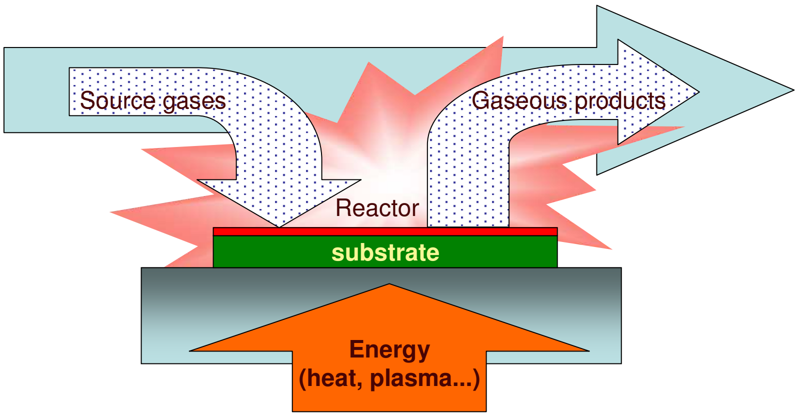
Chemical Vapor Deposition (CVD)



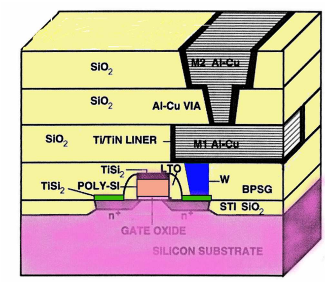
CVD

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

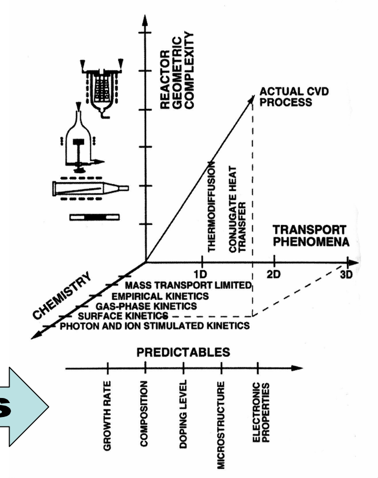
Applications:

- **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

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

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

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

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

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

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

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

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

$$SiH_{4(g)} + 2H_{2(g)} + O_{2(g)} \rightarrow$$
$$\rightarrow SiO_{2(s)} + 4HCl_{(g)} \qquad (1500^\circ C)$$

soot

$$2AlCl_{3(g)} + 3H_{2(g)} + 3CO_{2(g)} \rightarrow$$
$$\rightarrow Al_2O_{3(s)} + 3CO_{(g)} + 6HCl_{(g)} \qquad (1000^\circ C)$$

Compound Formation

hard surface coatings

$$SiCl_{4(g)} + CH_{4(g)} \rightarrow SiC_{(s)} + 4HCl_{(g)} \qquad (1400^\circ C)$$

$$TiCl_{4(g)} + CH_{4(g)} \rightarrow TiC_{(s)} + 4HCl_{(g)} \qquad (1000^\circ C)$$

$$BF_{3(g)} + NH_{3(g)} \rightarrow BN_{(s)} + 3HF_{(g)} \qquad (1100^\circ C)$$

MOCVD:

$$(CH_3)_3Ga_{(g)} + AsH_{3(g)} \rightarrow GaAs_{(s)} + 3CH_{4(g)} \qquad (650 - 750^\circ C)$$

Disproportionation

a chemical reaction in which a single substance acts as both oxidizing and reducing agent, resulting in the production of dissimilar substances

300 C →

$$2GeI_{2(g)} \leftrightarrow Ge_{(s)} + GeI_{4(g)}$$

← 600 C

lower-valent state is more stable at high T

Al, B, Ga, In, Si, Ti, Zr, Be, Cr can be deposited this way

Reversible Transfer

750 C →

$$As_{4(g)} + As_{2(g)} + 6GaCl_{(g)} + 3H_{2(g)} \leftrightarrow 6GaAs_{(s)} + 6HCl_{(g)}$$

← 850 C

Thermal CVD Films

Thermal CVD Films and Coatings

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

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

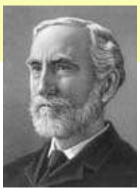
Thermodynamics of CVD

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 $\Delta G = \Delta H - T\Delta S$
- 2nd 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

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

\-

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

=

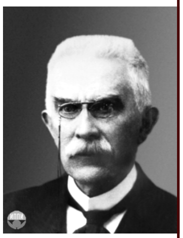
endothermic

$2C + H_2 = C_2H_2 - 260\,kJ$

Thermodynamics of CVD

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)



