \frac{T}{T} \cdot \frac{s_V - s_L}{v_V - v_L} = \frac{q}{T(v_V - v_L)}$$

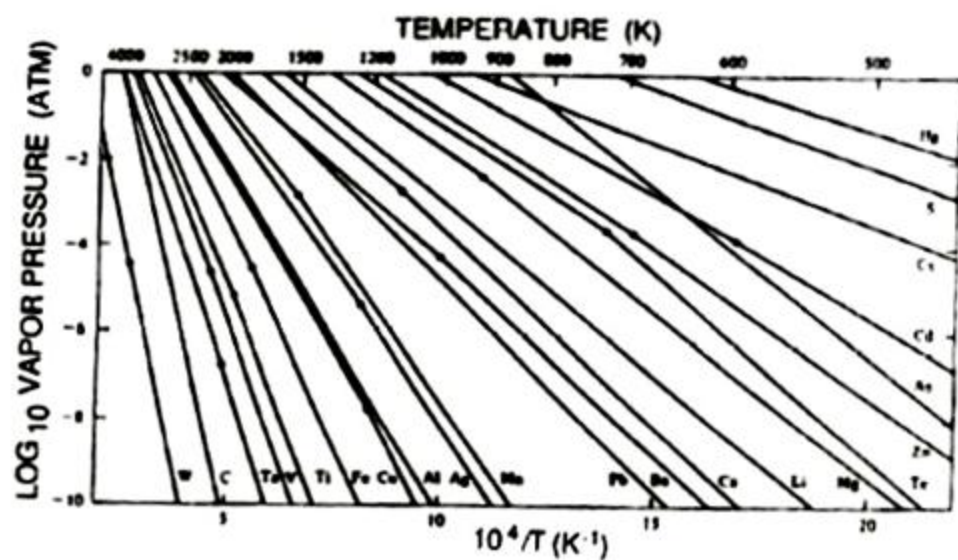
q : specific heat of evaporation

Fundamentals of Film Deposition

- Thermodynamics

$$\frac{dP}{dT} = \frac{q}{T(v_V - v_L)} \approx \frac{qP}{T \frac{RT}{\mu}}$$

$$\frac{dP}{P} = \frac{\mu q}{R} \frac{dT}{T^2} \rightarrow \ln P = -\frac{\mu q}{R} \frac{1}{T} + C$$



Vapor pressures of selected elements



Physical Vapor Deposition

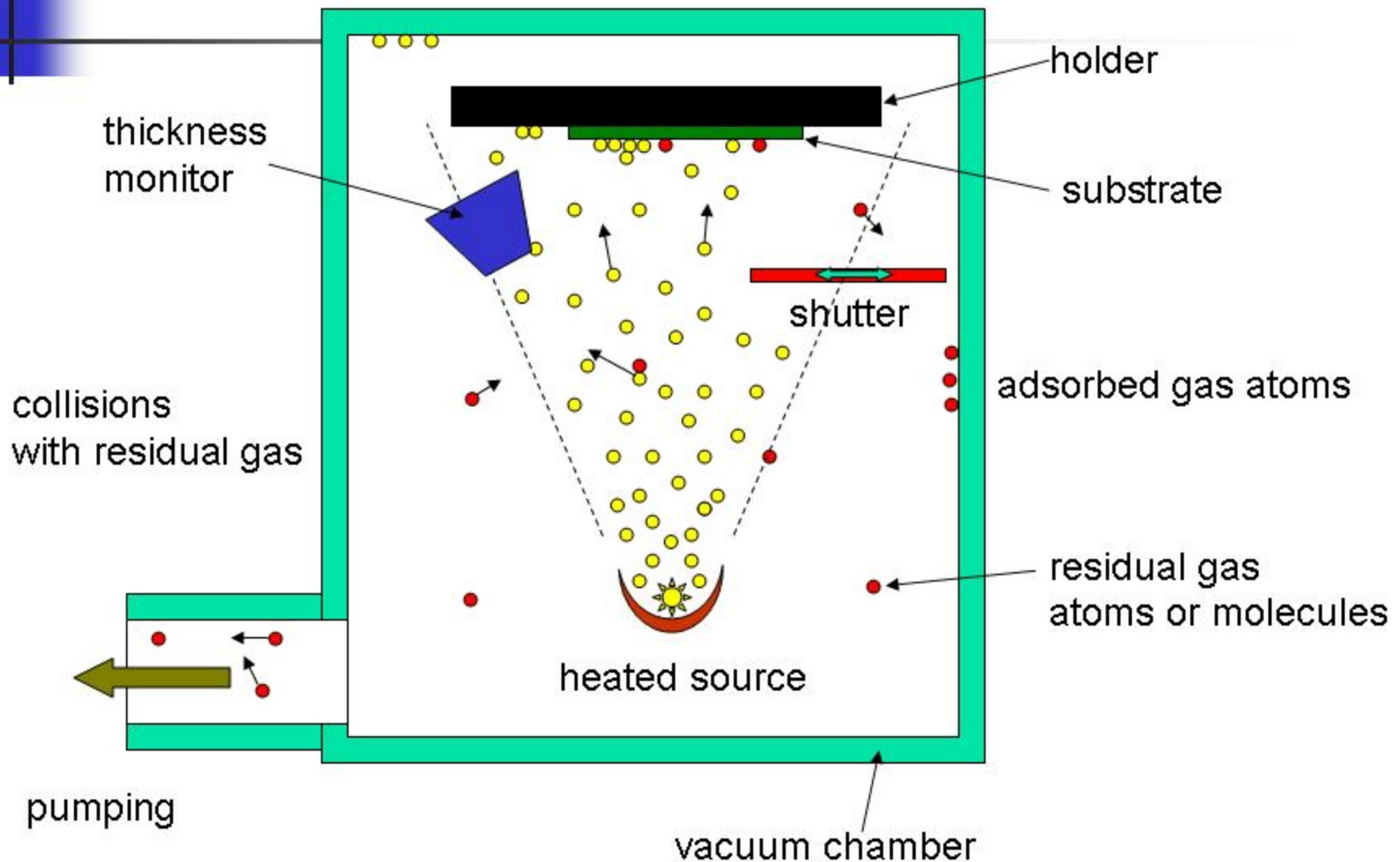
PVD involves the following sequence of steps:

- 1) the material is converted into vapor by heating;
- 2) the vapor is transported from its source to the substrate in a vacuum
- 3) the vapor condense on the substrate and forms the thin film.

The *advantages* of PVD by evaporation are:

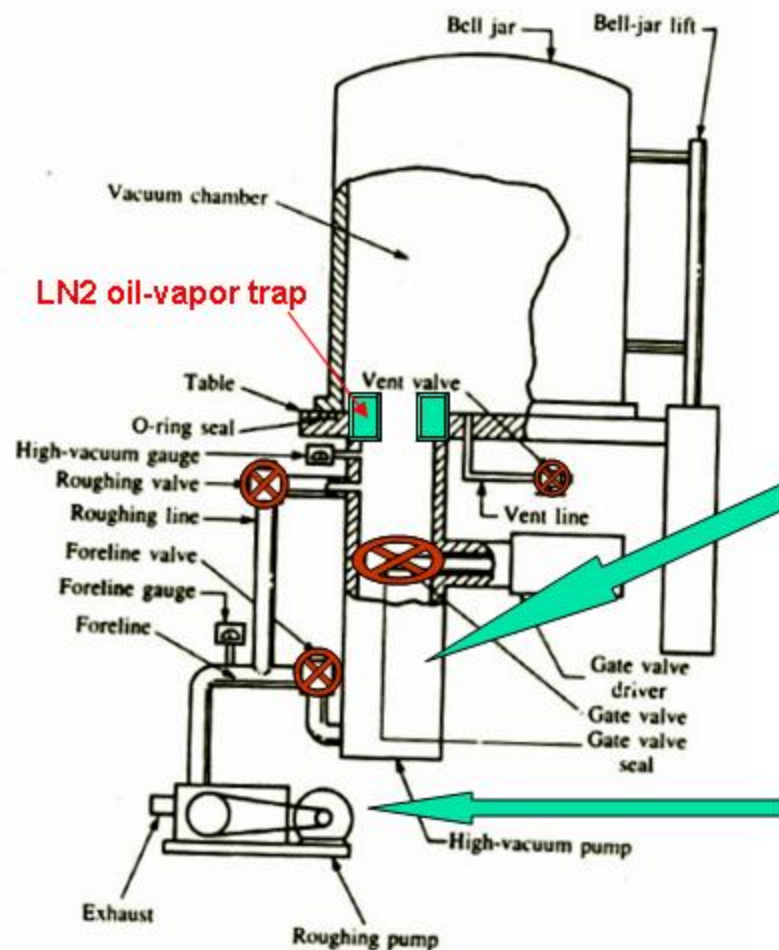
- 1) high purity of the thin film thanks to the high-vacuum environment;
- 2) no substrate damage from impinging atoms during the thin-film formation (unlike sputtering that produces some damage because of high-energy particles);
- 3) high deposition rates;
- 4) relatively small substrate heating.

