Vékonyrétegek előállítása és alkalmazásai

2010. november 15.

Dr. Geretovszky Zsolt

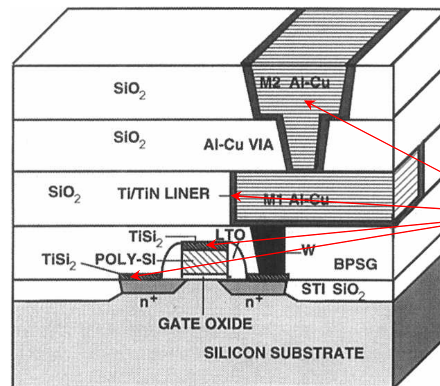
Chemical Vapour Deposition (CVD)

Chemical vapor deposition primarily relies on gas phase and gas-solid chemical reactions to produce thin films. It is a process in which a volatile compound of the material to be deposited reacts with other gases in order to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate.
Because they are subject to thermodynamic and kinetic limitations and constrained by the flow of gaseous reactants and products, CVD processes are more complex than those involving PVD.
Appreciation of the relevant theories will aim to ensure that the gas-phase precipitation occurs at decent rates, to yield amorphous, polycrystalline or epitaxial films with desired chemical composition, morphology and structure.
Since CVD processes do not require vacuum or unusual levels of electric power, they were practiced prior to PVD (e.g. protective W coating on the carbon filaments of incandescent light bulbs).

Diverse applications:

solid-state electronic devices, microelectronics,
coating ball bearings and cutting tools
components of rocket engines, nuclear reactors

The biggest player is microelectronic industry



The entire structure except the shaded or dark components are deposited by some variant of CVD.

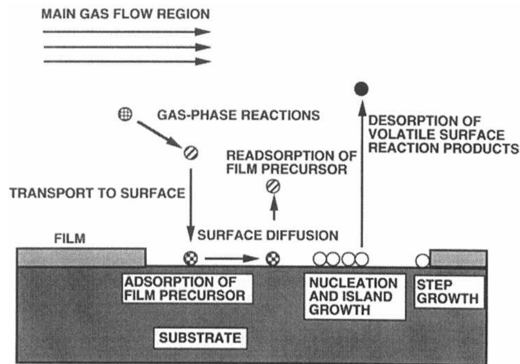
Figure 6-1 Schematic cross-sectional view of a MOS transistor structure with multilevel metallization scheme. Film materials deposited by CVD except those indicated.
LTO = low temperature oxide, BPSG = borophospho-silicate glass, STI = silicon trench insulator.

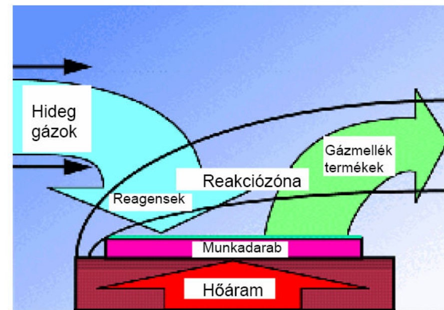
after K. P. Rodbell, IBM, T. J. Watson Research Division

Benefits

- large variety of films (metals, semiconductors, inorganic and organic compounds) can be grown in either crystalline or vitreous form
- Ability to control the stoichiometry of the layers
- High purity layers can be made (up to 99.999%)
- Compact layers can be formed (density is close to bulk density)
- Conformal coverage is not a problem
- Affordable cost of equipment + running costs
- Compatibility with other processing steps
- Suitable for both batch and semicontinuous operation

Major steps



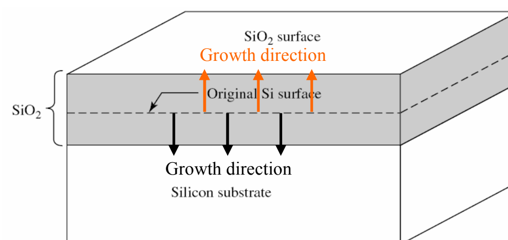


- Transport of reactants to the reaction zone.
- Chemical reactions in the gas phase to produce new reactive species and by-products.
- Transport of the initial reactants and their products to the substrate surface.
- Adsorption (chemical and physical) and diffusion of these species on the substrate surface.
- Heterogeneous reactions catalyzed by the surface leading to film formation.
- Desorption of the volatile by-products of surface reactions.
- Transport of the reaction by-products away from the reaction zone.

