ECE 416/516
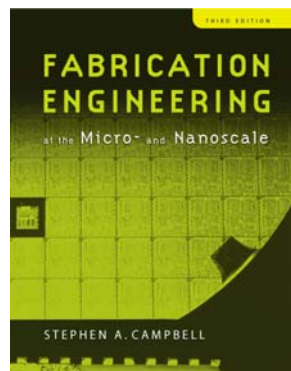# IC Technologies
Lecture 15:
Chemical Vapor Deposition (CVD)
& Epitaxial Growth

Professor James E. Morris
Spring 2012

Chapter 13

Chemical Vapor Deposition

Lecture Topics & Objectives

Topics

- Introduction
  - CVD Reactors
  - CVD Reactions
  - CVD Temperatures
  - CVD Process
- Reaction Thermodynamics
- Gas Transport
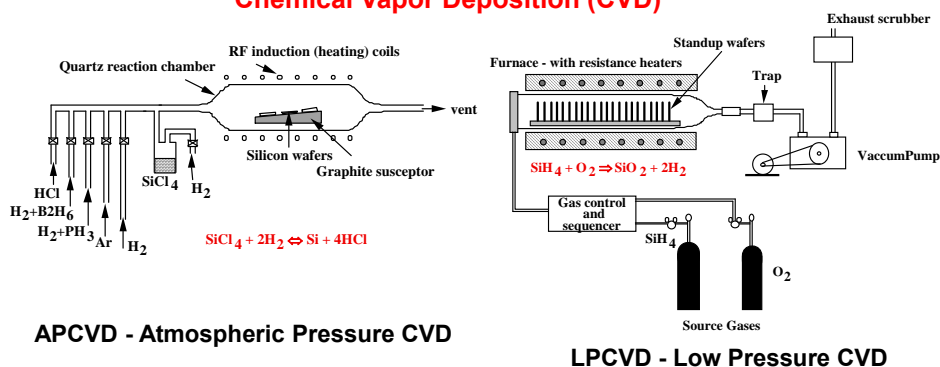- Growth Kinetics

Objectives

- Become familiar with CVD concepts
- Be able to calculate reagent concentrations, growth rates

Historical Development and Basic Concepts

Two main deposition methods are used today:
1. Chemical Vapor Deposition (CVD)   **2. Physical Vapor Deposition (PVD)**
   - APCVD, LPCVD, PECVD, HDPCVD   **- evaporation, sputter deposition**

Chemical Vapor Deposition (CVD)

RF induction (heating) coils

Quartz reaction chamber

vent

Silicon wafers

Graphite susceptor

HCl
H_2+B2H_6
H_2+PH_3 Ar H_2
$SiCl_4$ H_2

$SiCl_4 + 2H_2 \Leftrightarrow Si + 4HCl$

APCVD - Atmospheric Pressure CVD

Exhaust scrubber

Standup wafers

Furnace - with resistance heaters

Trap

VaccumPump

$SiH_4 + O_2 \Rightarrow SiO_2 + 2H_2$

Gas control
and
sequencer

SiH_4

O_2

Source Gases

LPCVD - Low Pressure CVD

4

Basic CVD concepts

Example: Si deposition by CVD (assume atmospheric pressure (APCVD))

Silane $\qquad$ $SiH_4(g) \leftrightarrow Si(s) + 2H_2(g)$

1% SiH_4 in H_2

Inlet pressure P
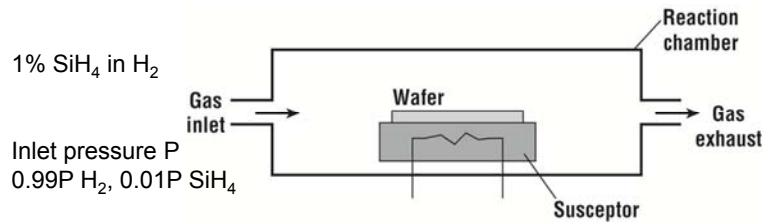0.99P H_2, 0.01P SiH_4
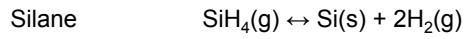

Figure 13.1 A simple prototype thermal CVD reactor.

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Micro- and Nanoscale $\qquad$ Campbell $\qquad$ Copyright © 2009 by Oxford University Press, Inc.

Actually: $\qquad$ $SiH_4(g) \leftrightarrow SiH_2(g) + 2H(g)$
with reaction constant : $\qquad$ $K_P(T) = p_{SiH2}\, p_H{}^2/p_{SiH4} = K_0 exp\text{-}\Delta G/kT$

Then: $\quad SiH_2(g) \leftrightarrow SiH_2(a)$
$SiH_2(a) \leftrightarrow Si(s) + H_2(g)$
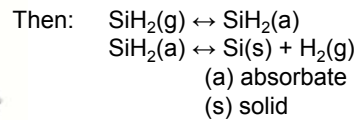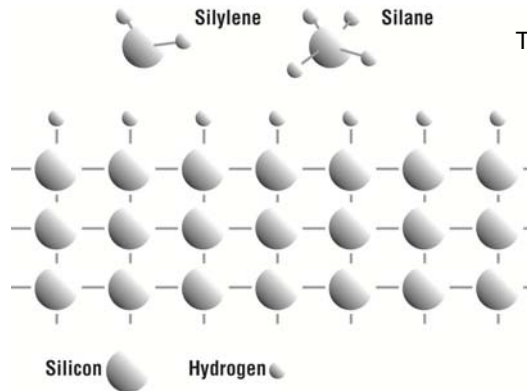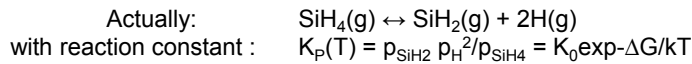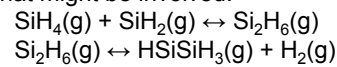(a) absorbate
(s) solid

Figure 13.3 A simple model of the surface of the wafer
during silane CVD includes adsorbed SiH_4 and SiH_2.

Other reactions that might be involved:
$SiH_4(g) + SiH_2(g) \leftrightarrow Si_2H_6(g)$
$Si_2H_6(g) \leftrightarrow HSiSiH_3(g) + H_2(g)$

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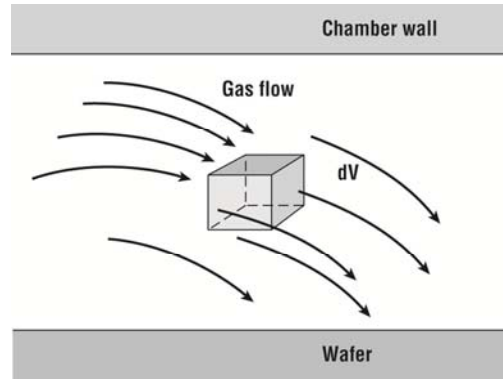
Chemistry:

$$P = p_{SiH4} + p_{SiH2} + p_H + p_{H2}$$

Figure 13.2 A volume element *dV* at some point in the gas above the surface of the wafer.

$$\frac{Si}{H} = \frac{f_{SiH_4}}{4f_{SiH_4} + 2f_{H_2}} = \frac{p_{SiH_4}}{4p_{SiH_4} + 2p_{H_2} + p_H} \text{ where f's are flow rates}$$

Ex. 13.1: For source gas AB & reaction AB↔A+B @ 1 atmos & 1000K, calculate partial pressures