Physical Vapor Deposition (PVD)

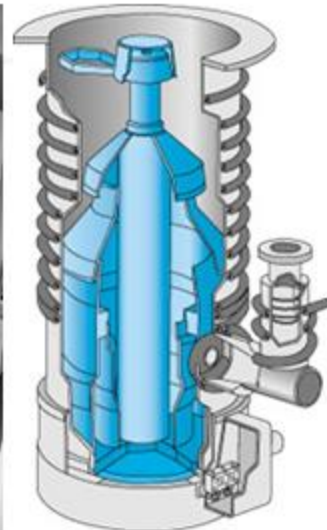
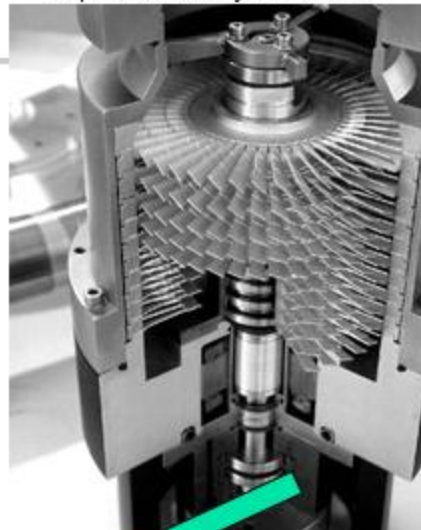


Physical Vapor Deposition

■ Vacuum Chamber



<http://www.fz-juelich.de>



Physical Vapor Deposition

■ Uniformity

$$\frac{d}{d_0} = \left(1 + \left(\frac{l}{h} \right)^2 \right)^{-1.5}$$

(point source), and

$$\frac{d}{d_0} = \left(1 + \left(\frac{l}{h} \right)^2 \right)^{-2}$$

(surface source)

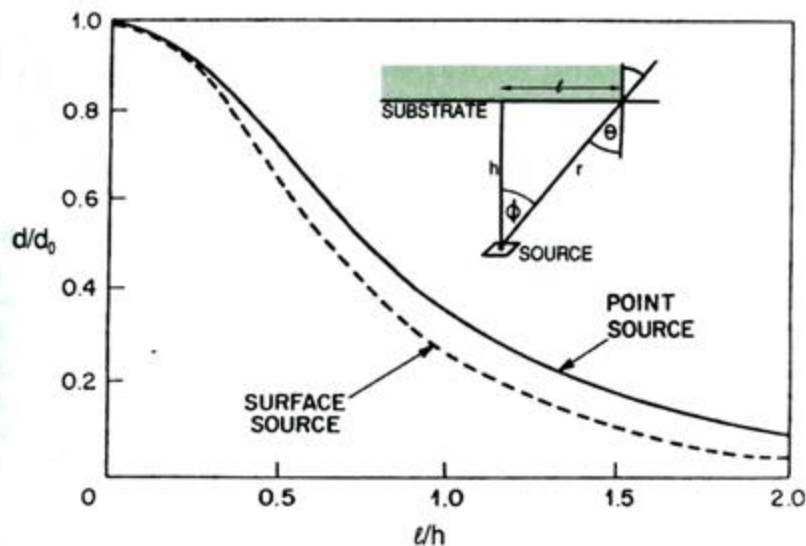
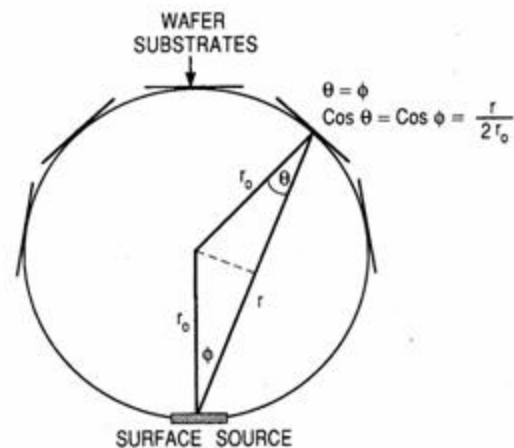


Figure 3-6 Film thickness uniformity for point and surface sources. (Insert) Geometry of evaporation onto parallel plane substrate.



Uniformity

- Lower deposition rate gives better uniformity, but increases risk for contamination in low-vacuum chambers.
- Larger distance from the source to the substrate improves uniformity, but also lowers the deposition rate.
- Rotating holder improves uniformity

Physical Vapor Deposition

Alloys

When evaporating alloys the composition changes with time of evaporation

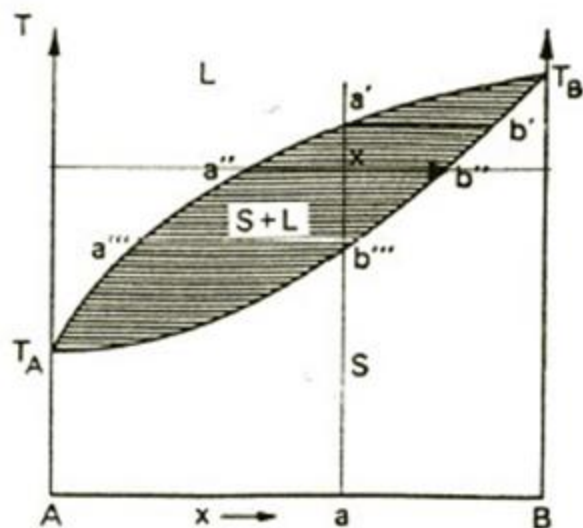


FIG. 4.6.2. Phase diagram for systems with a complete series of solid solutions ($P = \text{const.}$). Example: A = Ag, B = Au, $T_A = 960^\circ\text{C}$, $T_B = 1063^\circ\text{C}$ (from M. Hansen, see ref. on p. 100).