CVD coatings

Films produced by CVD fall into one of two categories:

Conversion layer: in this type one component of the coating already resides on the surface prior to introducing the reactant(s). E.g. surface oxidation of Si.



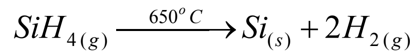
Deposited layers: All of the components of the layer arrives from the gas phase. (majority of CVD reactions are of this type)

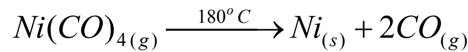
Types of chemical reactions

1. Pyrolysis
2. Reduction
3. Oxidation
4. Compound formation
5. Disproportionation

1. **Pyrolysis**

Thermal decomposition of (gaseous) species (on hot substrates).

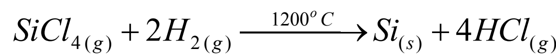


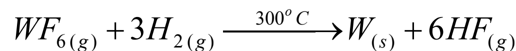


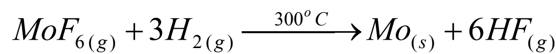
typical for hydrides, carbonyls and organometallic compounds

2. **Reduction**

Reducing the (gaseous) species via reaction with hydrogen gas.



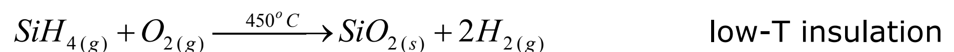


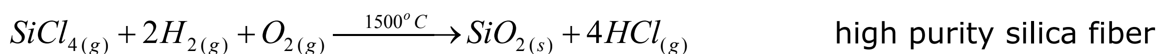


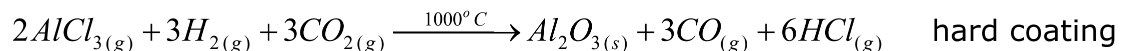
typical for halides, carbonyl halides, oxyhalides and other oxygen containing compounds

3. **Oxidation**

Reaction of the (gaseous) species with oxygen or O-containing material.

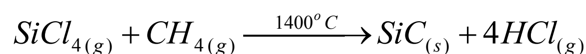


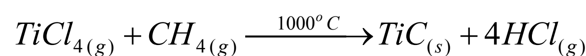


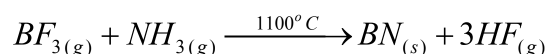


4. **Compound formation**

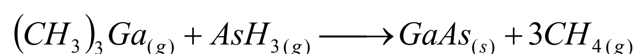
Reaction of a sufficiently volatile and reactive precursor compound with simple gaseous molecules like CH_4, NH_3, AsH_3, etc.







typical for carbide, nitride, borid film formation but compound semiconductor layers and complex oxides are also gaining wider interest.

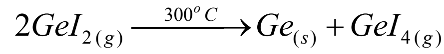


5. **Disproportionation**

Parallel oxidation and reduction in one chemical reaction, leading to the formation of a nonvolatile metal. The volatile compounds have different degree of temperature stability.

e.g. net reaction:

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



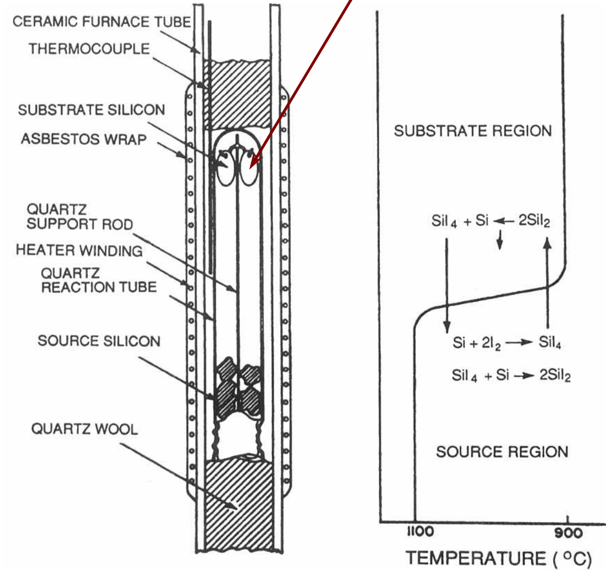
$$2GeI_{2(g)} \xrightarrow{300^{o}C} Ge_{(s)} + GeI_{4(g)}$$

$$2GeI_{2(g)} \xleftarrow[600^{o}C]{} Ge_{(s)} + GeI_{4(g)}$$

epitaxial growth of Si

If metal halides exists in two valance states the lower-valent state is usually more stable at higher temperature.

It works well with elements, like Al, B, Ga, In, Si, Ti, Zr, Be or Cr.



Vékonyrétegek előállítása és alkalmazásai

2010. november 16.

Dr. Geretovszky Zsolt

CVD *vs.* CVT

A clear distinction exists between chemical vapor deposition (CVD) and chemical vapor transport reactions (CVT).

In CVD one or more gaseous species enter the reactor from gas tanks or liquid bubbler *sources maintained outside the system*. The reactants then react at the hot surface to produce the solid film.

In CVT reactions, solid or liquid *sources are contained within the reactor* and the externally introduced carrier or reactant gases flow over the sources, lifting them into the vapor stream where they are transported along the reactor. Subsequently, deposition of solid from the gas phase occurs at the substrate.

What makes a good CVD precursor?

- Volatility (equilibrium vapor pressure and its T-dependence)
- Chemical and thermal stability (bond strength, dissociation energy)
- Reactivity (selective reactivity is preferred)
- Most common precursors

hydrides (MH_x: e.g. SiH_4, GeH_4, $AlH_3(NMe_3)_2$, NH_3)

halides: (MX_y: $TiCl_4$, $TaCl_5$, MoF_6, WF_6)

metal-organics:

alkils: $AlMe_3$, $AlBu_3$, $Ti(CH_2tBu)_4$

alkoxides: $Ti(OiPr)_4$, $[Cu(OtBu)]_4$

dialkyl amines: $Ti(NMe_2)_4$, $Cr(NEt_2)_4$

diketonates: $Cu(acac)_2$, $Pt(hfac)_2$

carbonyls: $Fe(CO)_5$, $Ni(CO)_4$

Me=methyl
Et=ethyl
Bu=buthyl
iPr=izo-propyl
acac=acetyl-acetonate
hfac=hexafluoroacetylacetonate

Thermal CVD

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.

Major steps to model

Thermodynamics

Main role: addresses the issue whether the chemical reaction is feasible.

CVD is *an empirical science* with thermodynamic guidelines.

Gas transport

Thickness uniformity and efficient utilisation of expensive reactants depends on proper transport.

In closed systems: T distr. -> p distr. -> transport

In open systems: volumetric flow rates -> p distr. -> transport

- Diffusion
  - Involves the motion of individual atomic or molecular species.
- Bulk flow
  - Parts of the gas move as a whole (plug flow).
    - Viscous flow
    - Convection

Film growth

Thermodynamics 1

Thermodynamics, TD can provide information on the concentration or partial pressures of the involved gaseous species and the direction of transport if the reaction is reversible.

TD therefore provides an upper limit of what to expect under the specified conditions.

However, it does NOT address questions related to the speed of reactions and the extent of transformation.