Also given: reaction constant at equilibrium

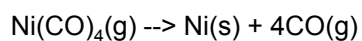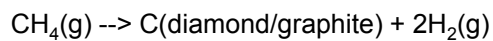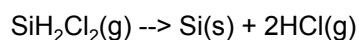$$K(T)=1.8x10^9 \text{ torr.exp} -(2.0eV/kT) = 0.15 \text{ torr}$$

so $0.15 = \dfrac{p_A p_B}{p_{AB}}$ and $P = p_A + p_B + p_{AB}$ and $p_A = p_B$

so $p_A^2 + 0.3p_A - 0.15P = 0$

For $P = 760$torr, $p_A = p_B = 10.5$ torr, $\& \ p_{AB} = 739$ torr

CVD Reactions #1

Pyrolysis: thermal decomposition

$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

$SiH_2Cl_2(g) \rightarrow Si(s) + 2HCl(g)$

$CH_4(g) \rightarrow C(diamond/graphite) + 2H_2(g)$

$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$

Oxidation:

$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$

$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12H_2(g)$

Hydrolysis:

$2AlCl_3(g) + 3H_2O(g) \rightarrow Al_2O_3(s) + 6HCl(g)$

Reduction:

$WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$
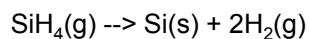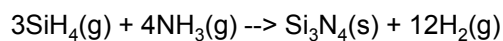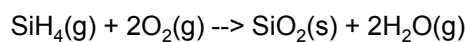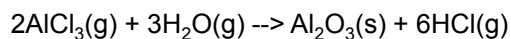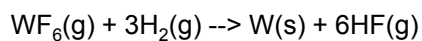
CVD Reactions #2

Displacement:

$Ga(CH_3)_3(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g)$

$ZnCl_2(g) + H_2S(g) \rightarrow ZnS(s) + 2HCl(g)$

$2TiCl_4(g) + 2NH_3(g) + H_2(g) \rightarrow TiN(s) + 8HCl(g)$

Disproportionation:

Assume low flow rates, incompressible gases, for laminar flow

Then

$$v(r) = \frac{1}{4\eta}\frac{dp}{dz}\left(a^2 - r^2\right)$$ (parabolic flow rate)

$\downarrow 2a$

U$_\infty$ → v

z →

U=0 at surfaces after

$$z_v = \frac{a}{25}N_{Re}$$ (Reynolds number)

$$= \frac{a}{25}U_\infty\frac{L}{\mu} = \frac{a}{25}U_\infty\frac{L\rho}{\eta}$$

L characteristic of chamber (~a)   μ kinematic viscosity
P density   η dynamic viscosity

Flow is turbulent for N$_{Re}$>2300 (H$_2$)

Figure 13.4 Flow development in a tubular reactor. The gas enters with a simple plug flow on the left and exits with a fully developed parabolic flow.

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Boundary layer approximation:

$$\delta \approx 5\sqrt{\frac{\mu z}{U_\infty}}$$

Diffusion coefficient:

$$D_e \propto T^{3/2}\frac{p_g}{P}$$

z→

Figure 13.5 (A) Gas flow as predicted by a parabolic flow model and in the stagnant layer approximation. (B) Stagnant layer thickness versus position assuming a plug flow inlet.
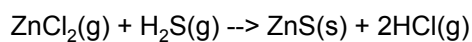
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Gas Transport

Viscous Flow: $p \geq 0.01 \text{atmos}$

Laminar Flow: 10's cm/sec

Flow: Flat Plate
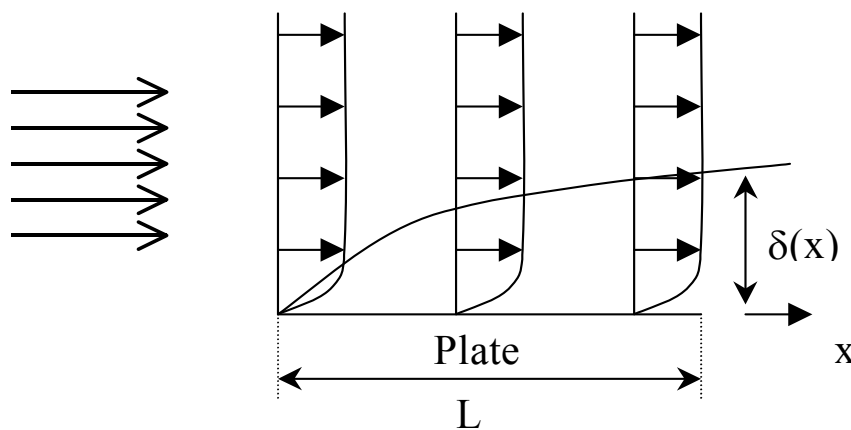
Development of Boundary Layer

$\delta(x)=5x/(Re_x)^{1/2}$

Re_x = Reynolds number = $V_0 \rho x/\eta$

ρ = gas density

η = gas viscosity

Average boundary layer thickness

$\delta_{AV} = L^{-1}\int_0^L \delta(x)dx \qquad = (10/3)L(\eta/V_0\rho L)^{1/2}$

$$= (10/3)L(Re_L)^{-1/2}$$

Need Re < 2100 or goes turbulent

Flow in Tube

Effect of plate, e.g. wafer susceptor

plate
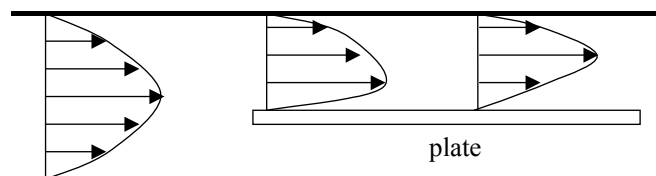
Flow in Tube: Fully Developed

All boundary layer beyond $L_e \approx 0.07\, r_0\, Re$
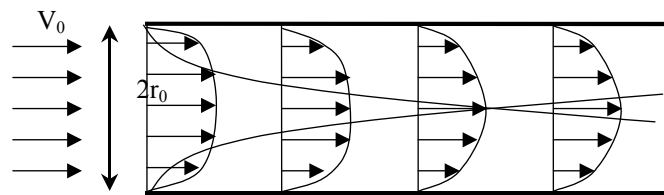
Axial flow (Hagen-Poiseuille)

Volumetric flow rate

$$V = (\Pi r_0^4 / 8\, \eta)\, \Delta P/\Delta x = \Pi r_0^2\, v$$

$$v(r) = v_{max}(1 - r^2/r_0^2)$$

η for gases independent of P

$\eta \propto T^{1/2}$ (theory); $\eta \propto T^n$ (expt) where $0.6 < n < 1.0$

Gas Flux & Diffusion

$J_i = C_i\, v_i$ where concentration $C_i = P_i / RT$ from gas law

$v_i = V / \pi r_0^2$, so $J_i = (P_i / RT)(r_0^2/8\eta)\Delta P_i/\Delta x)$

For diffusion: $J_i = - (D/RT)(dP_i/dx)$

$$= - D\,(P_i - P_{io}) / \delta RT$$

for diffusion across boundary layer

Diffusion constant in gases:-

$D = D_0\,(P_0/P)(T/T_0)^n$, where $n \approx 1.8$; D_0, P_0, T_0 at NTP

[Note LPCVD for increased D]

Convection

$$\rho = \frac{nm}{V} = \frac{Pm}{kT}$$

Gas heated at susceptor (center)
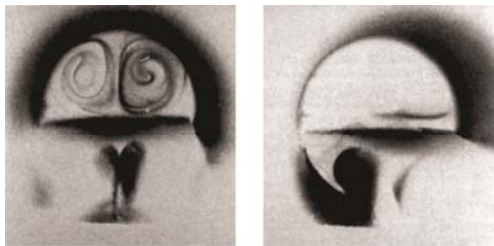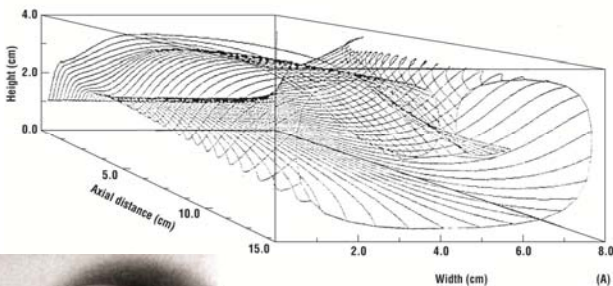
Figure 13.6 Flow field for a square cross section CVD reactor showing roll cells *(after Moffat).* Roll cells in hemispherical tubes at 760 torr (left) and 160 torr (right) *(after Takahashi et al., reprinted by permission of the publisher, The Electrochemical Society).*

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Use convection ↑ to oppose flow ↓

High flow/low pressure   Low flow/high pressure

Figure 13.7   Buoyancy-driven recirculation cells.