One can compensate for the changes

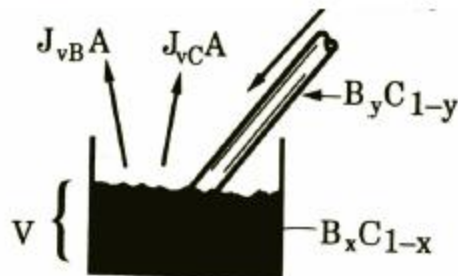
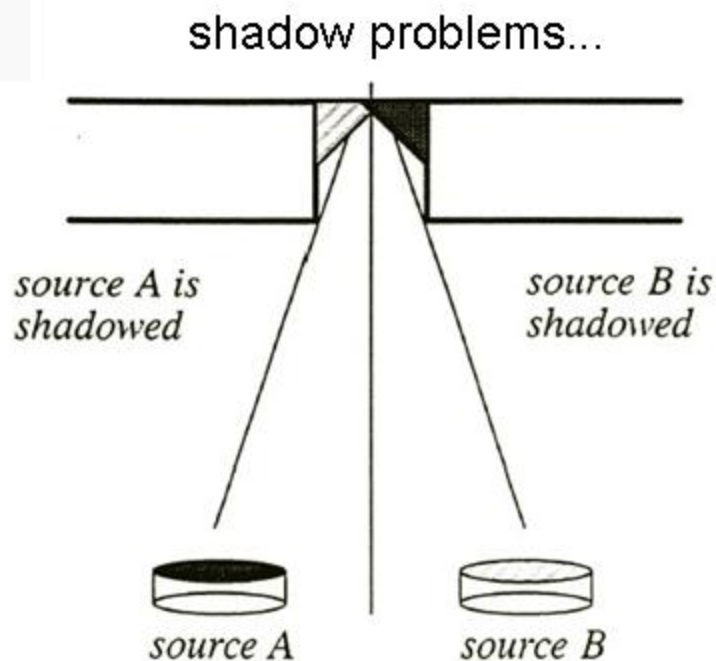
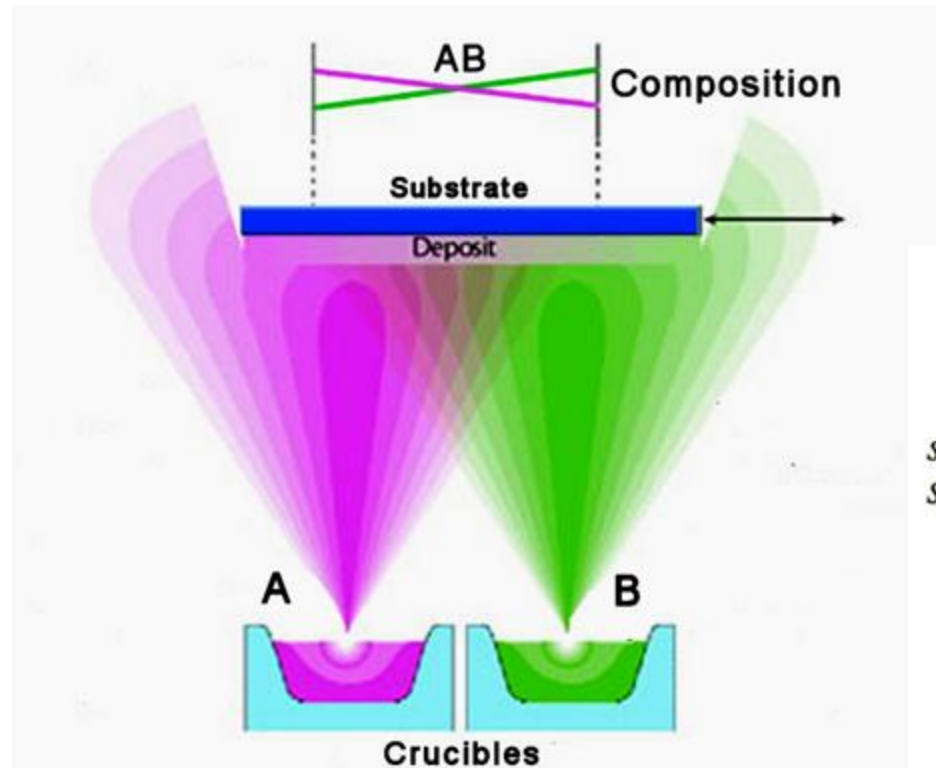


Figure 4.5 Alloy evaporation with continuous feed.

Physical Vapor Deposition

- Co-evaporation

Lateral composition change



Physical Vapor Deposition

■ Deposition Rate

- The deposition rate depends on the position and orientation of the substrate in the chamber.
- The evaporation rate Γ_e is the rate at which a material vaporizes. It can be calculated according to the equation :

$$\Gamma_e \left[\frac{\text{g}}{\text{cm}^2 \text{ s}} \right] \approx 0.06 \sqrt{\frac{M}{T}} P_v(T) [\text{Torr}]$$

where M is the molecular mass, P_v is the vapor pressure, and T is the temperature.

- A reasonable deposition rate ($0.1 \text{ mg/cm}^2 \text{ s}$) requires a vapor pressure above 10^{-2} torr.
- Refractory metals, such as W, need temperatures in excess of 3000°C to reach such a vapor pressure. Other metals, for instance Au, Ag, Cu, In, require much less heating.

Physical Vapor Deposition

■ Sources



HAIRPIN



SPIRAL

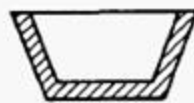


BOAT



BASKET

- Alloying of material with boat (Al-W)
- Metals can wet boat



CRUCIBLE



CRUCIBLE WITH BASKET

Possible contamination from boat or crucible

Resistive boats: refractory metals W, Ta, Mo
ceramic crucible or ceramic coating

Physical Vapor Deposition

■ E-Beam Evaporation

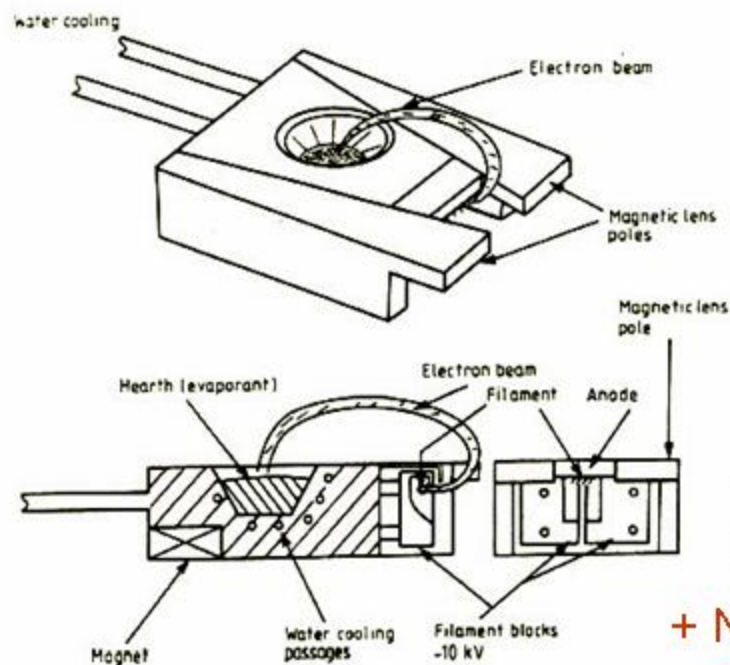
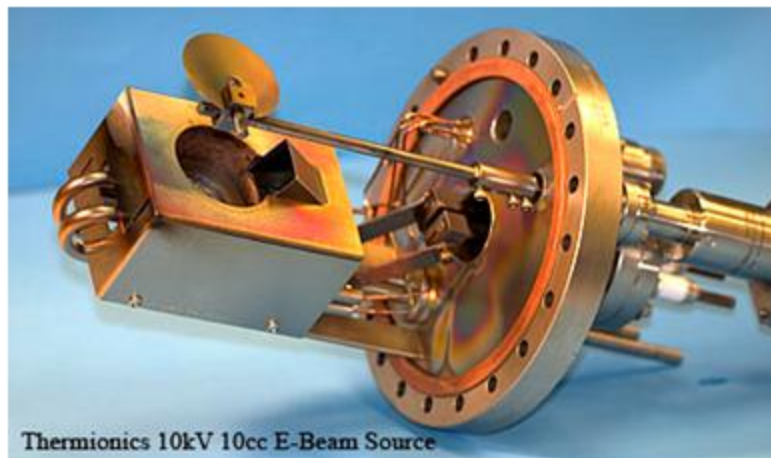


Figure A1.2.1. Electron beam heated evaporation source.