Remember, that TD *assumes* that (chemical, thermal) *equilibrium* has been attained in the system. This may occur in a closed system, while it is generally NOT the case in a flow reactor where gaseous reactants and products are continuously introduced and removed.

Since usually more species are present in the reactor than initially envisioned, the exact calculation of concentrations is more complex, but still possible in certain cases.

Thermodynamics 2

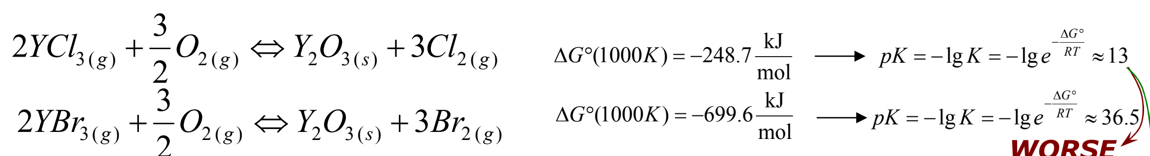
Thermodynamics may assist in selecting the suitable reaction for growing *single crystal* films. An example is given below.

According to nucleation theory a small negative value of the chemical free energy per unit volume, ΔG_V is required to foster a low nucleation rate of large critical-sized nuclei. This, in turn, would require a $\Delta G°$ value close to zero. When this happens, large amounts of reactants and products are simultaneously present.

If, however, ΔG_V (i.e. $\Delta G°$) were large and negative the likelihood of a high rate of heterogeneous nucleation, or even homogeneous nucleation of solid particles within the gas phase, would be enhanced.

The large driving force for chemical reaction tends to promote polycrystal formation, while smaller driving forces favor single crystal formation.

e.g.

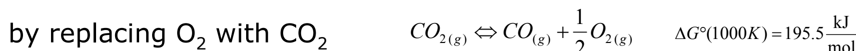


$$2YCl_{3(g)} + \frac{3}{2}O_{2(g)} \Leftrightarrow Y_2O_{3(s)} + 3Cl_{2(g)} \qquad \Delta G°(1000K) = -248.7\,\frac{\text{kJ}}{\text{mol}} \longrightarrow pK = -\lg K = -\lg e^{-\frac{\Delta G°}{RT}} \approx 13$$

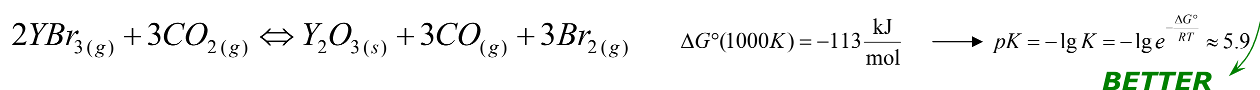
$$2YBr_{3(g)} + \frac{3}{2}O_{2(g)} \Leftrightarrow Y_2O_{3(s)} + 3Br_{2(g)} \qquad \Delta G°(1000K) = -699.6\,\frac{\text{kJ}}{\text{mol}} \longrightarrow pK = -\lg K = -\lg e^{-\frac{\Delta G°}{RT}} \approx 36.5$$

WORSE

by replacing O_2 with CO_2



$$CO_{2(g)} \Leftrightarrow CO_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta G°(1000K) = 195.5\,\frac{\text{kJ}}{\text{mol}}$$



$$2YBr_{3(g)} + 3CO_{2(g)} \Leftrightarrow Y_2O_{3(s)} + 3CO_{(g)} + 3Br_{2(g)} \qquad \Delta G°(1000K) = -113\,\frac{\text{kJ}}{\text{mol}} \longrightarrow pK = -\lg K = -\lg e^{-\frac{\Delta G°}{RT}} \approx 5.9$$

BETTER

Diffusion

Mass transport driven by the concentration difference of the material. Fick's I. and II. laws apply.