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

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 + ... → xX + yY + ...
- [forward rate] ∞ k_1 $[A]^a$ $[B]^b$ ···
- [reverse rate] ∞ k_{-1} $[X]^x$ $[Y]^y$ ···
- in equilibrium, k_1 $[A]^a$ $[B]^b$ ··· = k_{-1} $[X]^x$ $[Y]^y$ ···

(Waage, Peter)
(1833-1900)

(Guldberg, Cato)
(1836-1902)

Thermodynamics of CVD

Law of Mass Action **(continued)**

- $H_2 + I_2 \leftrightarrow 2HI$;
  the direct reaction results from collision of H_2 and I_2 molecules =>
  reaction rate is proportional to the number of such collisions;
  the number of collisions is proportional to density of H_2 and I_2;
  the density is proportional to pressure =>
- the reaction rate is proportional to the partial pressures of H_2 and I_2 :
  $$k_1 P_{H_2} P_{I_2}$$
- similarly, the reverse reaction rate is proportional to the number of collisions between HI molecules => the reaction rate is
  $$k_{-1} P_{HI}^2$$
- in equilibrium $k_1 P_{H_2} P_{I_2} = k_{-1} P_{HI}^2$
- we define the constant of equilibrium as
  $$K(T) = k_{-1} / k_1 = P_{H_2} P_{I_2} / P_{HI}^2$$
- presenting $H_2 + I_2 = 2HI$ in the form $H_2 + I_2 - 2HI = 0$ (= $a_1A_1 + a_2A_2 + a_3A_3 + ...$) the Law of Mass Action can be rewritten in terms of partial pressures P_i:
  $$\boldsymbol{P_1^{a_1} P_2^{a_2} P_3^{a_3} ... = K(T)}$$

Thermodynamics of CVD

Law of Mass Action (continued)

$$P_1^{a_1} P_2^{a_2} P_3^{a_3} \ldots = K(T) \text{ (partial pressures)}$$

$$P_i = c_i P$$

$$c_1^{a_1} c_2^{a_2} c_3^{a_3} \ldots = K(T) P^{-(a_1 + a_2 + a_3 \ldots)}$$

(total pressure and concentrations)

$$N_2\ (g) + 3H_2\ (g) = 2NH_3\ (g)$$

$$\frac{c_{N_2} c_{H_2}^3}{c_{NH_3}^2} = \frac{K(T)}{P^2}$$

An increase of P means increase of c_{NH_3} in accordance with Le Châtelier's principal

at 1 atm and 298K (standard state)

Finally: $\Delta G = \Delta G^0 + RT \ln K,$

i.e in equilibrium:

$$-\Delta G^0 = RT \ln K$$

Gas Transport

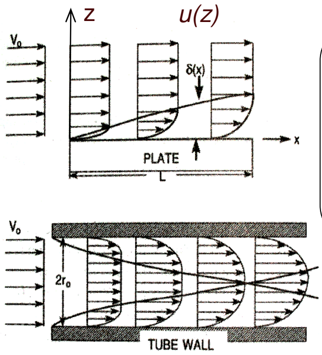
- Viscous flow (moment transfer)
- Diffusion (particle transfer)
- Convection
- Thermal conductivity (energy transfer)

Issues:

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

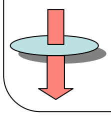
Gas Transport

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

$$\Lambda=-\eta\frac{du}{dz}$$

$$[\eta]=\frac{g}{cm\cdot s}$$

1 Poise

Viscosity (dynamic)

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

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

(velocity diffusion)

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

← density

Viscosity (kinetic)

Tells about rate of velocity equalization

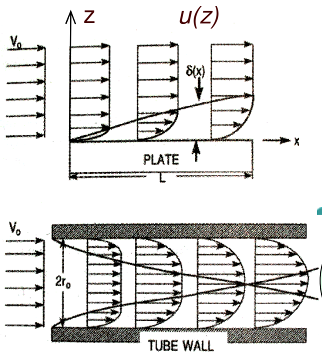
(20 C)	*η*	*ν*
air	1.8 e-4	0.15
water	0.01	0.01
Hg	0.016	0.0014
glycerine	15	12

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

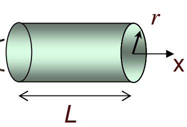
+strong temperature dependence

Gas Transport

Viscous Flow
(laminar)



Let's pick a part of liquid inside the tube...