- Heat conduction of the hearth limits temperature

+ No reaction between the hearth and the evaporated material; many materials can be evaporated, like W, Mo, Al_2O_3 , SiO_2

High power density: 10 kV, 1.5A, $0.2\text{-}1\text{cm}^2 \rightarrow 15\text{-}75 \text{ kW/cm}^2$

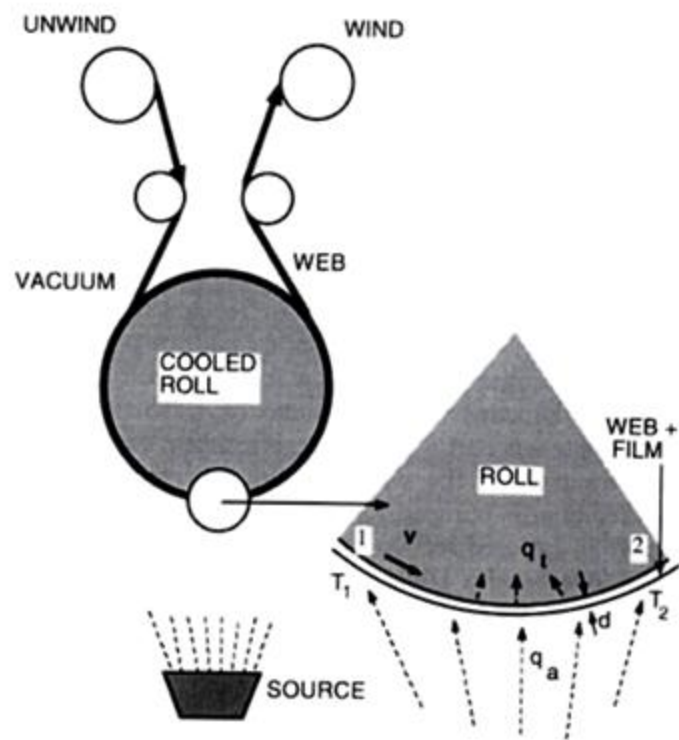
thermal conduction + evaporation + electron reflection + radiation losses

Physical Vapor Deposition

■ Web Coating

4000 miles² /year (packaging 60%)

Problems: plastic film can melt if the deposition rate (=energy flux) is too high



Clean and high-density vapor flux in e-beam PVD systems

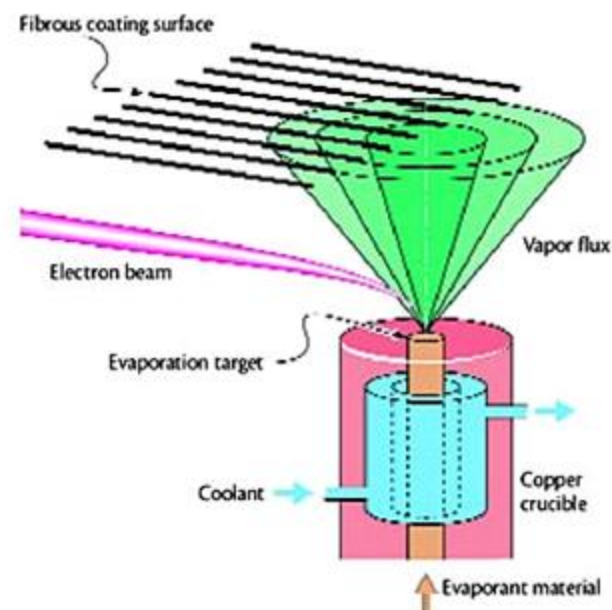
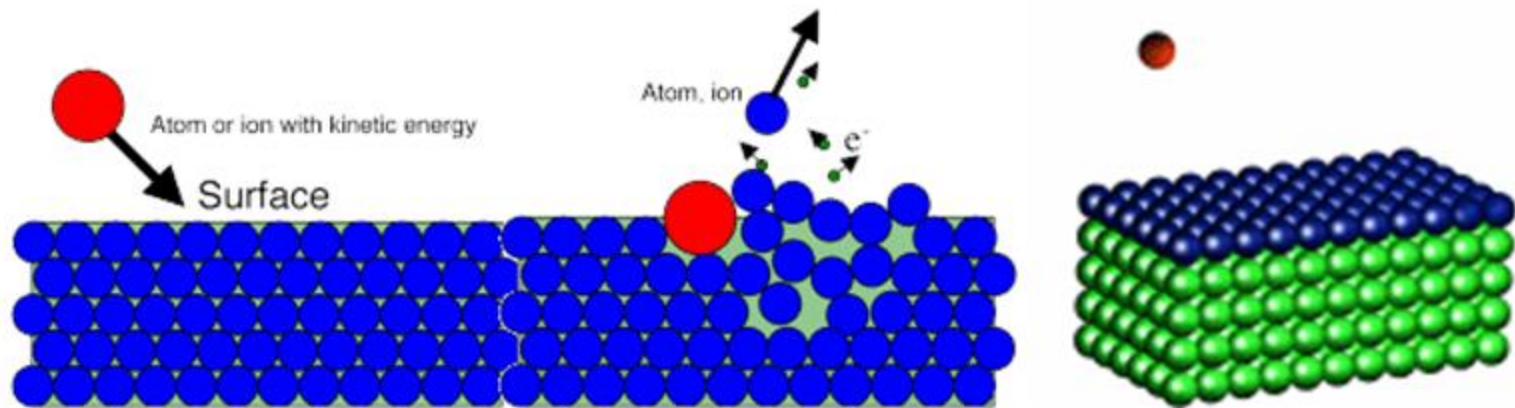


Figure 3-17 Schematic of web coating system including heat-transfer model describing web temperature.

Sputtering

- The impact of an atom or ion on a surface produces sputtering from the surface as a result of the *momentum transfer* from the in-coming particle. Unlike many other vapor phase techniques *there is no melting* of the material.



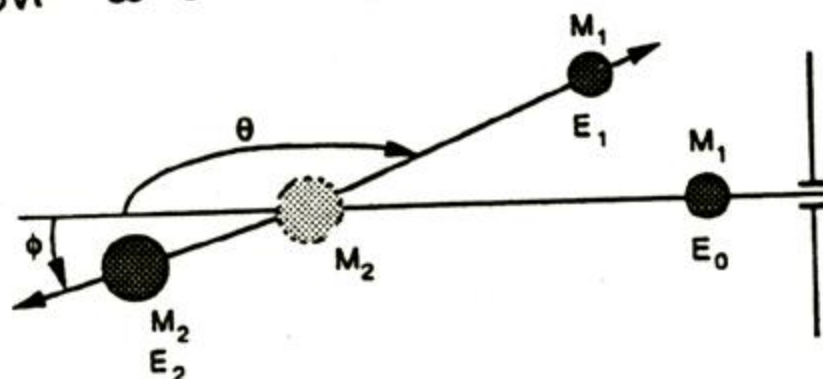
History of Sputtering

- The verb to SPUTTER originates from Latin SPUTARE (to blow one's nose).
- Grove (1852) and Plücker (1858) were first to report vaporization and film formation of metal films by sputtering.
- Key to understanding sputtering was discovery of electrons and positive ions in low pressure gas discharges and atom structure (J.J. Thomson, Rutherford), 1897--

