Thin Film Deposition

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 kÅ/s	Low	Moderate	Moderate, 2.5 kÅ/s
Species	Atoms & ions	Atoms & ions	Atoms, ions & clusters	molecules →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

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2} = \frac{k_B T}{\sqrt{2}\pi P d^2},$$

d : molecular diameter,

n : concentration of the gas,

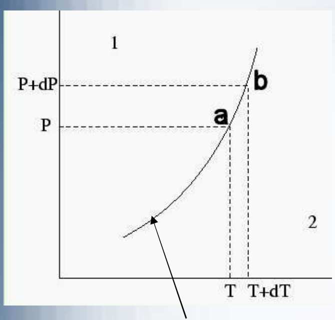
P : pressure, T : temperature

Have a good vacuum !

P (mbar)	λ (cm)	Collisions (1/s)	Impinging flux (1/cm^{2}s)	Monolayer /s
1	$7\cdot10^{-3}$	$7\cdot10^{6}$	$3\cdot10^{20}$	$3\cdot10^{5}$
10^{-3}	$7\cdot10^{0}$	$7\cdot10^{3}$	$3\cdot10^{17}$	$3\cdot10^{2}$
10^{-6}	$7\cdot10^{3}$	$7\cdot10^{0}$	$3\cdot10^{14}$	$3\cdot10^{-1}$
10^{-9}	$7\cdot10^{6}$	$7\cdot10^{-3}$	$3\cdot10^{11}$	$3\cdot10^{-4}$

Fundamentals of Film Deposition

- Thermodynamics



$g1 = g2$

Thermodynamic Gibbs potential G,

$dG = -SdT + VdP$

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

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

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

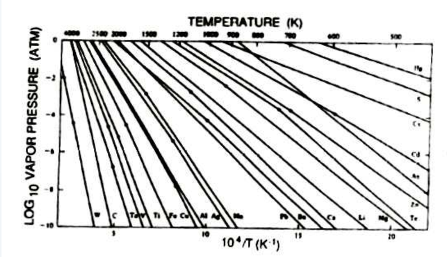
q : specific heat of evaporation

Fundamentals of Film Deposition

- Thermodynamics

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

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



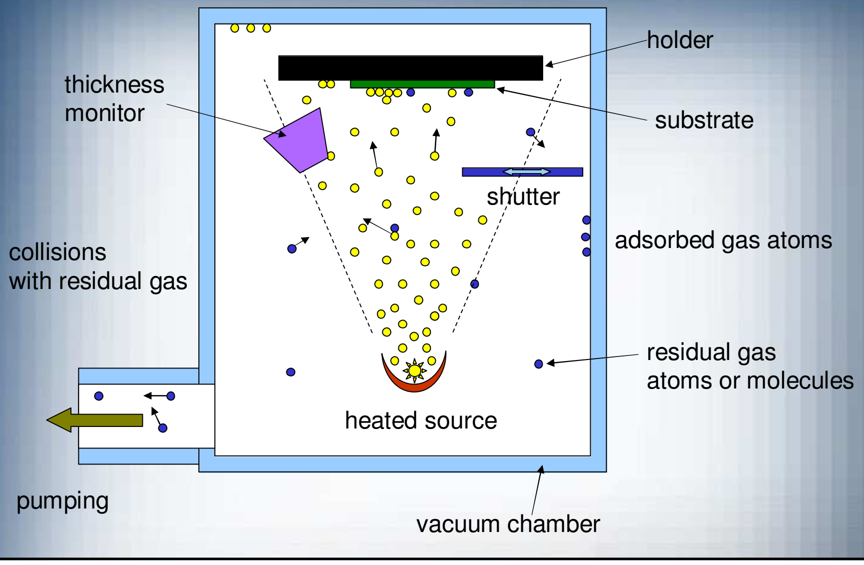
Vapor pressures of selected elements

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.

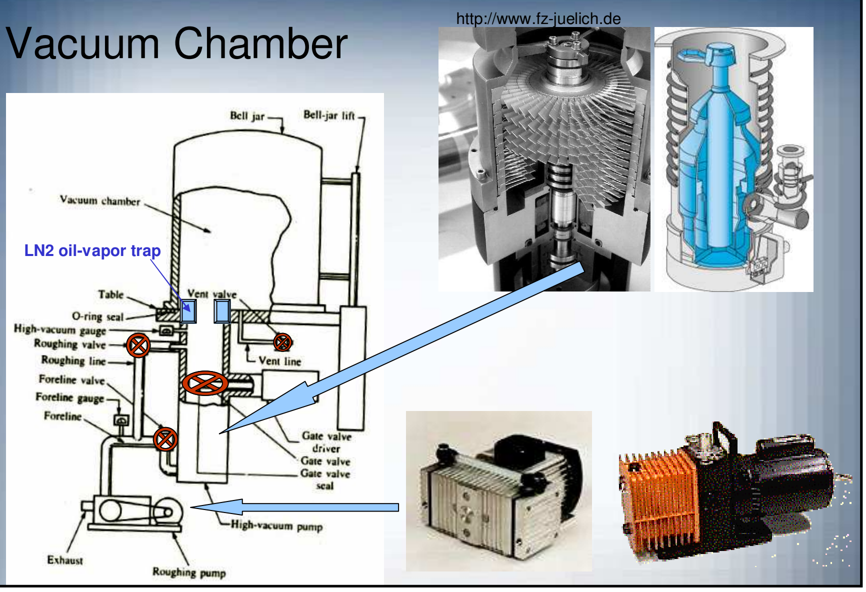
The *advantages* of PVD by evaporation are:
1) high purity of the thin film thanks to the high-vacuum environment;
2) no substrate damage from impinging atoms during the thin-film formation (unlike sputtering that produces some damage because of high-energy particles);
3) high deposition rates;
4) relatively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

Physical Vapor Deposition



Physical Vapor Deposition

- Vacuum Chamber



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)

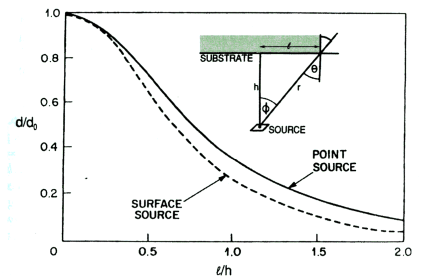


Figure 3-6 Film thickness uniformity for point and surface sources. (Insert) Geometry of evaporation onto parallel plane substrate.