$$J = -D\frac{dC}{dx} \quad \text{and} \quad \frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

kinetic theory of gases predicts that $D \approx \frac{T^{3/2}}{P}$

experimentally

$$D = D_0 \frac{P_0}{P}\left(\frac{T}{T_0}\right)^n$$

$0.1\frac{cm^2}{s} < D_0 = D(P_0,T_0) < 10\frac{cm^2}{s}$

$P_0 = 1atm$

$T_0 = 273K$

$n \approx 1.8$

diffusional transfer is enhanced at reduced pressure → LPCVD

Fick's first law: $J = -D\frac{dC}{dx}$

for a dilute component $C_i = \frac{P_i}{RT}$

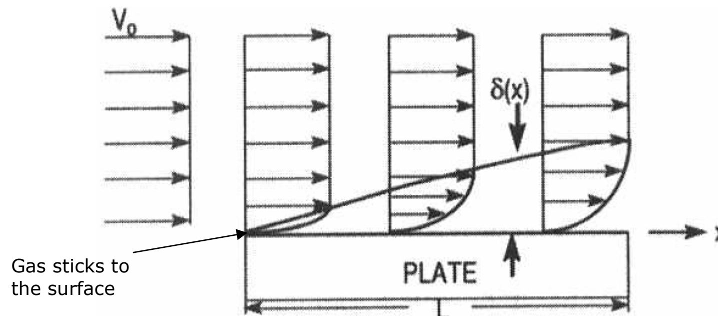
$$J_i = -\frac{D}{RT}\frac{dP_i}{dx}$$

$$J_i = -\frac{D}{RT}\frac{(P_g - P_s)}{\delta}$$

through a stagnant boundary layer

Viscous flow

Viscous flow is operative when gas transport occurs at P>=0.01atm, which is the pressure range characteristic of most CVD systems. At typical flow velocities of tens of cm/s the flow is laminar.



Gas sticks to the surface

Experimentally: $\eta \propto T^n$, $0.6<n<1.0$ and indep. of pressure

$$\delta(x) = \frac{5x}{\mathrm{Re}_x^{1/2}} \qquad \mathrm{Re}_x = \frac{v_0 \rho x}{\eta}$$

average thickness of the boundary layer over a plate of length L

$$\bar{\delta}(x) = \frac{1}{L}\int_0^L \frac{5x}{\mathrm{Re}_x^{1/2}}dx = \frac{10}{3}\frac{L}{\mathrm{Re}_L^{1/2}}$$

low value of δ is desirable

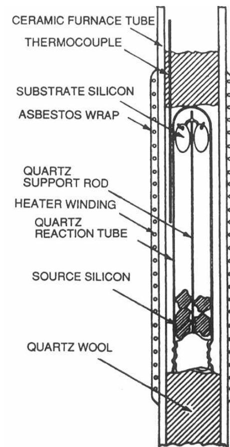
↓

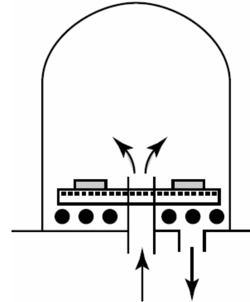
increase v_0, but keep it below $v_o(Re_x=2100)$!

Re~ few 100 is typical of CVD

Convective flow

Convection arises from the response of the fluidum to gravitational, centrifugal, electric, and magnetic forces. It is manifested in CVD reactors when there are vertical gas-density or temperature gradients.



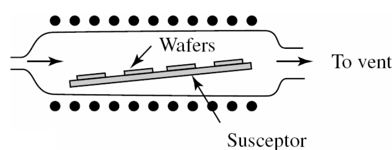


In cold-wall reactors heated susceptors are surrounded – above as well as on the sides – by the cooler walls. Cooler, more dense gases then lie above hotter, less dense gases. The resultant convective instability causes an overturning of the gas by buoyancy effects.

In vertical reactors the cooler region should be placed over the hotter one in order to enhance convective circulation.