Sputtering yield

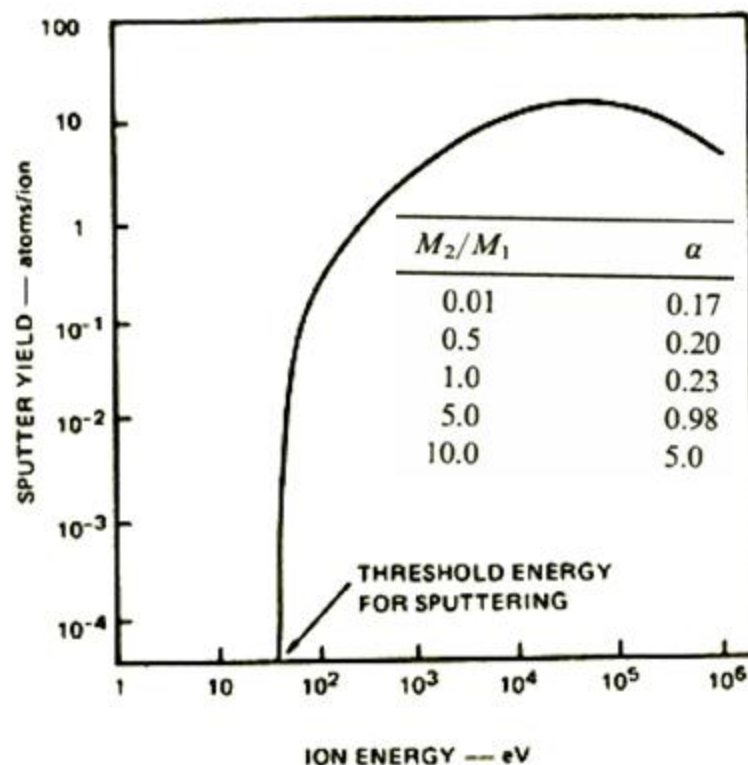
Sputtering Yield of Elements at 500 eV

Gas	He	Ne	Ar	Kr	Xe
Element					
Be	0.24	0.42	0.51	0.48	0.35
C	0.07	—	0.12	0.13	0.17
Al	0.16	0.73	1.05	0.96	0.82
Si	0.13	0.48	0.50	0.50	0.42
Ti	0.07	0.43	0.51	0.48	0.43
V	0.06	0.48	0.65	0.62	0.63
Cr	0.17	0.99	1.18	1.39	1.55
Cu	0.24	1.80	2.35	2.35	2.05
Fe	0.15	0.88	1.10	1.07	1.00
Ni	0.16	1.10	1.45	1.30	1.22
Nb	0.03	0.33	0.60	0.55	0.53
Mo	0.03	0.48	0.80	0.87	0.87
Pd	0.13	1.15	2.08	2.22	2.23
Ag	0.20	1.77	3.12	3.27	3.32
Ta	0.01	0.28	0.57	0.87	0.88
W	0.01	0.28	0.57	0.91	1.01
Re	0.01	0.37	0.87	1.25	—
Os	0.01	0.37	0.87	1.27	1.33
Ir	0.01	0.43	1.01	1.35	1.56
Pt	0.03	0.63	1.40	1.82	1.93
Au	0.07	1.08	2.40	3.06	3.01
Au	0.10	1.3	2.5	—	7.7
Pb	1.1	—	2.7	—	—



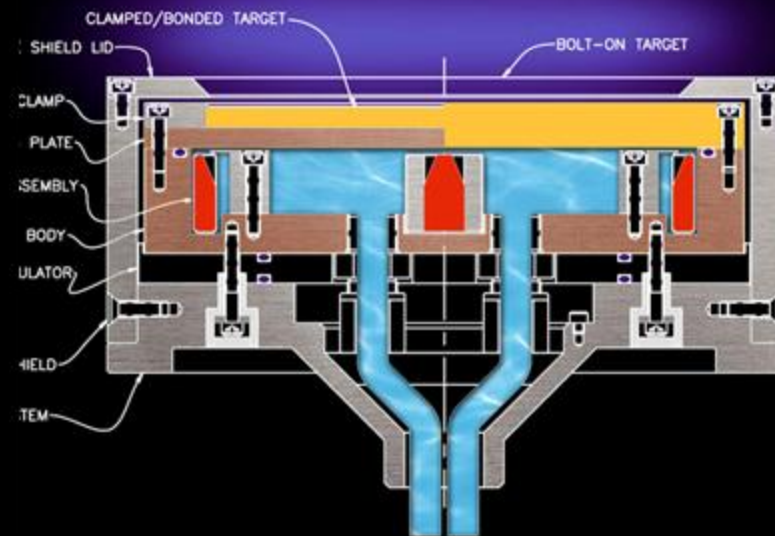
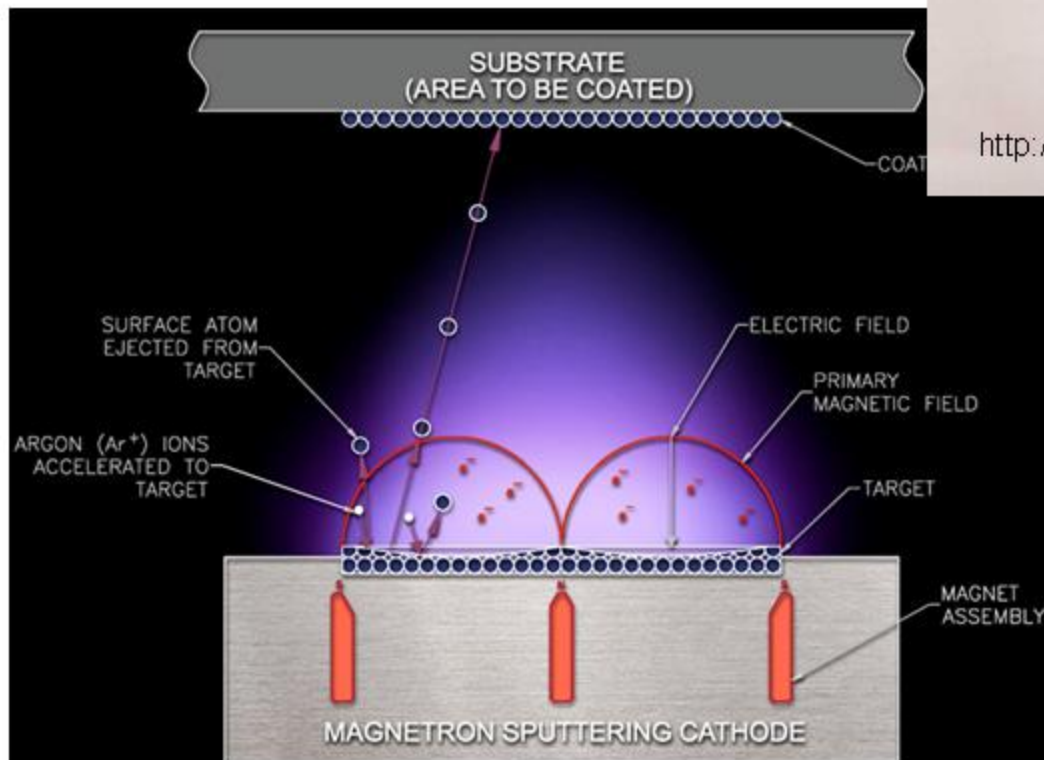
$$S(E) = \frac{3}{4\pi^2} \alpha \frac{4M_1M_2}{(M_1 + M_2)^2} \frac{E}{U_0}$$