$$\Lambda=-\eta\frac{du}{dr}$$

Momentum flux through the surface:
(a friction force acting on the cylinder from the rest of the gas / liquid)

$$2\pi r L\Lambda=-2\pi r L\eta\frac{du}{dr}$$

The friction force is balanced by the force due to the pressure difference *ΔP along L*

$$-2\pi r L\eta\frac{du}{dr}=\pi r^2\Delta P$$

By integration we get:

$$u=-\frac{r^2}{4L\eta}\Delta P+\mathrm{const}$$

From the boundary condition $u(r_0)=0$

$$u(r)=\frac{r_0^2-r^2}{4L\eta}\Delta P$$

$$dM(r)=\left(2\pi r\,u(r)dr\right)\cdot\rho=2\pi r\frac{r_0^2-r^2}{4L\eta}\Delta P\rho\,dr$$

$$M(r_0)=\frac{\pi r_0^4\rho}{8L\eta}\Delta P$$

Poiseuille relation

Poiseuille, Jean (1797-1869)

Gas Transport

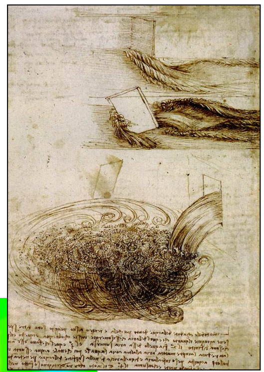
Viscous Flow
(turbulent)

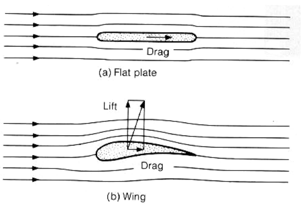
Turbulence is a very complex physical phenomena and even today we do not fully understand how turbulence works.
Richard Feynman: turbulence is the most important unsolved problem of classical physics.

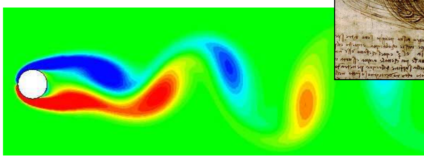
The first person that described and studied turbulence was probably **Leonardo da Vinci** (1452-1519). Since then many famous scientists have worked on the problem of turbulence like for example L. Euler (1707-1783), H. L. F. von Helmholtz (1821-1894), William Thompson (Lord Kelvin) (1824-1907), Lord Rayleigh(1842-1919) and A. N. Kolmogorov (1903-1987)...

$$\mathrm{Re} = \frac{d\,u\rho}{\eta}$$

Reinolds number







Re<1000

Diffusion

$$j = -D\frac{\mathrm{d}c}{\mathrm{d}x} \qquad [D] = \frac{\mathrm{cm}^2}{\mathrm{s}}$$

	D [cm²/s]
H_2 in O_2	0.7
CO_2 in air	0.14
O_2 in O_2	0.18
sugar in water	3e-6

In gases:

$$D \sim vl \sim \frac{v}{n\sigma} \sim \frac{v\,\mathrm{k_B}T}{P\sigma}$$

$$u = BF$$

Mobility *B*, force *F*, drift velocity *u* of ions

Time of equalization $t \sim \dfrac{L^2}{D}$

$$D = \mathrm{k_B}T\,B$$

Einstein's equation

L

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 (m^2/s), g = gravitational constant, $\Delta T = T_{hot} - T_{cold}$, T_r = reference temperature, $\dot{R}_g$ = gas reaction rate (mol/m^3-s), $\dot{R}_s$ = surface reaction rate (mol/m^2-s), C_{in} = input gas concentration (mol/m^3).
Adapted from Refs. 22, 23.

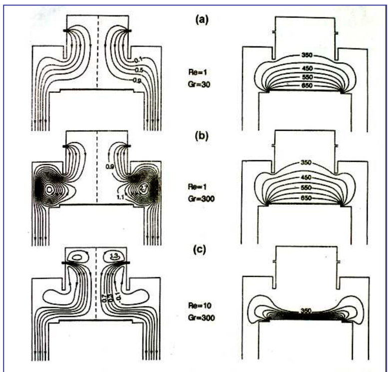


Figure 6-9 Gas streamlines (left) over the range 0–1, and corresponding isotherms in K (right) for different combinations of Reynolds and Grashof numbers. The reactor profile is outlined. (a) Re = 1, Gr = 30; (b) Re = 1, Gr = 300; (c) Re = 10, Gr = 300. (From C. R. Kleijn, "Transport Phenomena in Chemical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