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Figure 13.8 Typical deposition rates for CVD
as a function of the temperature with flow rate as a parameter.

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CVD Process Steps

- Transport & Homogeneous Reaction

- Deposition
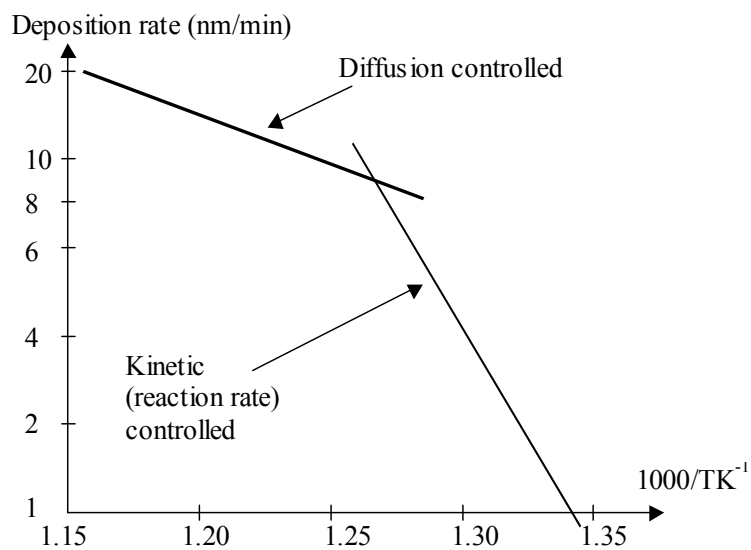
Deposition Rate #1

Deposition Rate #2

Gas Flow
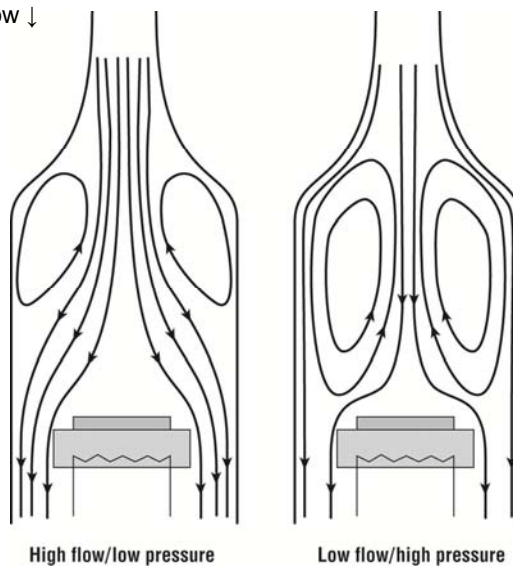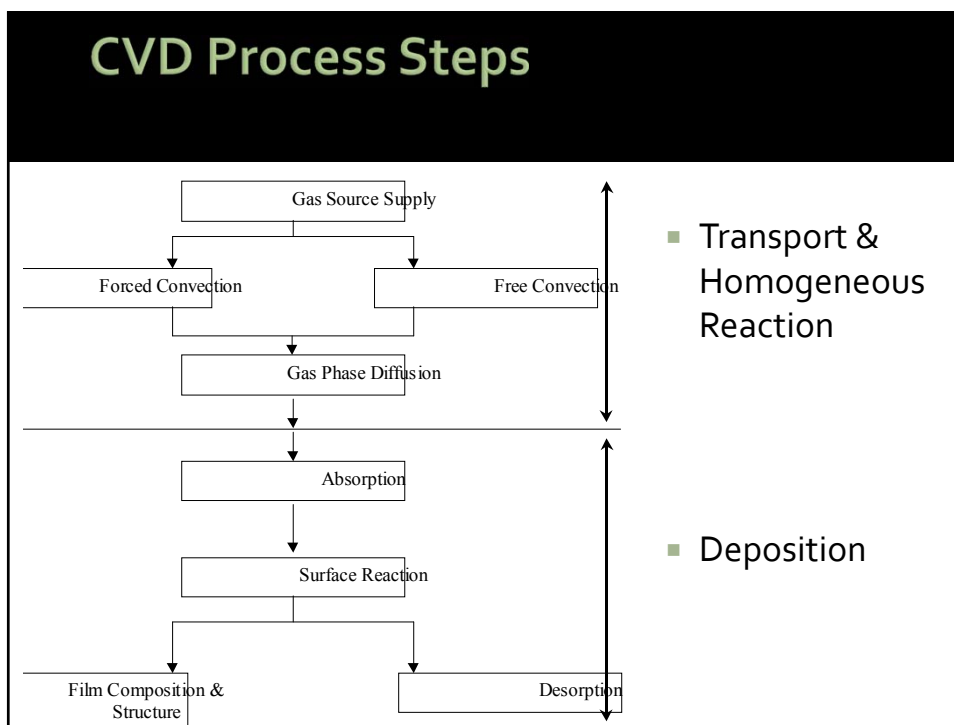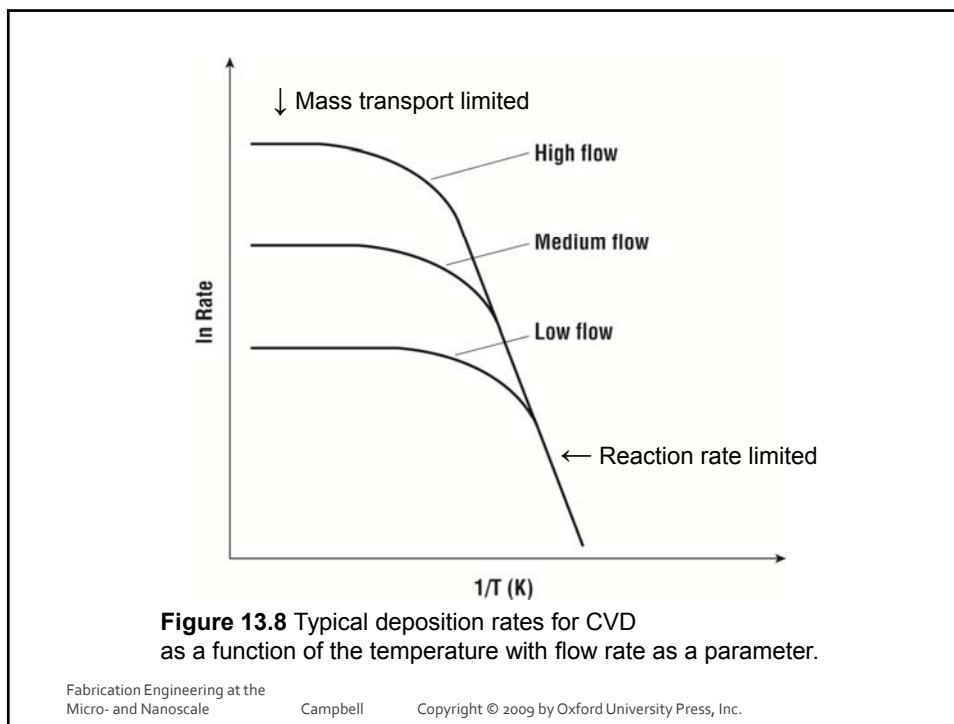
Mainstream flow