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

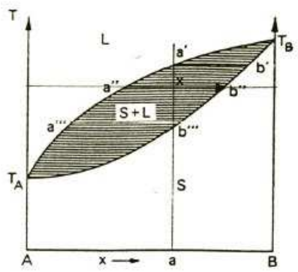


Fig. 4.6.2. Phase diagram for systems with a complete series of solid solutions (P = const.). Example: A = Ag, B = Au, T_A = 960°C, T_B = 1063°C (from M. Hansen, see ref. on p. 100).

One can compensate for the changes

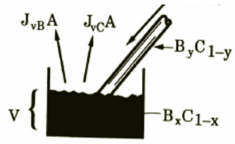
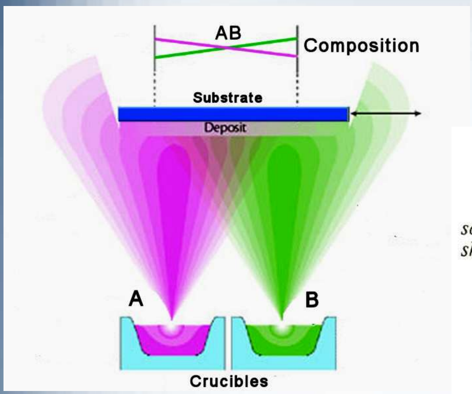


Figure 4.5 Alloy evaporation with continuous feed.

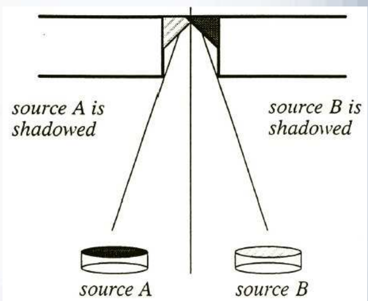
Physical Vapor Deposition

- Co-evaporation

Lateral composition change



shadow problems...



Physical Vapor Deposition

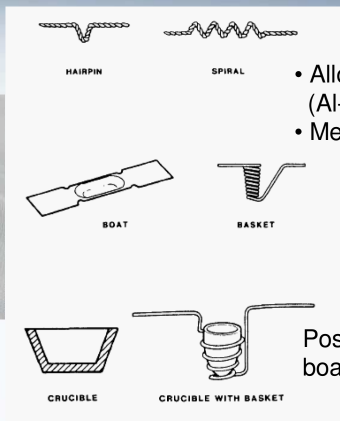
- Deposition Rate
  - The deposition rate depends on the position and orientation of the substrate in the chamber.
  - The evaporation rate Γ_e is the rate at which a material vaporizes. It can be calculated according to the equation :

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

  where M is the molecular mass, Pv is the vapor pressure, and T is the temperature.
  - A reasonable deposition rate (0.1 mg/cm^2 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



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

Possible contamination from boat or crucible

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

Physical Vapor Deposition

- E-Beam Evaporation

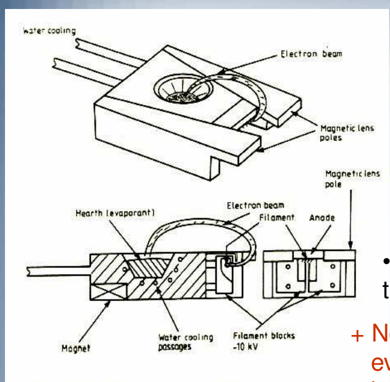
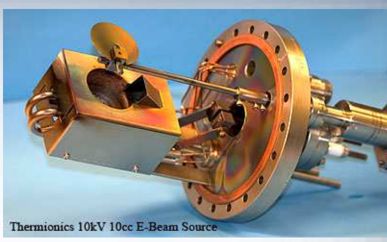


Figure A1.2.1. Electron beam heated evaporation source.



Thermionics 10kV 10cc E-Beam 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, 0.2-1cm^2 → 15-75 kW/cm^2

thermal conduction + evaporation + electron reflection + radiation losses

Physical Vapor Deposition

- Web Coating

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

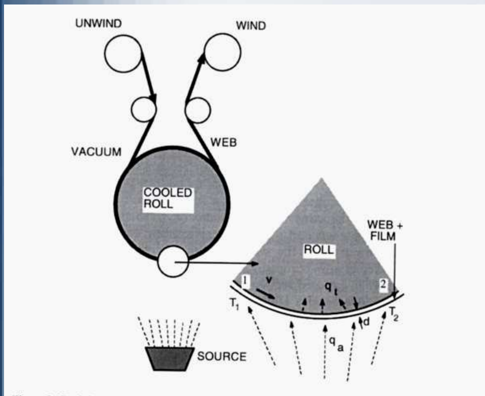
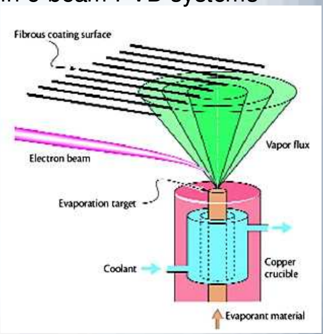


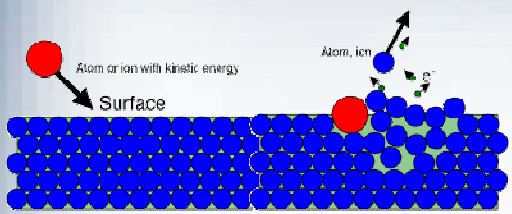
Figure 3-17 Schematic of web coating system including heat-transfer model describing web temperature.

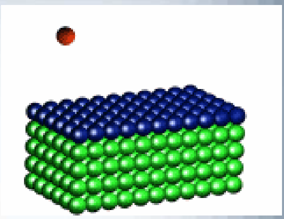
Clean and high-density vapor flux in e-beam PVD systems



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.