Film growth

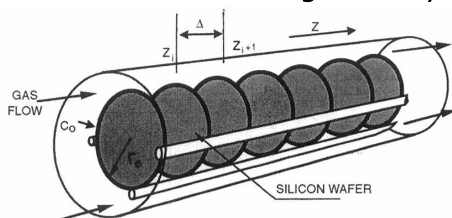
Horizontal reactor geometry



The susceptor is tilted to compensate for the increasing thickness of the boundary layer along the susceptor via forcing the velocity of the gas flow to increase in the tapered space above the substrates.

Enhanced transport across the stagnant layer compensates for reactant depletion. Continuously increasing the temperature downstream is another way to enhance deposition uniformity.

Hot-wall tubular reactor geometry (LPCVD)

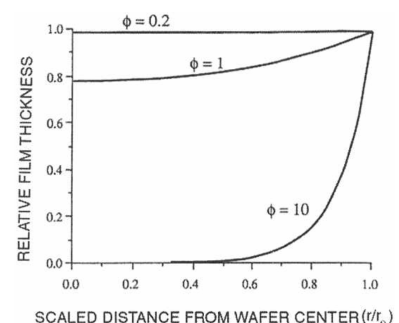


$$\Phi = \sqrt{\frac{2r_0^2 k}{\Delta \cdot D}}$$

r_0 wafer radius
k reaction rate constant
Δ interwafer separation
D diffusivity

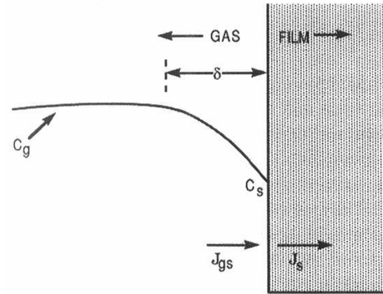
Φ describes the relative strength of diffusion and surface reaction. When
$\Phi << 1$ diffusion dominates
$\Phi >> 1$ reaction is faster

Plug/viscous flow is considered in the annular region, while diffusional transfer carries the species between the wafers.



The effect of temperature 1.

Film growth is effected by temperature



Andrew Stephen GROVE
Gróf András István
/1936 - /

mass flux to the surface

$$J_{gs} = h_g\left(C_g - C_s\right)$$

mass flux to the film

$$J_s = k_s C_s$$

if 1st order kinetics is assumed

$$J_{gs} = J_s$$

$$C_s = \frac{C_g}{1 + k_s/h_g}$$

Mass-transfer or diffusion control ($k_s >> h_g$)

Slow gas transport through the boundary layer limits the otherwise rapid surface reaction. C_s approaches zero.

Surface-reaction control ($k_s << h_g$)

Surface reaction is sluggish even though sufficient gas is available. C_s approaches C_g.

The effect of temperature 2.

The film growth rate

$$\dot{G} = \frac{J_s}{N_0} = \frac{k_s h_g C_g}{\left(h_g + k_s\right)N_0}$$

N_0 number of atoms incorporated into the film per unit volume

The temperature dependence of film growth rate is dominated by the temperature “sensitivity” of k_s and h_g.

$$J_{gs} = h_g\left(C_g - C_s\right)$$

$$J_i = -\frac{D}{RT}\frac{(P_g - P_s)}{\delta}$$

$\longrightarrow$ $h_g \propto \frac{D}{\delta}$

$D \propto T^2$ at most

δ only weakly depends on T

$\longrightarrow$ h_g is fairly insensitive to T

$k_s \propto e^{-\frac{E}{RT}}$ $\longrightarrow$ k_s is very sensitive to T

Low temperatures
k_s is small
surface-reaction control

$$\dot{G} = \frac{k_s C_g}{N_0}$$

High temperatures
k_s is large
mass-transfer control

$$\dot{G} = \frac{h_g C_g}{N_0}$$

The effect of temperature 3.