Stagnation layer
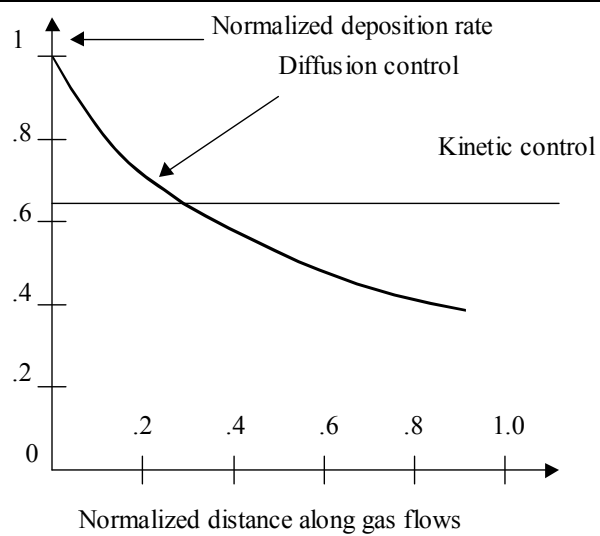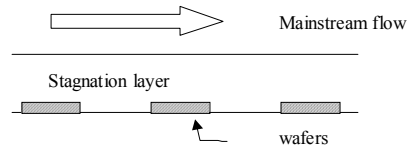
wafers

Flow perpendicular to wafers

wafer

flow

flow
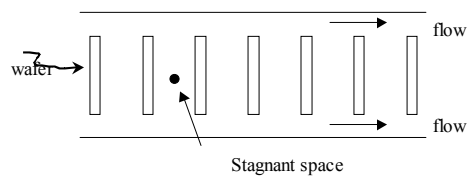
Stagnant space

Reactants Diffuse into stagnant space

Atmospheric Pressure Chemical Vapor Deposition (APCVD)

Gas stream

① ② ⑥ ⑦

③ ④ ⑤

Wafer

Susceptor
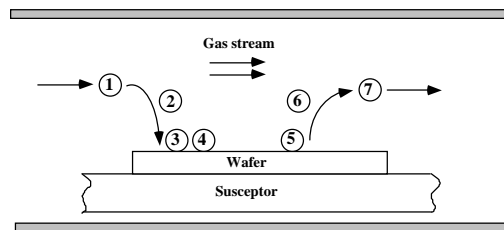
1. Transport of reactants to the deposition region.
*2. Transport of reactants from the main gas stream through the boundary layer to the wafer surface.
*3. Adsorption of reactants on the wafer surface.
*4. Surface reactions, including: chemical decomposition or reaction, surface migration to attachment sites (kinks and ledges); site incorporation; and other surface reactions (emission and redeposition for example).
*5. Desorption of byproducts.
6. Transport of byproducts through boundary layer.
7. Transport of byproducts away from the deposition region.

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Reaction/Diffusion Rate Control
See back to oxide growth

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

h_g gas phase mass transfer coefficient

$J_s = k_S C_s$

k_S surface reaction rate constant

$J_s = J_{gs}$ gives $C_s = C_g / (1 + k_s / h_g)$
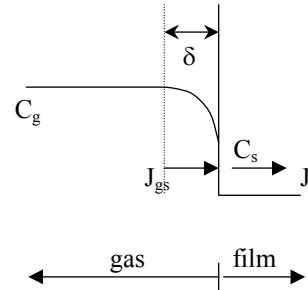
Film growth rate $g = J_s/N_0 = [k_s h_g/(k_s + h_g)](C_g/N_0)$

(N_0 = atomic density/unit vol. of film)

Mass Transfer (diffusion) rate control $h_g \ll k_s$

Reaction (kinetic) rate control $k_s \ll h_g$

Temperature Dependence₂

Boundary layer

Gas | Silicon

C_G

F_1 C_S

F_2

F_1 = diffusion flux of reactant species to the wafer
= mass transfer flux, step 2

$$F_1 = h_G(C_G - C_S) \qquad (4)$$

where h_G is the mass transfer coefficient (in cm/sec).

F_2 = flux of reactant consumed by the surface reaction
= surface reaction flux, steps 3-5

$$F_2 = k_S C_S \qquad (5)$$

where k_S is the surface reaction rate (in cm/sec).

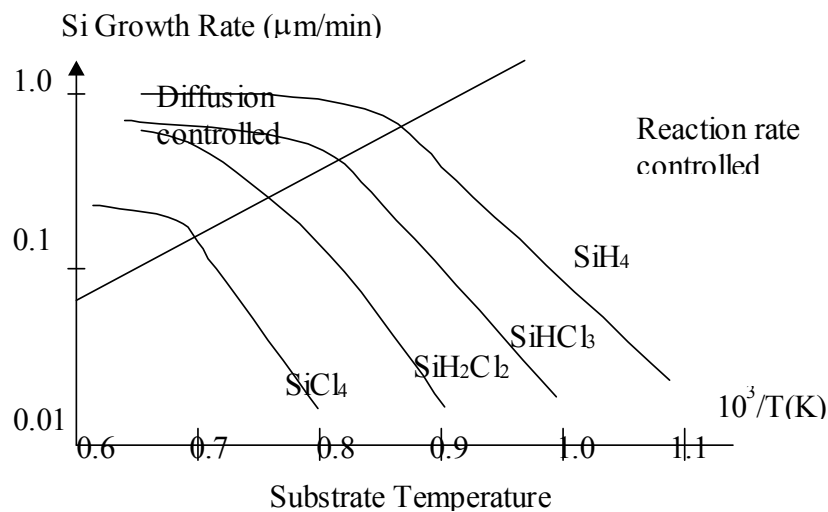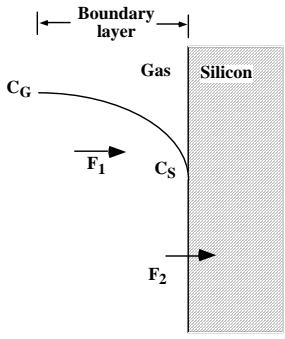In steady state: $F = F_1 = F_2$ $\qquad (6)$

Equating Equations (4) and (5) leads to $\qquad C_S = C_G\left(1 + \dfrac{k_S}{h_G}\right)^{-1} \qquad (7)$
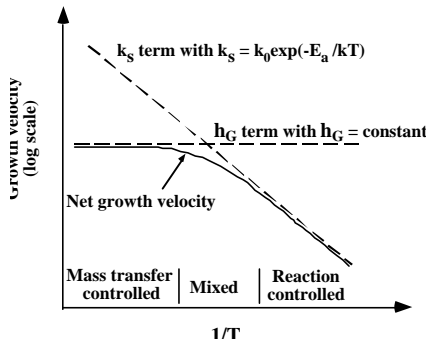
The growth rate of the film is now given by $v = \dfrac{F}{N} = \dfrac{k_S h_G}{k_S + h_G}\dfrac{C_G}{N} = \dfrac{k_S h_G}{k_S + h_G}\dfrac{C_T}{N}Y \qquad (8)$

where N is the number of atoms per unit volume in the film (5×10^{22} cm^{-3} for the case of epitaxial Si deposition) and Y is the mole fraction (partial pressure/total pressure) of the incorporating species.

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$$v = \frac{F}{N} = \frac{k_S h_G}{k_S + h_G}\frac{C_G}{N} = \frac{k_S h_G}{k_S + h_G}\frac{C_T}{N}Y$$

1. If $k_S \ll h_G$, then we have the surface reaction controlled case: $\qquad v \cong \dfrac{C_T}{N}k_S Y \qquad (9)$

2. If $h_G \ll k_S$, then we have the mass transfer, or gas phase diffusion, controlled case: $\qquad v \cong \dfrac{C_T}{N}h_G Y \qquad (10)$

Growth velocity (log scale)

k_S term with $k_S = k_0\exp(-E_a/kT)$

h_G term with h_G = constant

Net growth velocity

Mass transfer controlled | Mixed | Reaction controlled

1/T

• The surface term is Arrhenius with E_A depending on the particular reaction (1.6 eV for single crystal silicon deposition).
• h_G is ≈ constant (diffusion through boundary layer).
• As an example, Si epitaxial deposition is shown in the next slide (at 1 atm. total pressure). Note same E_A values and h_G ≈ constant. Rate is roughly proportional to (mol. wt.)$^{-1/2}$.