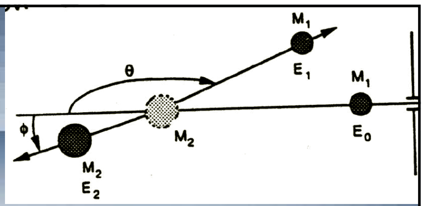


History of Sputtering

- The verb to SPUTTER originates from Latin SPUTARE (to blow one´s noise).
- 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--

http://www.gencoa.com/tech/whatsputtering.html

Sputtering yield

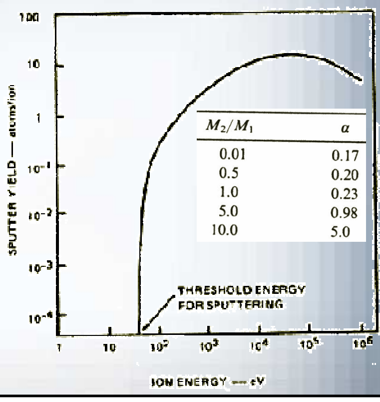


Sputtering Yield of Elements at 500 eV

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	—	—

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

$E < 1$keV; U_0 =binding energy

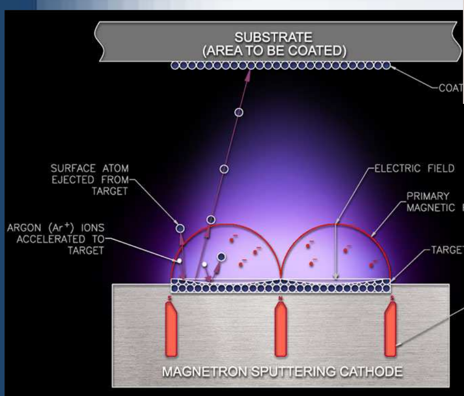


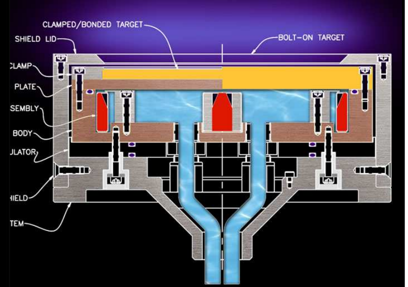
M_2/M_1	α
0.01	0.17
0.5	0.20
1.0	0.23
5.0	0.98
10.0	5.0

Sputtering

Magnetron sputtering

http://www.msi-pse.com/



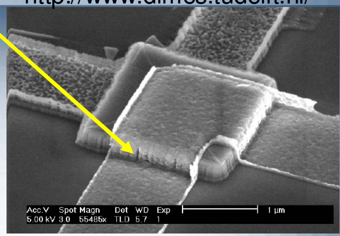


http://www.angstromsciences.com/technology/sputtering.htm

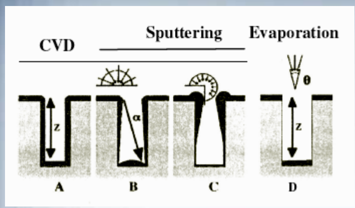
Sputtering

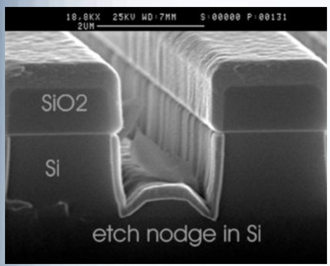
important that the film
is continuous at the step

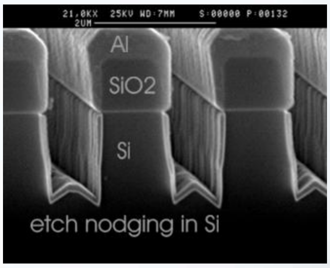
http://www.dimes.tudelft.nl/



- Step coverage







www.oxfordplasma.com

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

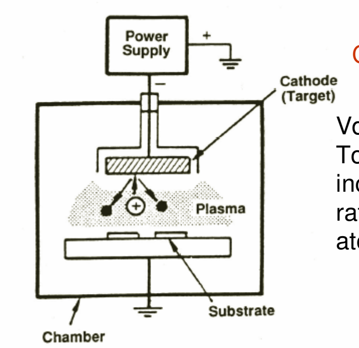


Figure A3.0.1. Schematic of a dc glow discharge sputtering system.

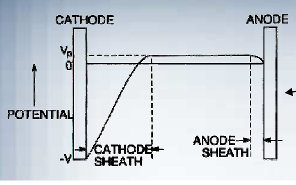
Cons: limited to conductive materials

Vdc ~ 500-5000 V; P ~20-100 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

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

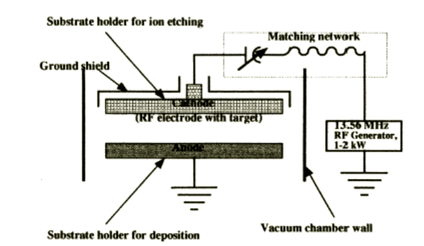


FIGURE 2.8 Two electrode set-up (diode) for RF ion sputtering or sputter deposition. For ion sputtering, the substrates are put on the cathode (target); for sputter deposition, the substrates to be coated are put on the anode.

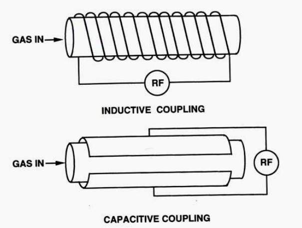
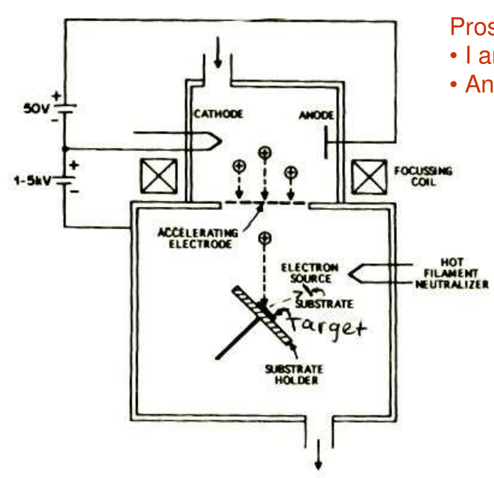


Figure 4-5 Inductively and capacitively coupled tubular RF plasma reactors.