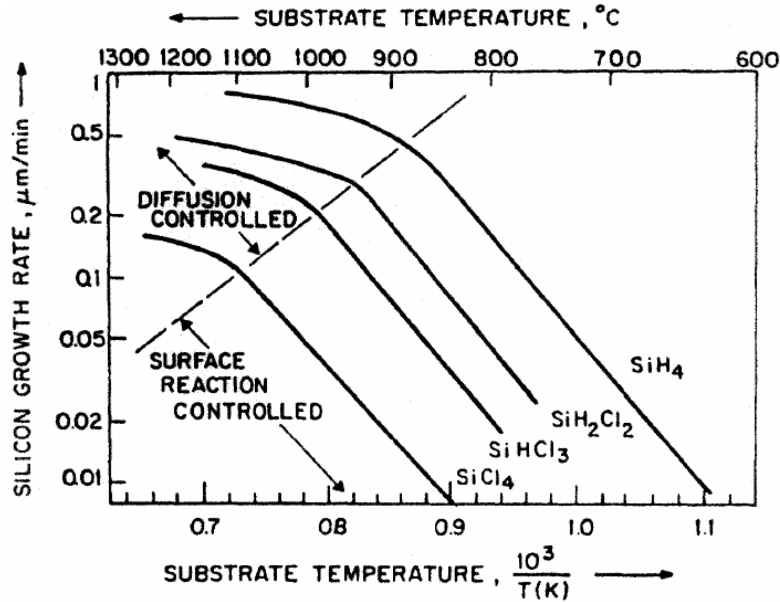
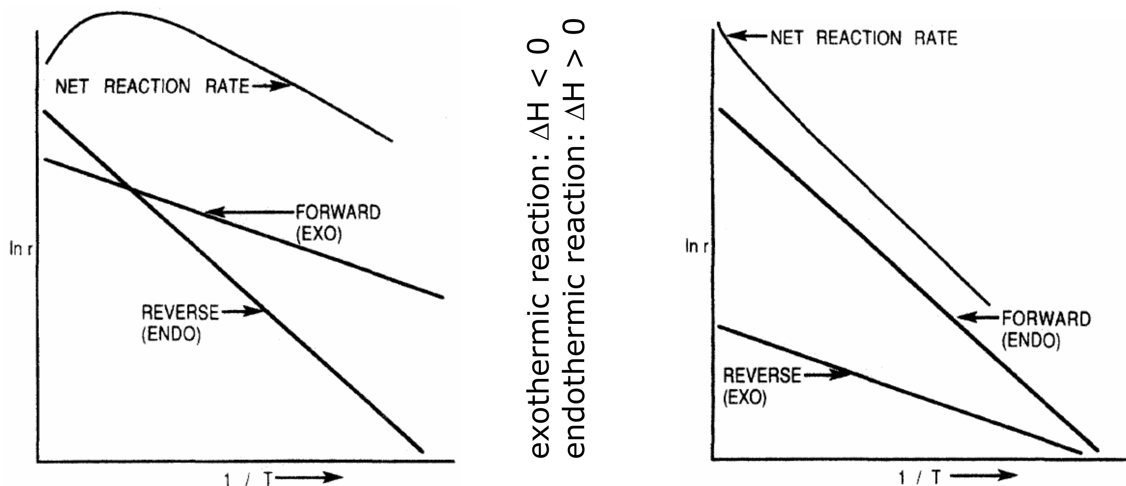


Figure 6-13 Deposition rate of Si from four different precursor gases as a function of temperature. (From W. Kern, in *Microelectronic Materials and Processes*, ed. R. A. Levy, reprinted with permission of Kluwer Academic Publishers, 1989.)

Film growth is carried out in the diffusion controlled region where the temperature response of the system is relatively flat.

The effect of temperature 4.

If the reaction leading to film formation is reversible



Reversible reaction

deposition at low T
etching at high T

deposition at every T

Hot-wall reactors are used to prevent deposition on the walls (e.g. GaAs deposition).

Thermodynamics transfers material (e.g. Si) from the cooler regions to the hotter ones → ***cold-wall*** reactors