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Temperature (ᵒC)

Growth rate (microns min⁻¹)

Mass transfer limited

Reaction limited

$SiH_4(N_2)$

SiH_4

SiH_2Cl_2
SiHCl₃
$SiCl_4$

$10^3/T(K) \longrightarrow$

Key points:
- k_S limited deposition is VERY temp sensitive.
- h_G limited deposition is VERY geometry (boundary layer) sensitive.

- Si epi deposition often done at high T to get high quality single crystal growth. ∴ h_G controlled. ∴ horizontal reactor configuration.
- h_G corresponds to diffusion through a boundary layer of thickness δ_S.

Assumed $F_1 = h_g(C_g - C_s)$
Fick's Law for the boundary layer → $\quad F_1 = -D_g \frac{\partial C}{\partial x} = \frac{D_g}{\delta_s}(C_g - C_s)$

- But typically δ_S is not constant as the gas flows along a surface.
∴ special geometry is required for uniform deposition.

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Concentration Example

e.g. Si/Cl/H systems:

$SiCl_4$

$SiCl_3H$

$SiCl_2H_2$

$SiClH_3$

SiH_4

$SiCl_2$

HCl

H_2

Si/Cl/H Reactions #1

$$SiCl_4(g) + 2H_2(g) \longleftrightarrow Si(s) + 4HCl(g)$$
$$\rightarrow K_1 = (a_{Si})P_{HCl}^4/P_{SiCl_4} P_{H_2}^2$$
$$SiCl_3H(g) + H_2(g) \longleftrightarrow Si(s) + 3HCl(g)$$
$$\rightarrow K_2=(a_{Si}) P_{HCl}^4 / P_{SiCl_3H} P_{H_2}$$
$$SiCl_2H_2(g) \longleftrightarrow Si(s) + 2HCl(g)$$
$$\rightarrow K_3=(a_{Si}) P_{HCl}^2 / P_{SiCl_2H_2}$$
$$SiClH_3(g) \longleftrightarrow Si(s) + HCl(g) + H_2(g)$$
$$\rightarrow K_4=(a_{Si}) P_{HCl} P_{H_2} / P_{SiClH_3}$$
$$SiCl_2(g) + H_2(g) \longleftrightarrow Si(s) + 2HCl(g)$$
$$\rightarrow K_5=(a_{Si}) P_{HCl}^2 / P_{SiCl_2} P_{H_2}$$
$$SiH_4(g) \longleftrightarrow Si(s) + 2H_2(g)$$
$$\rightarrow K_6 =(a_{Si}) P_{H_2}^2 / P_{SiH_4}$$
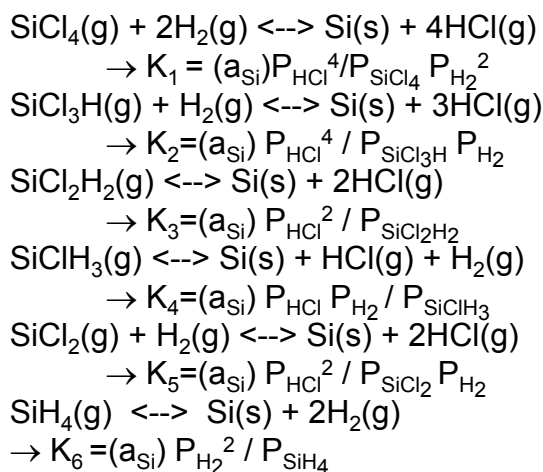
Si/Cl/H Reactions #2

Assume Si activity a_{Si}=1 and solve for 8 partial pressures

Need sum of partial pressures = total pressure

(Assume here, total = 1 atmosphere)

$$P_{SiCl_4} + P_{SiCl_3H}+ P_{SiCl_2H_2}+ P_{SiClH_3}+ P_{SiH_4}+ P_{SiCl_2}+ P_{HCl}+ P_{H_2} = 1$$

Cl/H ratio fixed

$$(Cl/H) = (4P_{SiCl_4} + 3P_{SiCl_3H}+ 2P_{SiCl_2H_2}+ P_{SiClH_3}+ P_{HCl}+ 2P_{SiCl_2})$$
$$\div (2P_{H_2}+ P_{SiCl_3Hm}+ 2P_{SiCl_2H_2} + 3P_{SiClH_3}+ P_{HCl}+ 4P_{SiH_4})$$

Find each term from (e.g. for Cl in $SiCl_4$):-

$$m_{Cl}=4M_{Cl}(m_{SiCl_4} / M_{SiCl_4}) \quad \& \ m_{SiCl_4}/ M_{SiCl_4} = P_{SiCl_4}V / RT$$

i.e. Number of moles Cl in $SiCl_4$ = m_{Cl} / M_{Cl} = $4P_{SiCl4}V / RT$

Si/Cl/H Reactions #3

To use, need K_i's

Ellingham diagram: $\Delta G° = \Delta H - T\Delta S$
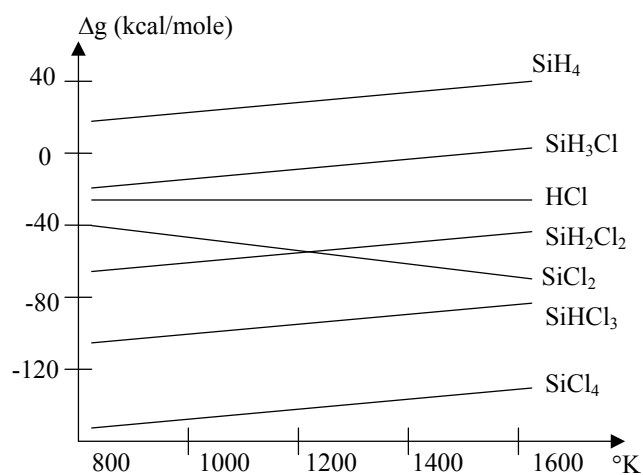
Si/Cl/H Reactions #4

For $SiCl_4$, HCl at 1500 K

$Si + 2Cl_2 \longleftrightarrow SiCl_4$ $\Delta G° = -106$ Kcal/mole

$(1/2)H_2 + (1/2)Cl_2 \longleftrightarrow HCl$ $\Delta G° = -25$ Kcal/mole

$\therefore SiCl_4 + 2H_2 \longleftrightarrow Si + 4HCl$
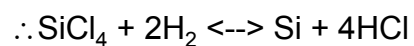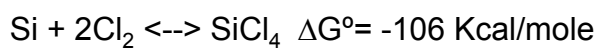
$\Delta G° = +106 + 4(-25) = +6$ Kcal/mole

& $K_1 = \exp -6000/(1.99)1500 = 0.13$

etc... for other K_i's

Si/Cl/H Reactions #5

Results (& for Si/Cl)

Reaction Example: Y_2O_3

$2YCl_3(g) + (3/2)O_2(g) \longleftrightarrow Y_2O_3(s) + 3Cl_2(g)$
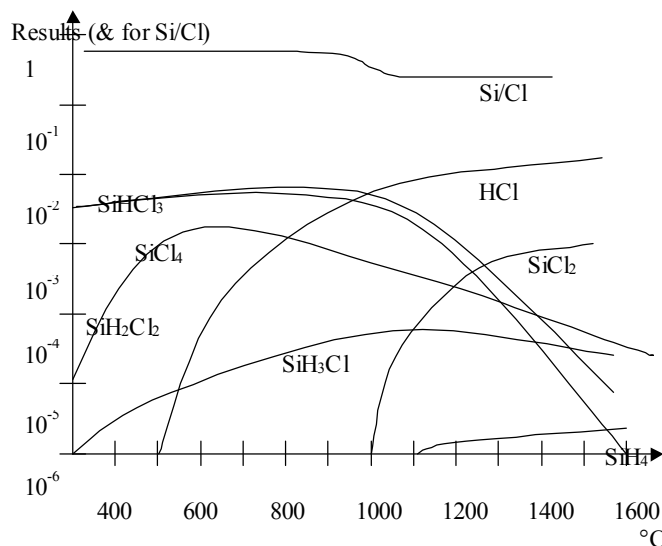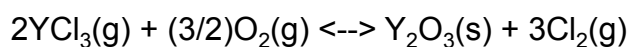
At 1000K; $\Delta G^o = -59.4$ Kcal/mole, i.e log K=+13
∴ Equilibrium too far right (Reaction too fast)