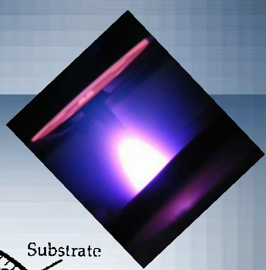
Sputtering systems

Ion-Beam Sputtering

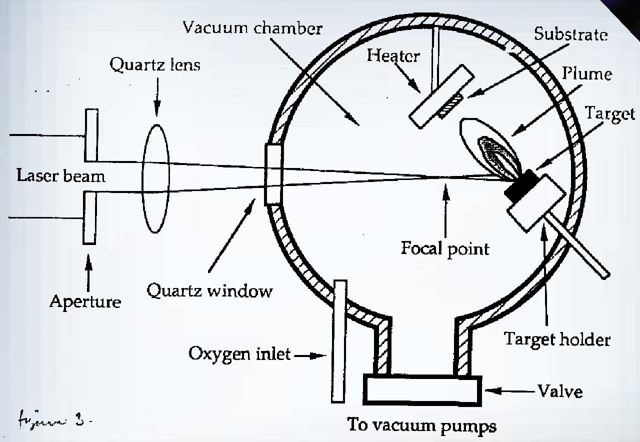


Pros:
- I and V controlled independently
- Angle of incidence can be changed

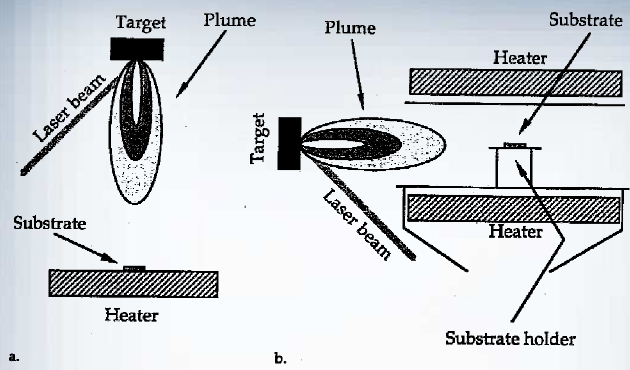
Pulsed-Laser Deposition



1 J/pulse; 3-5 J/cm^2
several targets → many-component materials
tailor-made properties



Pulsed-Laser Deposition

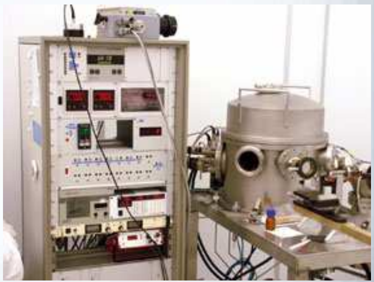


on-axis
+ stoichiometry
- particles

off-axis
+ less particles
- stoichiometry

Pulsed-Laser Deposition

- MC2- PLD "Twin" system



- MC2- PLD "Calas" system

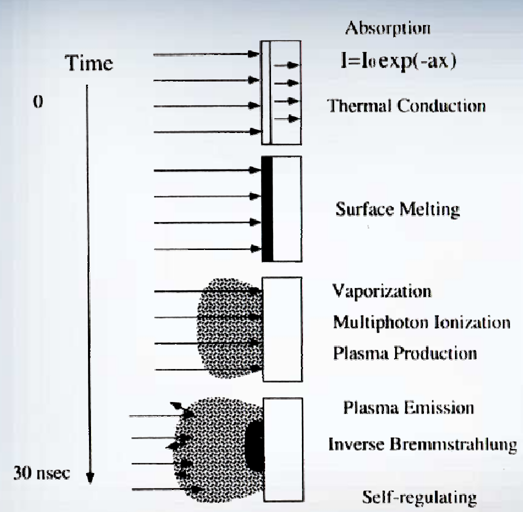
Pulsed-Laser Deposition

Ceramic Films Deposited by Pulsed Laser Methods

Property	Applications	Materials
High-temperature superconductivity	Microwave filters and delay lines, digital electronics, sensors	$YBa_2Cu_3O_7$, $Tl_2Ca_2Sr_2Cu_3O_x$, $Nd_{1.85}Ce_{0.15}CuO_4$
Ferroelectricity	DRAM capacitors, nonvolatile RAMS, optoelectronics, microwave devices	$Pb(Zr)TiO_3$, $(Sr, Ba)TiO_3$, $(Sr, Ba)Nb_2O_6$, $LiNbO_3$
Ferrimagnetism	Circulators, phase shifters, magnetic recording, antennas	$BaFe_{12}O_{19}$, $Y_3Fe_5O_{12}$, $(Mn, Zn)Fe_2O_4$, 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, In_2O_3/SnO_2, $(La, Sr)CoO_3$
Piezoelectricity	Microelectrical-mechanical (MEM) devices	$Pb(Zr)TiO_3$
Giant magnetoresistance	Magnetic recording head field sensors	$(La, Ca)MnO_3$
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



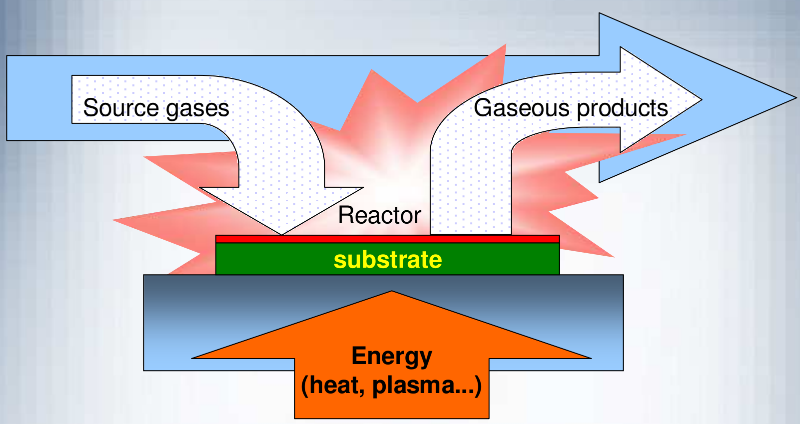
Pulsed-Laser Ablation

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

Chemical Vapor Deposition (CVD)



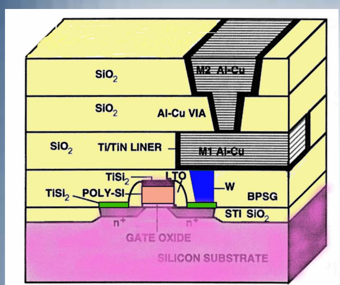
CVD

CVD is used to grow a thin layer of advanced materials on the surface of a substrate

Applications:

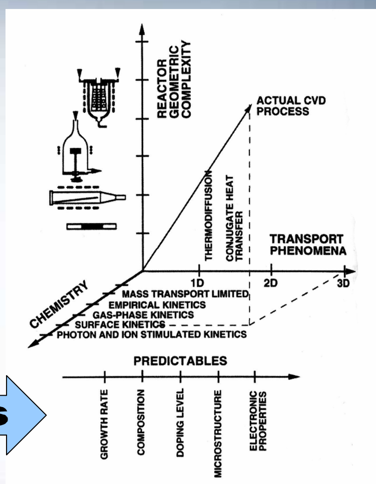
- **integrated circuits, optoelectronic devices and sensors**
- **catalysts**
- **micromachines, and fine metal and ceramic powders protective coatings**

CVD monopolizes the thin film deposition



MOS transistor structure

despite difficulties



CVD Reaction Types

- Pyrolysis
- Reduction
- Oxidation
- Compound formation
- Disproportionation
- Reversible transfer

Pyrolysis

chemical decomposition or change induced by heat

Silane   amorphous

$$SiH_{4(g)} \rightarrow Si_{(s)} + 2H_{2(g)} \quad (650^{\circ}C)$$

$$Ni(CO)_{4(g)} \rightarrow Ni_{(s)} + 4CO_{(g)} \quad (180^{\circ}C)$$

Ni carbonyl

Reduction

any process in which electrons are added to an atom or ion (as by removing oxygen or adding hydrogen); always occurs accompanied by oxidation of the reducing agent

epitaxial

$$SiCl_{4(g)} + 2H_{2(g)} \rightarrow Si_{(s)} + 4HCl_{(g)} \quad (1200^{\circ}C)$$

$$WF_{6(g)} + 3H_{2(g)} \rightarrow W_{(s)} + 6HF_{(g)} \quad (300^{\circ}C)$$

$$MoF_{6(g)} + 3H_{2(g)} \rightarrow Mo_{(s)} + 6HF_{(g)} \quad (300^{\circ}C)$$

In cooking, reduction is the process of thickening a sauce by evaporation.

Oxidation

is any electrochemical process which involves the formal oxidation state of an atom or atoms (within a molecule) being increased by the removal of electrons. E.g. iron(II) can be oxidized to iron(III):

Silane

$$SiH_{4(g)} + O_{2(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)} \quad (450^{\circ}C)$$

$$SiH_{4(g)} + 2H_{2(g)} + O_{2(g)} \rightarrow$$

soot

$$\rightarrow SiO_{2(s)} + 4HCl_{(g)} \quad (1500^{\circ}C)$$

$$2AlCl_{3(g)} + 3H_{2(g)} + 3CO_{2(g)} \rightarrow$$

$$\rightarrow Al_2O_{3(s)} + 3CO_{(g)} + 6HCl_{(g)} \quad (1000^{\circ}C)$$

Thermal CVD Films

Thermal CVD Films and Coatings

Deposited material	Substrate	Input reactants	Deposition temperature (°C)
Si	Single-crystal Si	$SiCl_2H_2$, $SiCl_3H$, or $SiCl_4 + H_2$	1050–1200
Si		$SiH_4 + H_2$	600–700
Ge	Single-crystal Ge	$GeCl_4$ or $GeH_4 + H_2$	600–900
GaAs	Single-crystal GaAs	$(CH_3)_3Ga + AsH_3$	650–750
InP	Single-crystal InP	$(CH_3)_3In + PH_3$	725
SiC	Single-crystal Si	$SiCl_4$, toluene, H_2	1100
AlN	Sapphire	$AlCl_3$, NH_3, H_2	1000
In_2O_3:Sn	Glass	In-chelate, $(C_4H_9)_2Sn(OOCH_3)_2$, H_2O, O_2, H_2	500
ZnS	GaAs, GaP	Zn, H_2S, H_2	825
CdS	GaAs, sapphire	Cd, H_2S, H_2	690
Al_2O_3	Si, cemented carbide	$Al(CH_3)_3 + O_2$, $AlCl_3$, CO_2, H_2	275–475 850–1100
SiO_2	Si	$SiH_4 + O_2$, $SiCl_2H_2 + N_2O$	450
Si_3N_4	SiO_2	$SiCl_2H_2 + NH_3$	750
TiO_2	Quartz	$Ti(OC_2H_5)_4 + O_2$	450
TiC	Steel	$TiCl_4$, CH_4, H_2	1000
TiN	Steel	$TiCl_4$, N_2, H_2	1000
BN	Steel	BCl_3, NH_3, H_2	1000
TiB_2	Steel	$TiCl_4$, BCl_3, H_2	>800

Note: E = epitaxial; P = polycrystalline; A = amorphous.
Adapted from Refs. 1, 2, 3.

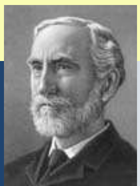
Thermodynamics of CVD

implies that the chemical equilibrium is attained; may not be true for flow reactors!

Chemical Reactions

enthalpy — entropy

- The Gibbs free-energy function G: $G = H - TS$, and $\Delta G = \Delta H - T\Delta S$
- 2[nd] Law of Thermodynamics: spontaneous reactions occur at P, T = const if $\Delta G < 0$



(Gibbs, J. W.)
(1839 - 1903)

- Thermal effect of a reaction only depends on initial and final states and does not depend on intermediate processes (Hess, 1840)

(Hess, H.I.)
(1802 - 1850)

$2C + H_2 = C_2H_2 + ?$ does not normally occur

exothermic:

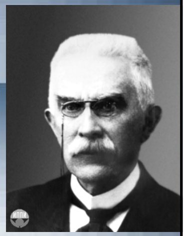
$2C + 2O_2 = 2CO_2 + 800\ \text{kJ}$; + $H_2 + \frac{1}{2}O_2 = H_2O + 240\ \text{kJ}$

\- $C_2H_2 + \frac{5}{2}O_2 = 2CO_2 + H_2O + 1300\ \text{kJ}$

endothermic:

= $2C + H_2 = C_2H_2 - 260\ \text{kJ}$

Thermodynamics of CVD



(Le Châtelier, Henri-Louis)
(1850-1936)

Chemical Equilibrium

- *The Principle (Le Châtelier 1884):*
  If the conditions of a system, initially at equilibrium, are changed, the equilibrium will shift in such a direction as to tend to restore the original conditions (counter reaction)