$E < 1\text{keV}$; U_0 = binding energy



Sputtering

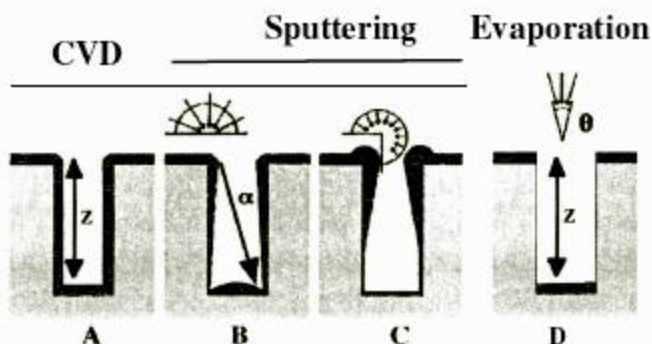
Magnetron sputtering



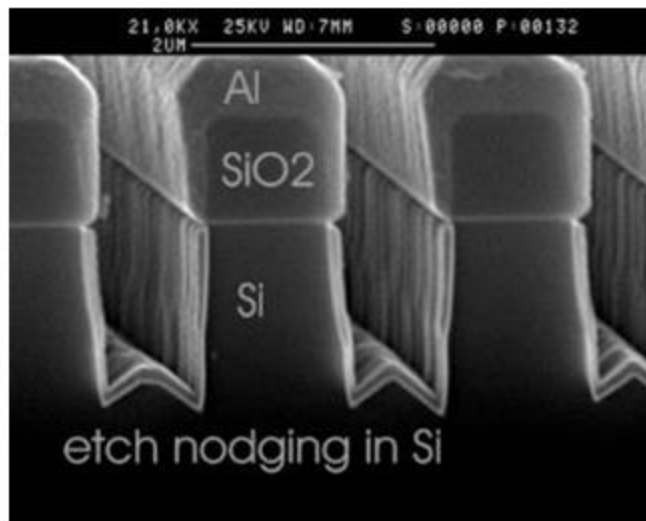
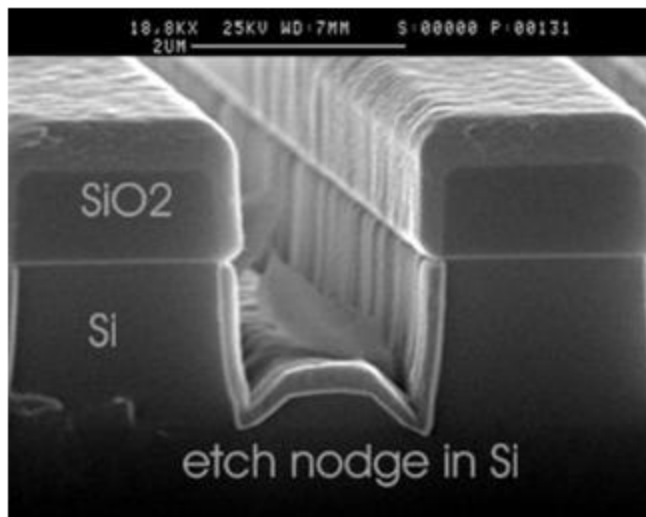
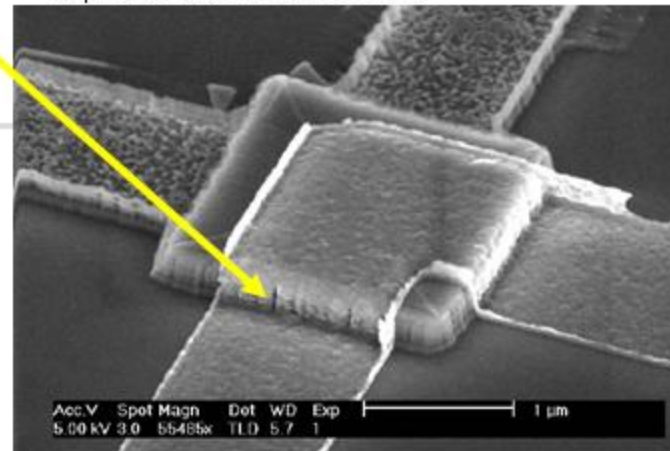
Sputtering

important that the film
is continuous at the step

■ Step coverage



<http://www.dimes.tudelft.nl/>





Sputtering

Pros:

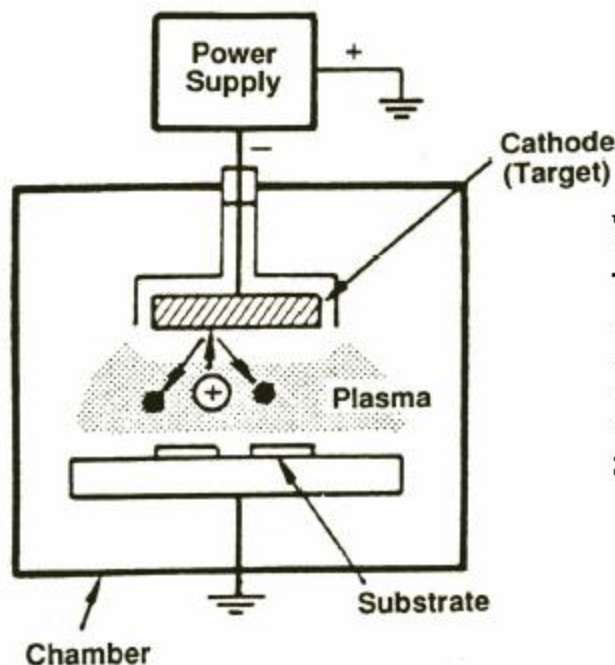
- Good coating and step coverage
- Preserves stoichiometry of multi-component compounds
- Good adhesion
- Majority of materials, ceramics, and refractory metals

Cons:

- Relatively low deposition rates
- Substrate heating
- Targets wear out non-uniformly → costs
- Gas atoms may be incorporated in film

Sputtering systems

DC glow discharge



Cons: limited to conductive materials

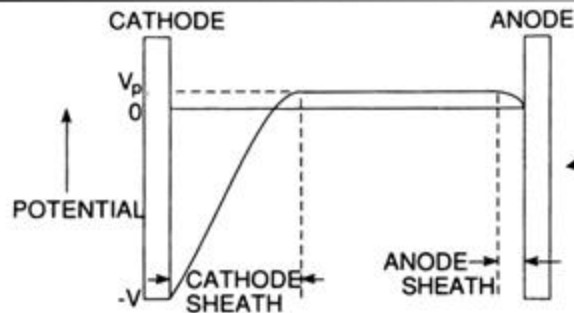
$V_{dc} \sim 500-5000 \text{ V}$; $P \sim 20-100 \text{ mTorr}$;
To increase the deposition rate one should increase P , but after a certain threshold the rate decreases due to scattering upon gas atoms or molecules

Figure A3.0.1. Schematic of a dc glow discharge sputtering system.

Sputtering systems

RF sputtering

Pros: not limited to conductive materials



- Negative self-bias due to mobility difference
- Higher ionization level; electrons stay longer in plasma

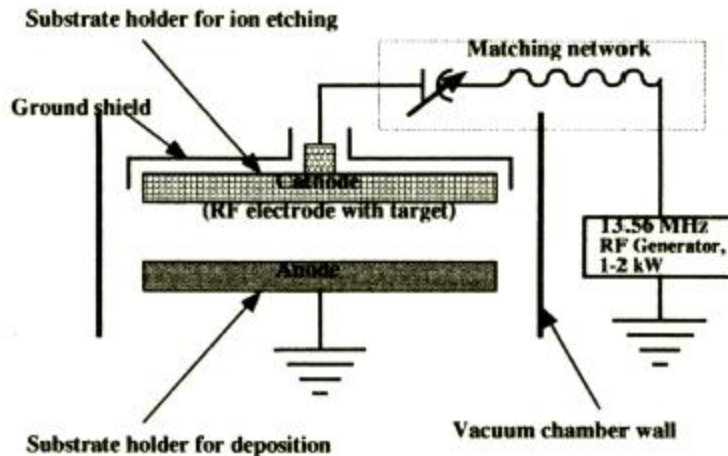


FIGURE 2.8 Two electrode set-up (diode) for RF ion sputtering or sputter deposition. For ion sputtering, the substrates are put on the cathode (target); for sputter deposition, the substrates to be coated are put on the anode.