YBr_3, YI_3 less stable; ΔG^o more negative

Add gas phase reaction with $\Delta G^o > 0$ to slow
e.g. $CO_2(g) \longleftrightarrow CO(g) + (1/2)O_2(g)$; $\Delta G^o = +46.7$ Kcal

So overall:
$2YCl_3(g) + 3CO_2(g) \longleftrightarrow (1/2)O_3(g) + 3CO(g) + Cl_2(g)$
with $\Delta G^o = -59.4 + 3(46.7) = +80.7$ Kcal, i.e. now to left
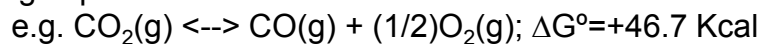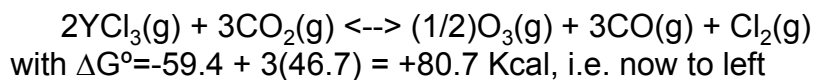
So use YBr_3 or YI_3. For YBr_3 now $\Delta G^o = -27$ Kcal/mole

Reaction Thermodynamics

aA +bB <--> cC
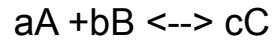
Free energy change: $\Delta G = cG_C - aG_A - bG_B$
where $G_i = G_i^o + RT \ln a_i$
where G_i^o is reference to free energy
and "activity" a_i is effective concentration

$\Delta G = \Delta G^o + RT \ln (a_C{}^c / a_A{}^a a_B{}^b)$
where $\Delta G^o = cG_C^o - aG_A^o - bG_B^o$

For equilibrium, $0 = \Delta G^o + RT \ln (a_{C(eq)}{}^c / a_{A(eq)}{}^a a_{B(eq)}{}^b)$
or $-\Delta G^o = RT \ln K$

So $\Delta G = RT \ln[(a_C / a_{C(eq)})^c / (a_B / a_{B(eq)})^b / (a_A / a_{A(eq)})^a]$

APCVD (high rate → thick dielectric)
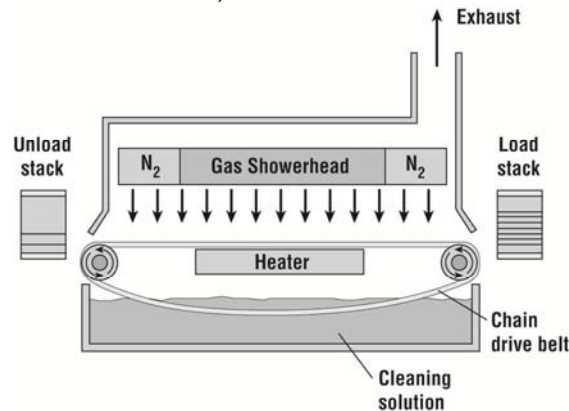
Figure 13.9 Simple continuous-feed atmospheric pressure reactor (APCVD).

$O_2 : SiH_4 \geq 3:1 \rightarrow SiO_2$
N_2 dilutes/slows reaction

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Add PH$_3$ for phosphosilicate glass (PSG)

SiH$_4$/PH$_3$ = 20:1
Diluent: N$_2$
Total gas flow: 11 l/min

Figure 13.10 Deposition rate of PSG in an APCVD system
(after Kern and Rosler, ®1977, AIP).

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Avoid premature reactions (gas phase nucleation)

Figure 13.11 Showerhead design used to minimize deposition at the
nozzle by maintaining an inert curtain between the reactants.

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Low Pressure Chemical Vapor Deposition (LPCVD)

- Atmospheric pressure systems have major drawbacks:
  - At high T, a horizontal configuration must be used (few wafers at a time).
  - At low T, the deposition rate goes down and throughput is again low.

- The solution is to operate at low pressure. In the mass transfer limited regime,

$$h_G = \frac{D_G}{\delta_S} \quad \text{But} \quad D_G \propto \frac{1}{P_{total}} \quad (12)$$

- D_G will go up 760 times at 1 torr, while δ_S increases by about 7 times. Thus h_G will increase by about 100 times.
- Transport of reactants from gas phase to surface through boundary layer is no longer rate limiting.
- Process is more T sensitive, but can use resistance heated, hot-walled system for good control of temperature and can stack wafers.

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LPCVD: reduces gas phase nucleation, and increases reactant transport

Hot wall:
More uniform temperature
Decreases convection
May deposit on walls

Cold wall (less wall deposits)

Figure 13.12 Common LPCVD reactor geometries.

Vertical LPCVD

5-zone heating element

Water cooled heating jacket

Figure 13.14 LPCVD process section: a low pressure process tube showing the heater, quartz tube, boat, and various gas and mechanical control mechanisms *(ASM Europe).*

Closed quartz pedestal

Paddle TC

Gas injection ring

N$^+$ doping:

POCl$_3$

AsH$_3$ or PH$_3$

Figure 13.15 Deposition rate of polysilicon as a function of temperature and of silane flow rate *(after Voutsas and Hatalis, reprinted by permission of the publisher, The Electrochemical Society).*

Use of TEOS (tetraethyloxysilane):

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2H_2O + 4C_2H_4$$
$$@ 700°C$$

$$Si(OC_2H_5)_4 + 12O_2 \rightarrow SiO_2 + 10H_2O + 8CO_2$$
$$@ 400\text{-}600°C$$

TEOS-BPSG
(O_2 = 140sccm, T_D = 640° , TMB = 6.5)
Boat d

x-axis: PH$_3$(15% in Ar) flow (sccm)
left y-axis: Dopant content [wt%]
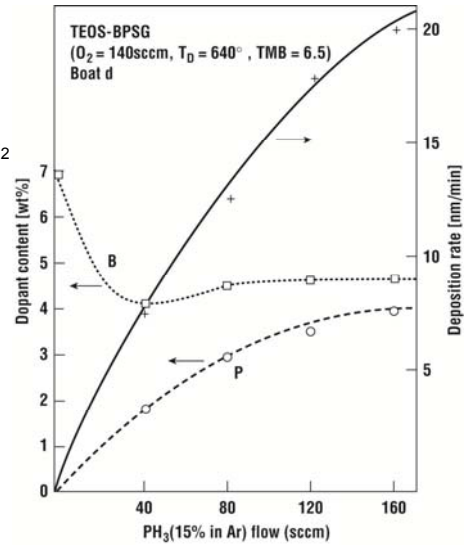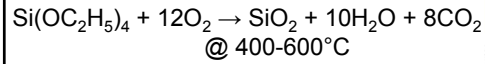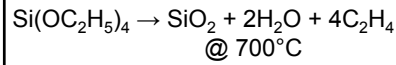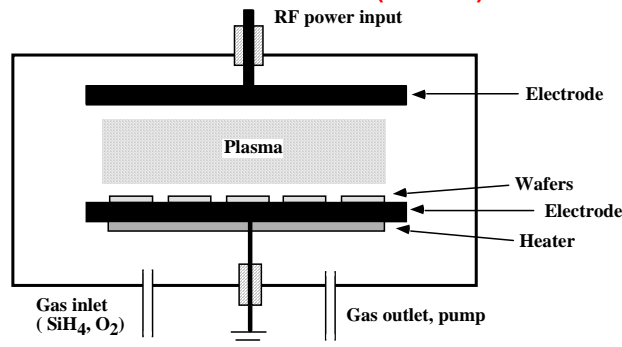*right y-axis:* Deposition rate [nm/min]