P → 200 bar; 600C

N_2 (g) + $3H_2$ (g) ↔ $2NH_3$ (g) + heat

← T

1901

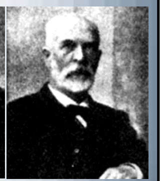
1906:
Haber & Claude

"I let the discovery of the ammonia synthesis slip through my hands. It was the greatest blunder of my scientific career." Le Châtelier

Law of Mass Action **(Waage & Guldberg 1867)**

- $aA + bB + \ldots \rightarrow xX + yY + \ldots$
- $[\text{forward rate}] \propto k_1\,[A]^a\,[B]^b \cdots$
- $[\text{reverse rate}] \propto k_{-1}\,[X]^x\,[Y]^y \cdots$
- in equilibrium, $k_1\,[A]^a\,[B]^b \cdots = k_{-1}\,[X]^x\,[Y]^y \cdots$

(Waage, Peter)
(1833-1900)



(Guldberg, Cato)
(1836-1902)

Gas Transport

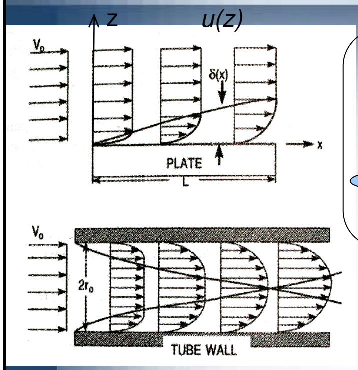
- Viscous flow (moment transfer)
- Diffusion (particle transfer)
- Convection
- Thermal conductivity (energy transfer)

Issues:

- film thickness uniformity
- growth rates
- efficient utilization of process gases
- computer modeling of CVD reactor

Gas Transport

Viscous Flow
(laminar)



$$[\Lambda] = \frac{\frac{g \cdot cm}{s}}{cm^2 \cdot s} = \frac{g}{cm \cdot s^2}$$

Momentum flow, Λ

1 sec
1 cm²

$$\Lambda = -\eta \frac{du}{dz} \qquad [\eta] = \frac{g}{cm \cdot s}$$

1 Poise

Viscosity (dynamic)

Tells about how quickly momentum is transferred (rate of momentum equalization)

$$[\nu] = \frac{cm^2}{s}$$

(velocity diffusion)

$$\nu = \frac{\eta}{\rho}$$

ρ ← density

Viscosity (kinetic)

Tells about rate of velocity equalization

(20 C)	*η*	*ν*
air	1.8 e-4	0.15
water	0.01	0.01
Hg	0.016	0.0014
glycerine	15	12

For gases, $\eta \sim mnVl \sim mV/\sigma$
(σ is the cross section)

+strong temperature dependence

Gas Transport, everything included

Dimensionless Parameter Groups in CVD

Name	Definition	Physical interpretation	Typical magnitude APCVD	Typical magnitude LPCVD
Knudsen	$Kn = \lambda/L$	Ratio of gas mean free path to characteristic length	10^{-6}–10^{-5}	10^{-3}–10^{-2}
Prandtl	$Pr = C_p\eta/K$	Ratio of momentum diffusivity to thermal diffusivity	~0.7	~0.7
Schmidt	$Sc = C_p\eta/D$	Ratio of momentum diffusivity to mass diffusivity	1–10	1–10
Reynolds	$Re = \rho v L/\eta$	Ratio of inertia forces to viscous forces	10^{-2}–10^{2}	10^{-2}–10^{2}
Peclet (mass)	$Pe_m = ReSc$	Ratio of convective mass flux to diffusive mass flux	10^{-1}–10^{3}	10^{-1}–10^{3}
Grashof (thermal)	$Gr_t = \frac{g\rho^2 L^3 \Delta T}{\eta^2 T_r}$	Ratio of buoyancy force to viscous force	10^{2}–10^{7}	0–10
Rayleigh	$Ra = GrPr$	Ratio of buoyancy force to viscous force	10^{2}–10^{7}	0–10
Damkohler (gas phase)	$Da_g = \frac{\dot{R}_g L}{C_{in} v}$	Ratio of chemical reaction rate to bulk flow rate	10^{-3}–10^{3}	10^{-3}–10^{3}
Damkohler (surface)	$Da_s = \frac{\dot{R}_s L}{C_{in} D}$	Ratio of chemical reaction rate to diffusion rate	10^{-3}–10^{3}	10^{-3}–10^{3}
Arrhenius	$Arrh = \frac{E}{RT_r}$	Ratio of activation energy to potential energy	0–100	0–100
Gay–Lussac	$Ga = \Delta T/T_r$	Ratio of temperature difference to reference temperature	1–1.3	0.6–1

Note: L = reactor dimension (m), C_p = specific heat (J/kg-K), η = viscosity (Pa-s), K = thermal diffusivity (m²/s), g = gravitational constant, $\Delta T = T_{hot} - T_{cold}$, T_r = reference temperature, $\dot{R}_g$ = gas reaction rate (mol/m³-s), $\dot{R}_s$ = surface reaction rate (mol/m²-s), C_{in} = input gas concentration (mol/m³).
Adapted from Refs. 22, 23.

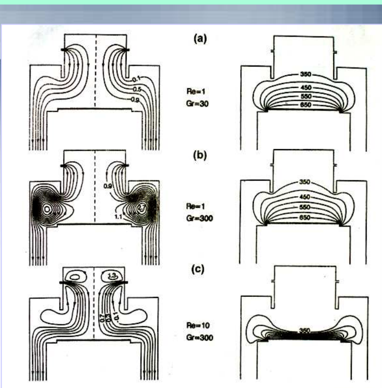


Figure 6-9 Gas streamlines (left) over the range 0–1, and corresponding isotherms in K (right) for different combinations of Reynolds and Grashof numbers. The reactor profile is outlined. (a) Re = 1, Gr = 30; (b) Re = 1, Gr = 300; (c) Re = 10, Gr = 300. (From C. R. Kleijn, "Transport Phenomena in Chemical Vapor Deposition Reactors." Ph.D. Thesis, Technical University of Delft, 1991. Reprinted with permission.)