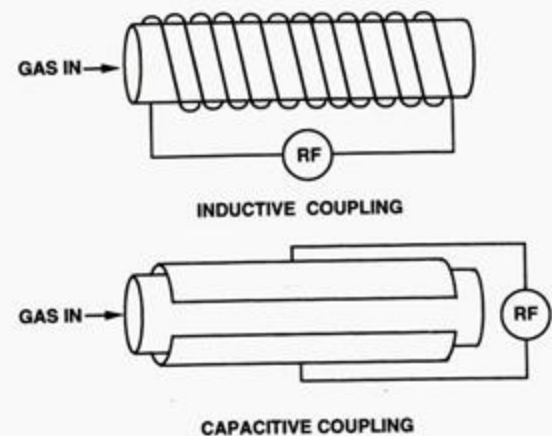
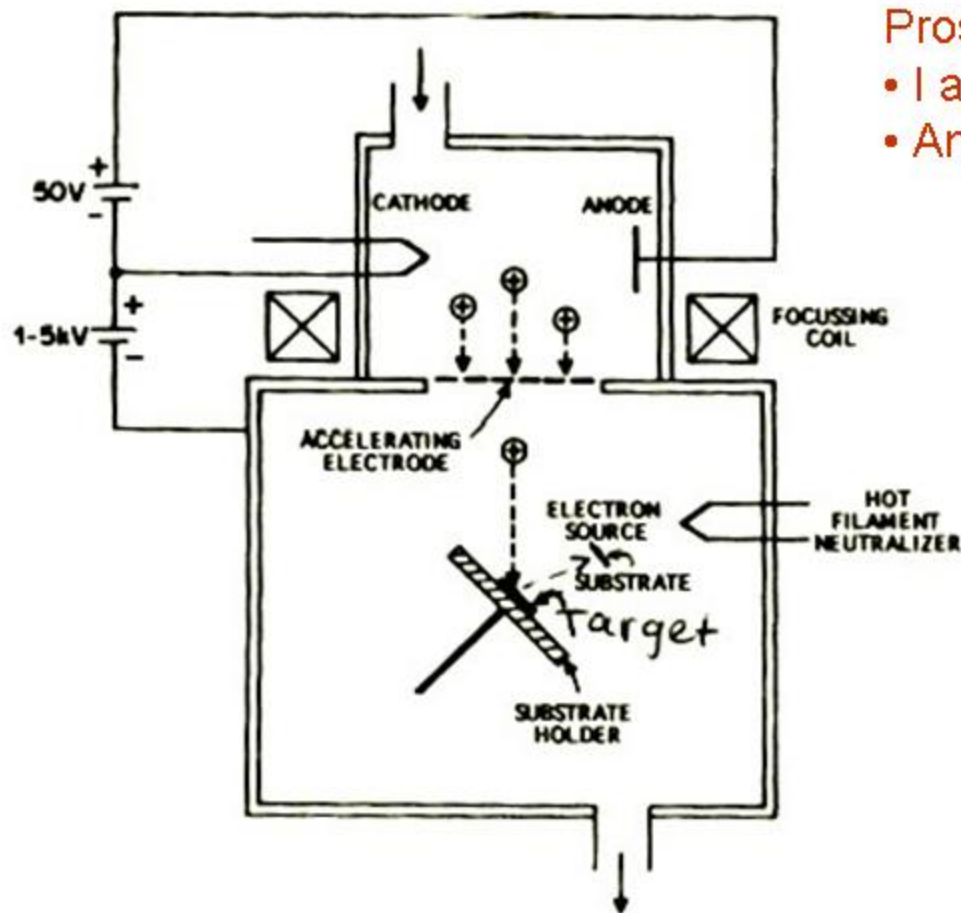


Figure 4-5 Inductively and capacitively coupled tubular RF plasma reactors.

Sputtering systems

Ion-Beam Sputtering



Pros:

- I and V controlled independently
- Angle of incidence can be changed

Pulsed-Laser Deposition

1 J/pulse; 3-5 J/cm²

several targets → many-component materials
tailor-made properties

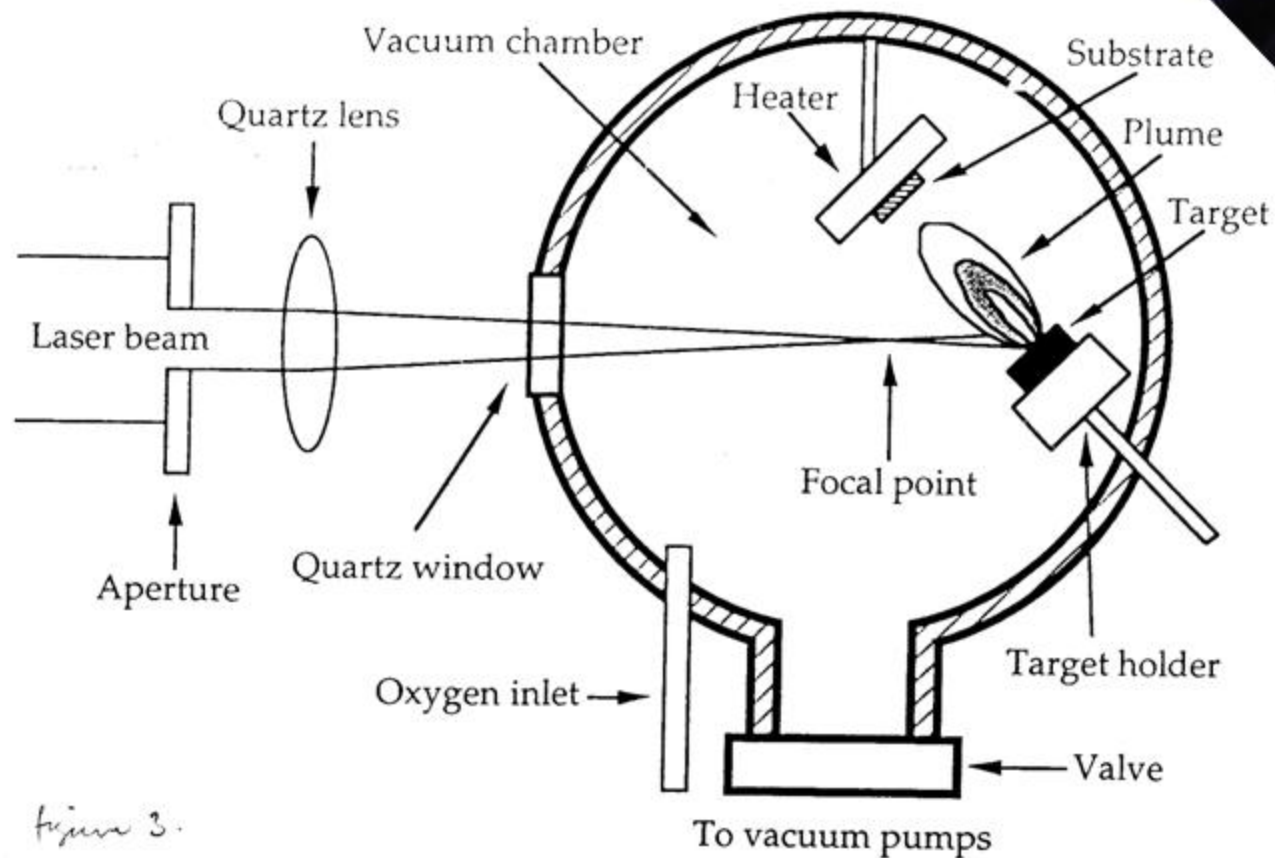
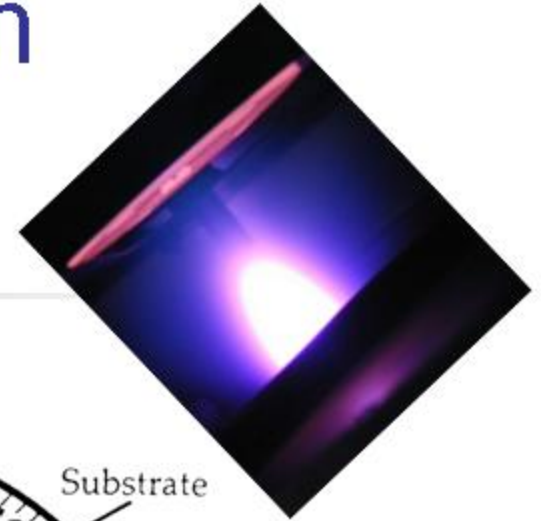
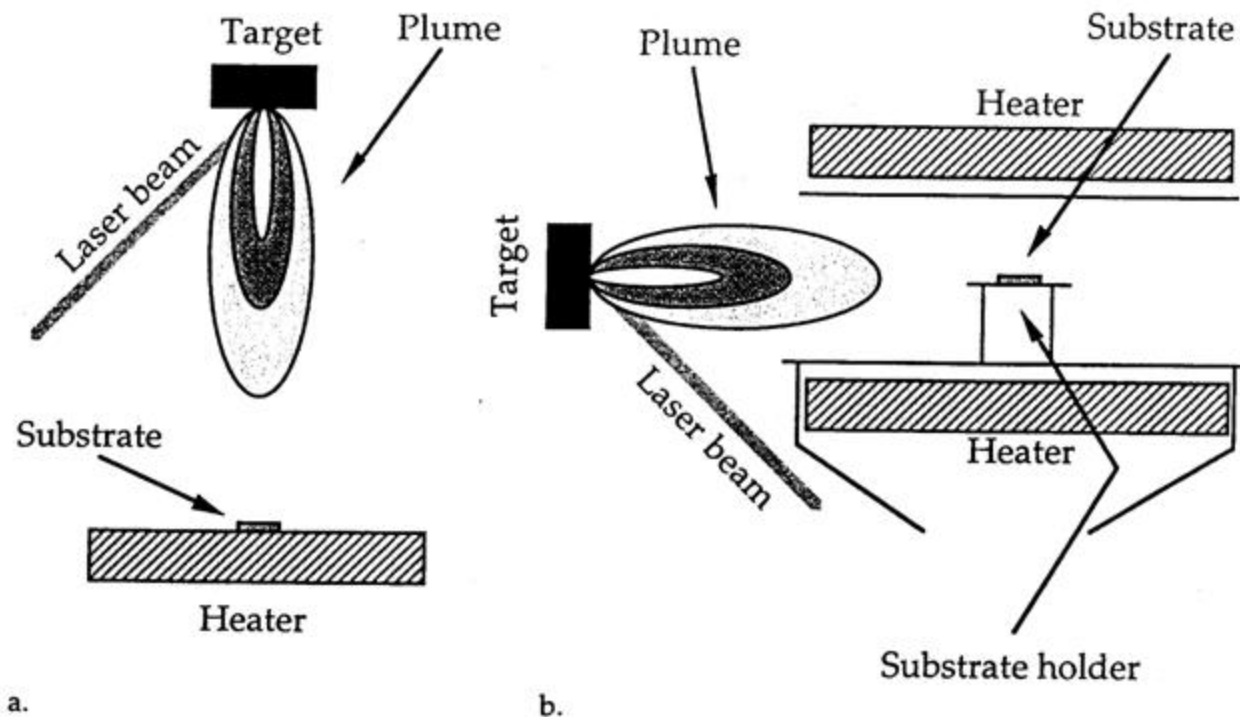