Figure 13.17 BPSG deposition rate and the boron and phosphorus concentrations as a function of phosphine flow in the TEOS/TMB system *(after Becker et al., ©1986, AIP).* *(TMB: tri-methyl bromine?)*

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Plasma Enhanced CVD (PECVD)

RF power input

Electrode

Plasma

Wafers
Electrode
Heater

Gas inlet
(SiH$_4$, O$_2$)

Gas outlet, pump

• **Non-thermal energy to enhance processes at lower temperatures.**
• **Plasma consists of electrons, ionized molecules, neutral molecules, neutral and ionized fragments of broken-up molecules, excited molecules and free radicals.**
• **Free radicals are electrically neutral species that have incomplete bonding and are extremely reactive. (e.g. SiO, SiH$_3$, F)**
• **The net result from the fragmentation, the free radicals, and the ion bombardment is that the surface processes and deposition occur at much lower temperatures than in non-plasma systems.**

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CVD Reaction Temperatures

- **Thermal SiO$_2$**
- **CVD Si$_3$N$_4$**
- **CVD SiO$_2$**
- **PECVD Si$_3$N$_4$**
- **PECVD SiO$_2$**
- **Photon-ECVD Si$_3$N$_4$**
- **Photon-ECVD SiO$_2$**

Deposition Temperature °C
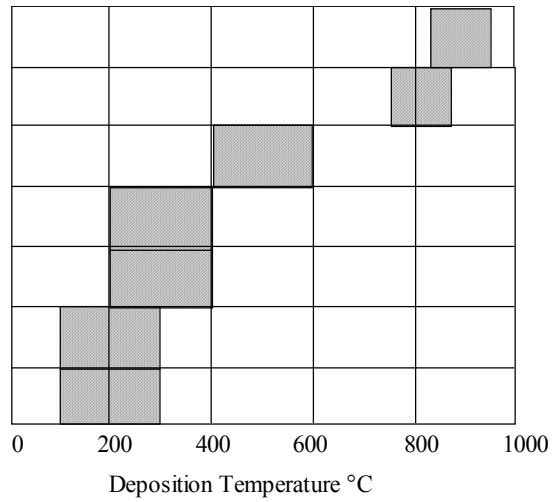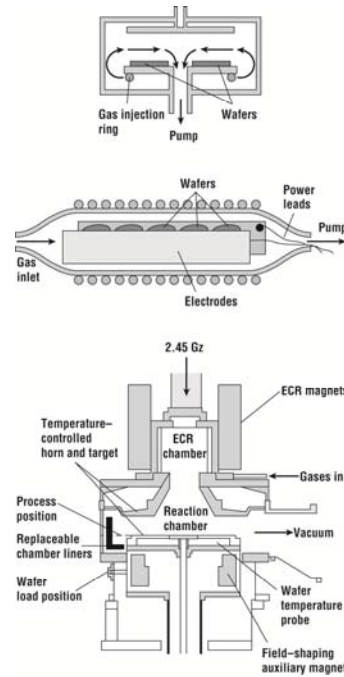
PECVD

Figure 13.18 Basic PECVD geometries: cold wall parallel plate, hot wall parallel plate, and ECR.

Figure 13.20 Deposition rate, density, and stoichiometry in the PECVD of Si₃N₄ *(after Clausen et al., reprinted by permission of the publisher, The Electrochemical Society).*

Figure 13.21 Results for the PECVD of SiO₂ *(after Van de Ven, ©1981, Solid State Technology).*
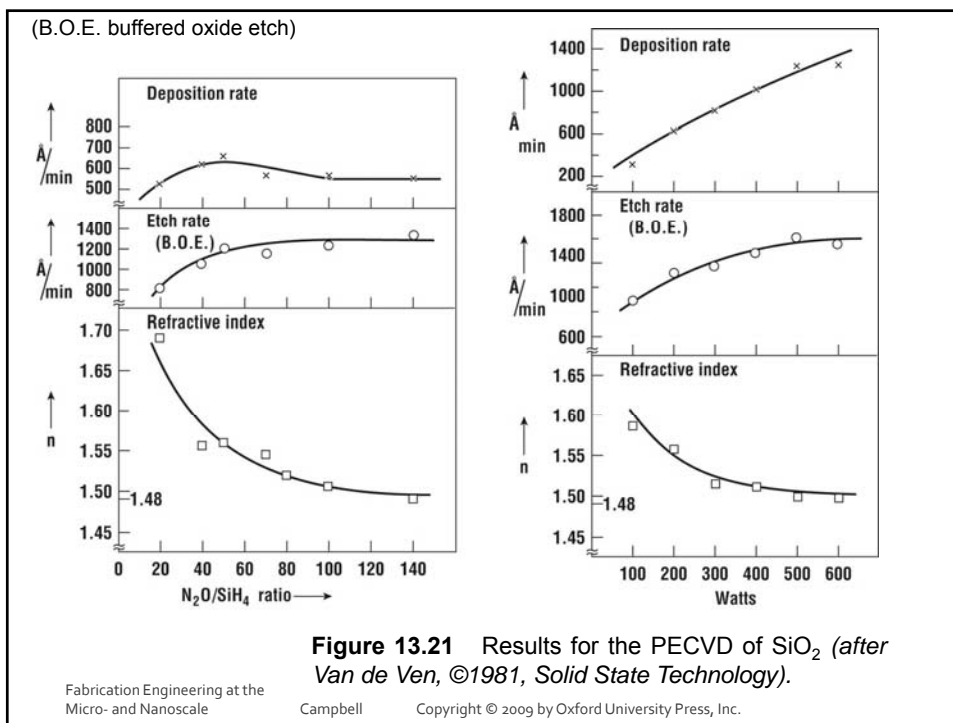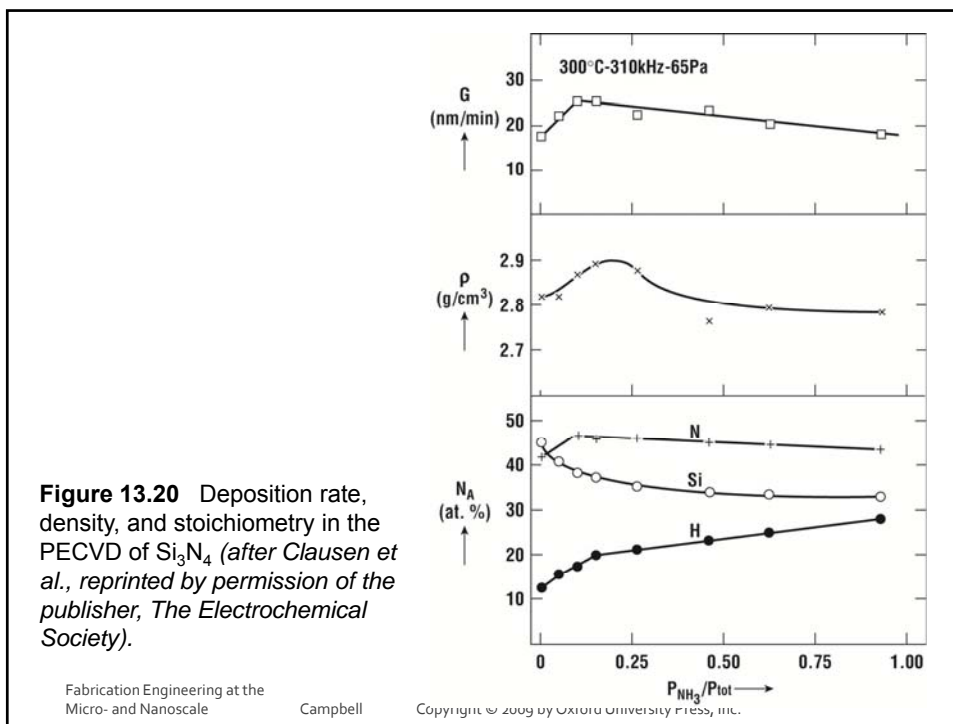
High Density Plasma (HDP) CVD