Film Growth Kinetics

Axial Growth Uniformity

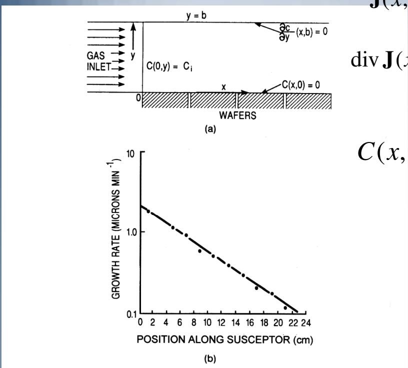


Figure 6-10 (a) Horizontal reactor geometry with conditions for flow. (b) Variation of growth rate with position along susceptor. Reactor conditions: $\bar{v} = 7.5$ cm/s, $b = 1.4$ cm, $T = 1200$°C, and $C_i = 3.1 \times 10^{-5}$ g/cm³. (From P. C. Rundle, *Int. J. Electron.* **24**, 405, © 1968 Taylor and Francis, Ltd.)

$$\mathbf{J}(x,y) = C(x,y)\bar{v} - D\nabla C(x,y)$$

$$\operatorname{div}\mathbf{J}(x,y) = D\left\{\frac{\partial^2 C(x,y)}{\partial x^2} + \frac{\partial^2 C(x,y)}{\partial y^2}\right\} + \frac{\partial C(x,y)}{\partial x}\bar{v} = 0$$

$$C(x,y) = \frac{4\bar{C}}{\pi}\sin\left(\frac{\pi y}{2b}\right)\cdot\exp\left(-\frac{\pi^2 Dx}{4\bar{v}b^2}\right)$$

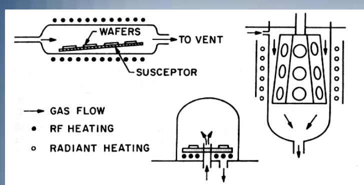
$$J(x) = D\left.\frac{\partial C(x,y)}{\partial y}\right|_{y=0}$$

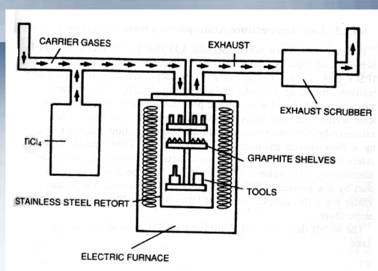
$$\dot{G}(x) = \frac{MJ(x)}{\rho M_0}$$

$$\dot{G}(x) = \frac{4\bar{C}MD}{b\rho M_0}\cdot\exp\left(-\frac{\pi^2 Dx}{4\bar{v}b^2}\right)$$

Thermal CVD

Atmospheric-Pressure Systems “APCVD”





High temperatures:

$$2\mathrm{TiCl_4} + \mathrm{CH_3CN} + 5/2\mathrm{H_2} \Rightarrow 2\mathrm{Ti(C,N)} + \mathrm{CH_4} + 4\mathrm{HCl};\ 700 < T < 850^\circ\mathrm{C}$$

$$2\mathrm{TiCl_4} + \mathrm{N_2} + 4\mathrm{H_2} \Rightarrow 2\mathrm{TiN} + 8\mathrm{HCl};\ 850 < T < 1200^\circ\mathrm{C}$$

Low temperatures:

$$\mathrm{SiH_4} + \mathrm{O_2} \xrightarrow{450^\circ\mathrm{C}} \mathrm{SiO_2} + 2\mathrm{H_2}$$

$$\mathrm{Si(OC_2H_5)_4} \xrightarrow{700^\circ\mathrm{C}} \mathrm{SiO_2} + \text{by-products}$$

Low-Pressure Systems “LPCVD” (1-10 mTorr)

- dense packing of wafers
- high deposition rates
- improved uniformity
- better step coverage
- fewer pinholes

Thermal CVD

Metalorganic CVD "MOCVD"

Laser-Enhanced CVD "LECVD"

MOCVD Precursors for Assorted Metals and Electroceramic Metal Oxides

Metals[a]	Alkoxides	β-Diketonates[c]	Alkyls
Ag		Ag(acac)	
Al			$AlMe_3$, $AlEt_3$
Au		Me_2Au(fhac)	
Cu	$Cu(OBu)_4$	$Cu(hfac)_2$, $Cu(acac)_2$	
Pt		$Pt(acac)_2$	$C_5H_5Pt(Me)_3$
Metal oxides[b]			
TiO_2	$Ti(OR)_4$ [b]		
ZrO_2	$Zr(OR)_4$	$Zr(acac)_4$, $Zr(thd)_4$	
Ta_2O_5, Nb_2O_5	$Ta(OEt)_5$ [c], $Nb(OEt)_5$		
(Ba, Sr)TiO_3	$Ti(OR)_4$, $Ti(OPr)_2(thd)_2$	$Ba(thd)_2$, $Ba(hfac)_2$, $Sr(thd)_2$	
Pb(Zr, Ti)O_3, (Pb, La)(Zr, Ti)O_3	$Zr(OR)_4$, $Ti(OR)_4$, $Ti(OR)_2(thd)_2$	$Pb(thd)_2$, $Pb(fod)_2$, $Zr(thd)_4$, $La(thd)_3$	$PbEt_4$, (neopentoxy)$PbEt_3$
Pb(Mg)NbO_3	$Nb(OEt)_5$	$Pb(thd)_2$, $Mg(thd)_2$, $Nb(thd)_4$	
(Ni, Zn)Fe_2O_4		$Ni(thd)_2$, $Ni(acac)_2$, $Zn(thd)_2$, $Zn(acac)_2$, $Fe(thd)_3$, $Fe(acac)_3$	
$YBa_2Cu_3O_{7-x}$		$Y(thd)_3$, $Ba(thd)_2$, $Ba(hfac)_2$, $Cu(thd)_2$, $Cu(hfac)_2$	

[a] From Ref. 36.
[b] From Ref. 40.
[c] Abbreviations for β-diketonate ligands: acac: 2,4-pentanedionate; thd: 2,2,6,6-tetramethyl-3,5-heptanedionate; hfac: 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; fod: 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate.
$R = (C_mH_{2m+1})$, Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl.