Film Growth Kinetics

Axial Growth Uniformity

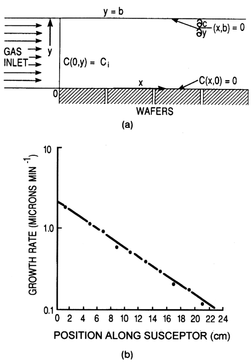


Figure 6-10 (a) Horizontal reactor geometry with conditions for flow. (b) Variation of growth rate with position along susceptor. Reactor conditions: $\bar{v}$ = 7.5 cm/s, b = 1.4 cm, T = 1200°C, and $C_i = 3.1 \times 10^{-5}$ g/cm³. (From P. C. Rundle, *Int. J. Electron.* **24**, 405, © 1968 Taylor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

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

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

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

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

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

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

Film Growth Kinetics

Radial Growth Uniformity on Wafers

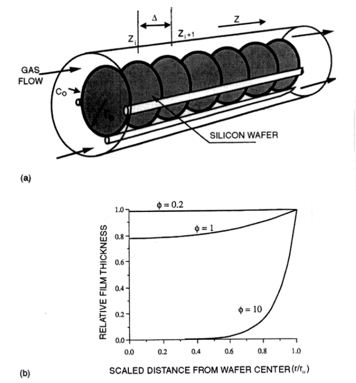


Figure 6-11 (a) Schematic representation of hot-wall, multiple wafer LPCVD reactor geometry with gas flow boundary conditions. (b) Film thickness variation as a function of the scaled radial distance along the wafer for different values of ϕ. (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

$$D\left\{\frac{\partial}{\partial r}\left(\frac{r\,\partial C(r,z)}{\partial r}\right)+\frac{\partial^2 C(r,z)}{\partial z^2}\right\}=0$$

$$D\left.\frac{\partial C}{\partial z}\right|_{z=z_i}=kC$$

$$\left.\frac{\partial C(r,z)}{\partial r}\right|_{r=0}=0 \qquad C(r_0,z)=C_0$$

$$\text{for } \frac{\Delta}{r_0}\le 0.05:\quad \frac{\partial^2 C(r,z)}{\partial z^2}\approx\frac{2kC}{D\Delta}$$

$$D\frac{\partial}{\partial r}\left(\frac{r\,\partial C(r)}{\partial r}\right)+\frac{2kC(r)}{\Delta}=0$$

$$\frac{d(r/r_0)}{d(1)}=\frac{C(r)}{C_0}=\frac{I_0\left(\sqrt{\frac{2r_0k}{\Delta D}}\,\frac{r}{r_0}\right)}{I_0\left(\sqrt{\frac{2r_0k}{\Delta D}}\right)}$$

φ

Film Growth Kinetics

Temperature Dependence

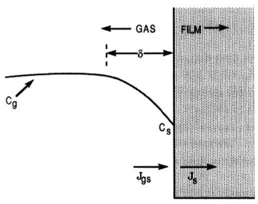


Figure 6-12 Model of CVD growth process. Gas flows normal to plane of paper. (From Ref. 26. Reprinted with permission from John Wiley & Sons, copyright © 1967.)

$$J_{gs}=h_g(C_g-C_s) \qquad J_s=k_sC_s$$

$$C_s=\frac{C_g}{1+k_s/h_g}\quad \text{for } J_{gs}=J_s$$

$$k_s\propto\exp\left(-\frac{E}{RT}\right)$$

$k_s >> h_g$: mass transfer

$k_s << h_g$: surface reaction

reversibility of chemical reactions can result in lower growth rates at high temperatures

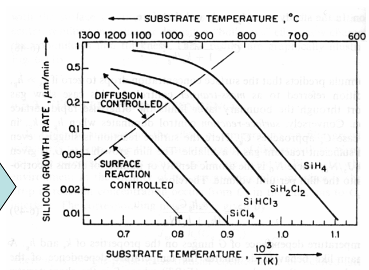
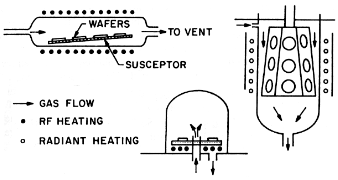
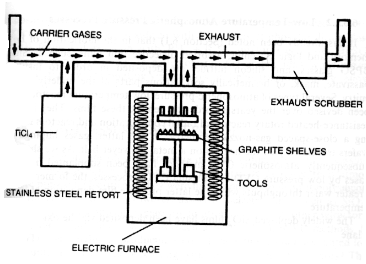


Figure 6-13 Deposition rate of Si from four different precursor gases as a function of temperature. (From W. Kern, in *Microelectronic Materials and Processes*, ed. R. A. Levy, reprinted with permission of Kluwer Academic Publishers, 1989.)