figure 3.

Pulsed-Laser Deposition



on-axis
+ stoichiometry
- particles

off-axis
+ less particles
- stoichiometry

Pulsed-Laser Deposition



- MC2- PLD "Twin" system

- MC2- PLD "Calas" system



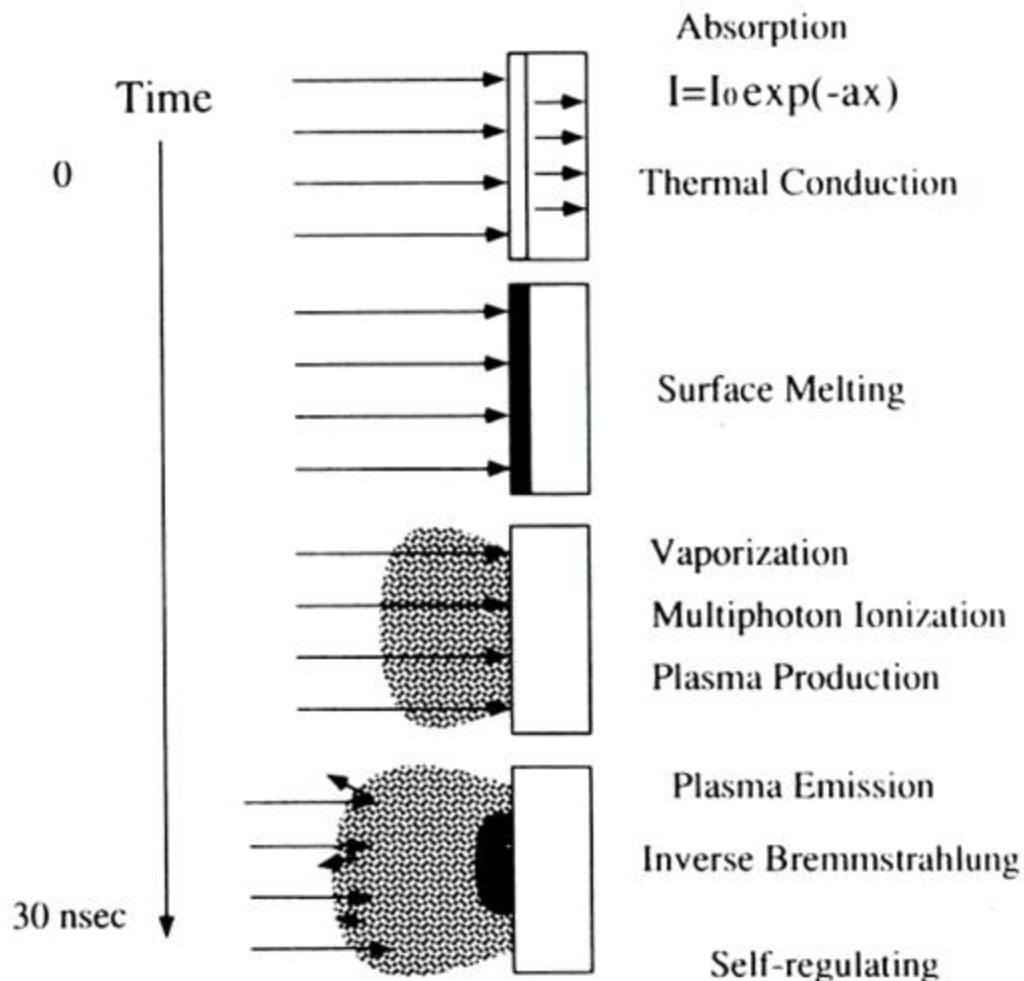
Pulsed-Laser Deposition

Ceramic Films Deposited by Pulsed Laser Methods

Property	Applications	Materials
High-temperature superconductivity	Microwave filters and delay lines, digital electronics, sensors	$\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Ti}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$
Ferroelectricity	DRAM capacitors, nonvolatile RAMS, optoelectronics, microwave devices	$\text{Pb}(\text{Zr})\text{TiO}_3$, $(\text{Sr}, \text{Ba})\text{TiO}_3$, $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$, LiNbO_3
Ferrimagnetism	Circulators, phase shifters, magnetic recording, antennas	$\text{BaFe}_{12}\text{O}_{19}$, $\text{Y}_3\text{Fe}_5\text{O}_{12}$, $(\text{Mn}, \text{Zn})\text{Fe}_2\text{O}_4$, Li_2FeO_4
Electrochromic effects	Optical modulators, sunroofs, sensor protection	WO_3 , MoO_3 , V_2O_5
Electro-optical effects	Transparent conductors, solar energy, photovoltaics	F-doped ZnO_2 , $\text{In}_2\text{O}_3/\text{SnO}_2$, $(\text{La}, \text{Sr})\text{CoO}_3$
Piezoelectricity	Microelectrical-mechanical (MEM) devices	$\text{Pb}(\text{Zr})\text{TiO}_3$
Giant magnetoresistance	Magnetic recording head field sensors	$(\text{La}, \text{Ca})\text{MnO}_3$
Thermal and corrosive stability	Oxidation and thermal protection coatings for turbine blades	Y-ZrO_2 , MgAl_2O_4
Friction and wear	Hard, low-friction, wear-resistant coatings	MoS_2 , BN , SiC , diamond-like carbon
Biocompatibility	Prostheses, hip/knee implants	Hydroxylapatite, Al_2O_3

From D. B. Crissey, J. S. Horwitz, P. C. Dorsey, and J. M. Pond, *Laser Focus World*, p. 155, May (1995).

Pulsed-Laser Ablation



Pulsed-Laser Ablation

Laser ablation with conventional lasers (Nd:Yag, CO2...):

- The laser pulses are absorbed if their wavelength is coupled with the material.
- The absorbed energy is transferred into heat
- The heat vaporizes the material and there is local ablation

Cons: The quality of ablation depends strongly on the laser wavelength.

Femtosecond laser:

- The photon density is so high at focus that a single electron can absorb several photons
- The absorbed photons allow electrons to reach the ionization-energy levels
- The ejected electrons hit other atoms, and amplify ionization
- All the energy is evacuated with the electrons and a cold plasma remains at the machined spot
- The cold plasma expands from the sample

All this happens in a few femtoseconds.

There is no time for heat to propagate over more than a few nanometers.

Pros for machining:

- No thermal damage:** High machining quality, heat sensitive material machining
- High accuracy:** down to 100nm
- No wavelength dependence:** any material can be ablated