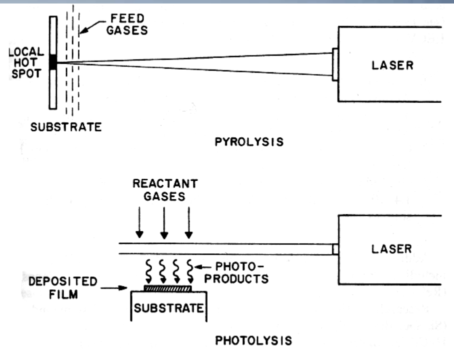


Figure 6-17 (a) Pyrolytic and (b) photolytic laser-induced chemical-vapor deposition of films (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

CVD Reactor Types

- **Chamber pressure:**
  - atmospheric-pressure (APCVD)
  - low-pressure
    - * LPCVD
    - * PECVD
- **Reactor heating:**
  - Hot-wall
  - Cold-wall

Reaction Mechanism
- mass transport, when *P* and *T* are high
- surface reaction, when *P* and *T* are low
- possible to switch from one to another by changing *P* or *T*

APCVD
± mass-transport limited region
+ fast deposition
– poor step coverage

LPCVD
± surface reaction rate limited
+ excellent purity, uniformity and step coverage
– low deposition rates
– requires vacuum system

Cold-wall
+ no reaction on the wall
– difficult to control the real T

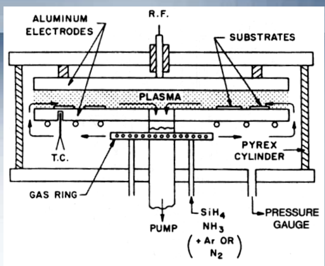
Hot-wall
– particle contamin. (peel off)
– requires periodic cleanup

Plasma-Enhanced CVD

PECVD Films, Source Gases, and Deposition Temperatures

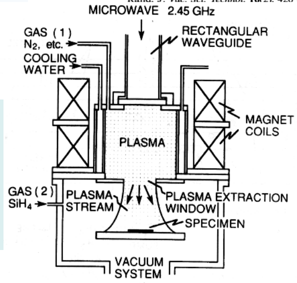
Film	Source gases	Deposition temperature (°C)
Elemental		
Al	$AlCl_3–H_2$	100–250
a-B	$BCl_3–H_2$	400
a-C	$C_xH_m–H_2/Ar$	25–250
a-Si	$SiH_4–H_2$	300
c-Si	$SiH_4–H_2$	400
Oxides		
Al_2O_3	$AlCl_3–O_2$	100–400
SiO_2	$SiCl_4–O_2$	100–400
TiO_2	$TiCl_4–O_2$	100–500
Nitrides		
AlN	$AlCl_3–N_2$	< 1000
BN	$B_2H_6–NH_3$	300–700
	$BCl_3–NH_3/Ar$	300–700
Si_3N_4	$SiH_4–NH_3–N_2$	25–500
TiN	$TiCl_4–N_2–H_2$	100–500
Carbides		
B_4C	$B_2H_6–CH_4$	400
BCN	$B_2H_6–CH_4–N_2$	~25
	$C_6H_{18}BN$	250
SiC	$SiH_4–C_xH_m$	140–600
TiC	$TiCl_4–CH_4–H_2$	400–900
Borides		
TiB_2	$TiCl_4–BCl_3–H_2$	480–650

Plasma can lower deposition *T*



Reinberg-type cylindrical radial-flow plasma reactor Rand, J. Vac. Sci. Technol. 16(2), 420 (1979).

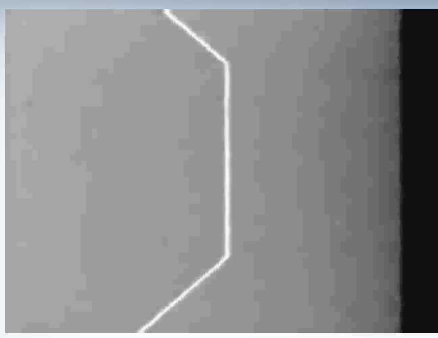
ECR vs RF:
- denser discharge
- lower pressures
- higher degree of ionization
- absence of electrodes



ECR plasma deposition reactor. (From S. Matuso, in *Handbook of Thin Film Deposition Processes and Techniques*, ed. K. K. Schuegraf. Noyes, Park Ridge, NJ, 1988.

FIB-Enhanced CVD

http://www.feic.com/products/strata-235m.htm

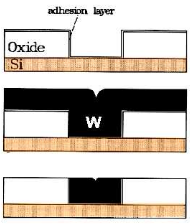


FEI

FEI Strata™ DB-STEM - Delivers integrated sample preparation, ultra-high resolution STEM imaging and microanalysis below 1nm, for high throughput semiconductor and data storage labs

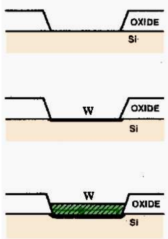
Selective CVD

Blanket (non-selective) CVD



- Most commonly used in industry.
- Due to the poor nucleation and adherence of CVD W on SiO_2. A "glue" layer is needed: predeposited TiN, or sputtered W, TiW and Mo.
- For contact hole and via fill purposes the process requires a subsequent etch back.

Selective CVD



- Fill contacts or vias is much simpler than the blanket approach: no adhesion layer and etch back needed. Less toxic waste
- Deposited on silicon, Al,etc.; not deposited on the dielectrics such as SiO_2.
- Drawbacks: encroachment phenomenon, selectivity loss.
- not used extensively in industry compared to blanket tungsten.

$$2WF_6 + 3H_2 \rightarrow W + 6HF \quad (300^{\circ}C) \qquad 2WF_6 + 3Si \rightarrow 2W + 3SiF_4$$

SAFETY

Hazardous Gases Employed in CVD

Gas	Corrosive	Flammable	Pyrophoric	Toxic	Bodily hazard
Ammonia (NH_3)	✚			✚	Eye and respiratory irritation
Arsine (AsH_3)		✚		✚	Anemia, kidney damage, death
Boron trichloride (BCl_3)	✚				
Boron trifluoride (BF_3)	✚				
Chlorine (Cl_2)	✚			✚	Eye and respiratory irritation
Diborane (B_2H_6)		✚	✚	✚	Respiratory irritation
Dichlorosilane (SiH_2Cl_2)	✚	✚			
Germane (GeH_4)		✚		✚	
Hydrogen chloride (HCl)	✚				
Hydrogen fluoride (HF)	✚				Severe burns
Hydrogen (H_2)		✚			
Phosphine (PH_3)		✚	✚	✚	Respiratory irritation, death
Phosphorus pentachloride (PCl_5)	✚				
Silane (SiH_4)		✚	✚	✚	
Silicon tetrachloride ($SiCl_4$)	✚				
Stibine (SbH_3)		✚		✚	

To be continued ...

- Epitaxy
- Thin-Film Nucleation & Growth