Thermal CVD

Atmospheric-Pressure Systems
"APCVD"





High temperatures:

$$2TiCl_4 + CH_3CN + 5/2H_2 \Rightarrow 2Ti(C,N) + CH_4 + 4HCl;\ 700 < T < 850^{\circ}C$$
$$2TiCl_4 + N_2 + 4H_2 \Rightarrow 2TiN + 8HCl;\ 850 < T < 1200^{\circ}C$$

Low temperatures:

$$SiH_4 + O_2 \xrightarrow{450^{\circ}C} SiO_2 + 2H_2$$
$$Si(OC_2H_5)_4 \xrightarrow{700^{\circ}C} SiO_2 + by-products$$

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"

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.

Laser-Enhanced CVD
"LECVD"

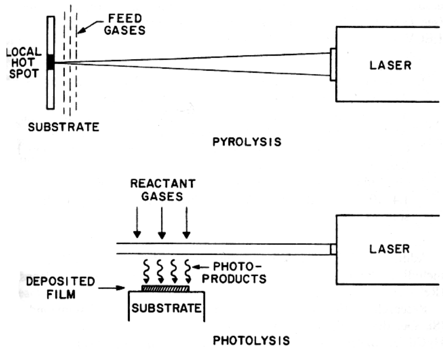


Figure 6-17 (a) Pyrolytic and (b) photolytic laser-induced chemical-vapor deposition of films (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

Thermal CVD

Injection MOCVD

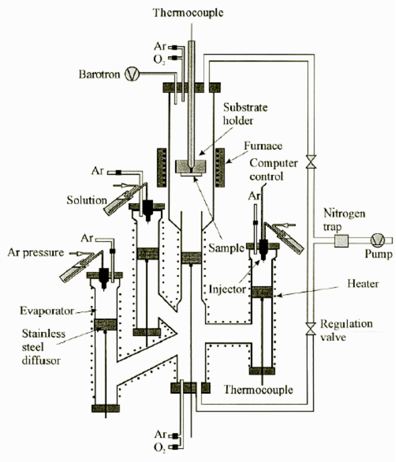


Figure 1. Injection CVD reactor.

Supercond. Sci. Technol. **10** (1997) 959–965. Printed in the UK PII: S0953-2048(97)85503-0

Thin YBCO films on $NdGaO_3$ (001) substrates grown by injection MOCVD

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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

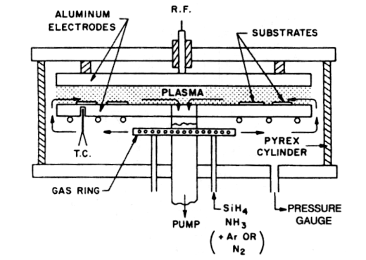
Hot-wall
– particle contamin. (peel off)
– requires periodic cleanup

Plasma-Enhanced CVD

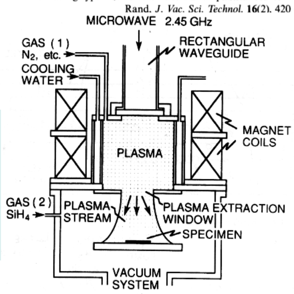
PECVD Films, Source Gases, and Deposition Temperatures

Film	Source gases	Deposition temperature (°C)
Elemental		
Al	$AlCl_3$–H_2	100–250
a-B	BCl_3–H_2	400
a-C	C_nH_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
	$C_8H_{18}BN$	250
SiC	SiH_4–C_nH_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).

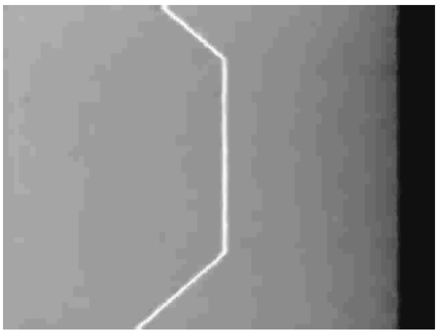


ECR vs RF:
- denser discharge
- lower pressures
- higher degree of ionization
- absence of electrodes

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

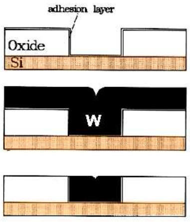
http://www.feic.com/products/strata-235m.htm



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

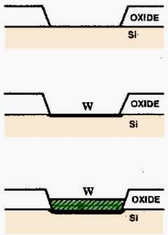
Selective CVD

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.

$$2WF_6 + 3H_2 \rightarrow W + 6HF \quad (300^\circ C)$$

$$2WF_6 + 3Si \rightarrow 2W + 3SiF_4$$

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)		✚		✚	

Home assignment #4 (p.350)