- **Remote high density plasma with independent RF substrate bias.**
- **Allows simultaneous deposition and sputtering for better planarization and void-free films (later).**
- **Mostly used for SiO$_2$ deposition in backend processes.**

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Metal CVD

Figure 13.22 The use of caps versus plug-filled contacts.

e.g. $WF_6 + 3 H_2 \leftrightarrow W + 6HF$ (WF6 liquid at 25°C)

CVD Example: CdTe #1

$CdTe(s) <--> Cd(g) + (1/2)Te_2(g)$

$\Delta G = 68.64 - 44.94 \times 10^{-3}T$ Kcal/mole

CdTe Source
T_1
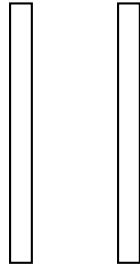
Substrate
T_2

$L \sim 1$ mm
$T_1 > T_2$
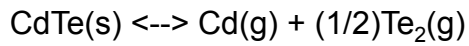
CVD Example: CdTe #2

At source:

$P_{Cd}(T_1)\ P_{Te_2}^{1/2}(T_1) = \exp - [\Delta G(T_1)/RT_1] = K(T_1)$

At substrate:

$P_{Cd}(T_2)\ P_{Te_2}^{1/2}(T_2) = \exp - [\Delta G(T_2)/RT_2] = K(T_2)$

For linear variation of concentration with distance:

$J_{Cd} = (D_{Cd}/L)\ [\ P_{Cd}(T_1)\ /\ RT_1 - P_{Cd}(T_2)\ /\ RT_2\ ]$

$J_{Te_2} = (D_{Te_2}/L)\ [\ P_{Te_2}(T_1)\ /\ RT_1 - P_{Te_2}(T_2)\ /\ RT_2\ ]$

if D independent of T

Stoichometry requires $J_{Cd} = 2\ J_{Te_2}$

$g(\mu m/min) = J_{Cd}M_{CdTe}\ (60 \times 10^4)\ /\ \rho$

& assume $P_i(T_1) >> P_i(T_2)$ for $T_1 - T_2 > 100ºC$

$\therefore P_{Cd}(T_1)\ /\ P_{Te_2}(T_1) = 2\ D_{Te_2}\ /\ D_{Cd}$

Growth Rate Uniformity #1

$\delta c/\delta y\,(x,b) = 0$

$c(0,y) = c_i$

$c(x,0) = 0$

wafers
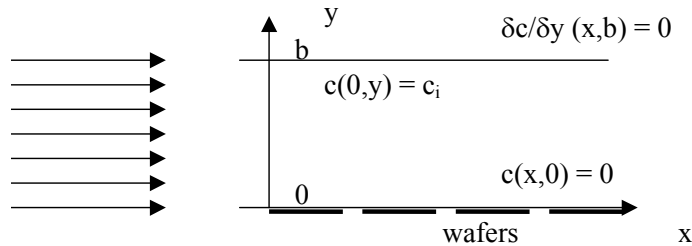
$J = C(x,y)v - D\,\nabla C(x,y)$

or Fick's law:

$\partial C(x,t)/\partial t = D[\partial^2 C(x,y)/\partial x^2 + \partial^2 C(x,y)/\partial y^2] - v[\partial C(x,y)/\partial x]$

$= 0$ for steady state

Also, $C=0$ for $y=0$, $x>0$ $\partial C/\partial y = 0$ for $y=b$, $x>0$ & $C=C_i$ for $x=0$, $b>y>0$

giving:

$C(x,y) = (4C_i/\pi)\int_{n=0}^{\infty}(2n+1)^{-1}\sin[(2n+1)(\pi y/2b)]\exp\{v/D - [(v/D)^2 + (2n+1)^2(\pi/b)2]^{1/2}x\}$

Growth Rate Uniformity #2

Approx: $vb \gg D\pi$, $x \gg 0$

$C(x,y) \approx (4C_i/\pi)\sin(\pi y/2b)\exp-(\pi^2 Dx/4vb^2)$

& $J(x) = -D[\partial C(x,y)/\partial y]_{y=0}$ at wafer surface

So growth rate $g(x) = (M_{si}/\rho M_S)J(x)$, where M_{si}, M_S molecular weights of Si, gas

$= (2C_i M_{Si}/b\rho M_s)D\exp-(\pi^2 Dx/4vb^2)$

Growth rate (μm/min)
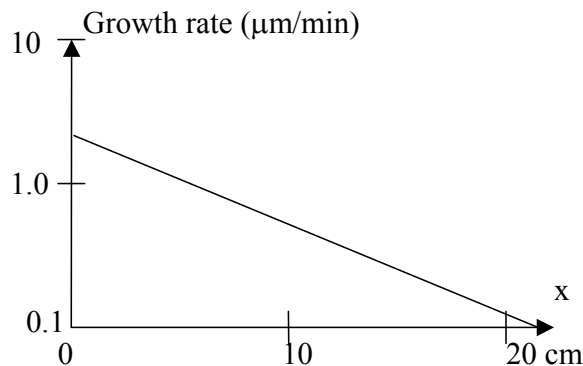
Selective W deposition:

Deposits preferentially on conductors (e.g. Si) rather than insulators (e.g. SiO_2)

Also barrier metals: (e.g. TiN, WN)

Adhesion promoters
Prevent chemical reactions

$6TiCl_4 + 8NH_3 \rightarrow 6TiN + 24HCl + N_2$
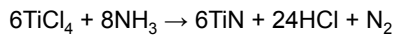
Cu CVD typically by organometallics

Atomic Layer Deposition (ALD)

Figure 13.25 Damage to the substrate produced by selective tungsten.

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Calibration of Models - Example: SPEEDIE
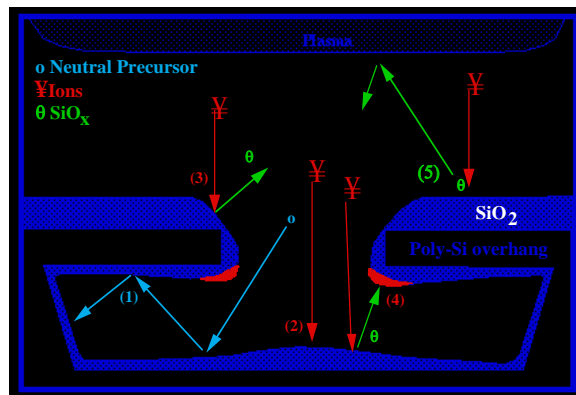
Overhang test structure allows calibration of different components

(1) CVD component
(2) Ion-induced deposition
(3) Sputtering with angle-dependent sputter yield
(4) Redeposition
(5) Backscattered deposition

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OVERHANG TEST STRUCTURE

DEPOSITION PRECURSORS

DIRECT DEPOSITION

POLY-Si OVERHANG

SURFACE DIFFUSION

INDIRECT DEPOSITION

1-4 µm

RE-EMISSION

OXIDE

SILICON SUBSTRATE

16 µm

BY OBSERVING DEPOSITION PROFILES IN THE CAVITY CONCLUSIONS CAN BE DRAWN ABOUT THE DEPOSITION MECHANISMS

* INFLUENCE OF CAVITY HIGHT ON DEPOSITION ON THE UNDERSIDE
* TAPERING OF THICKNESS ON TOP SURFACE

J.P. McVittie, J.C. Rey, L.Y. Cheng, and K.C. Saraswat, "LPCVD Profile Simulation Using a Re-Emmission Model", IEDM Tech. Digest, 917-919 (1990)

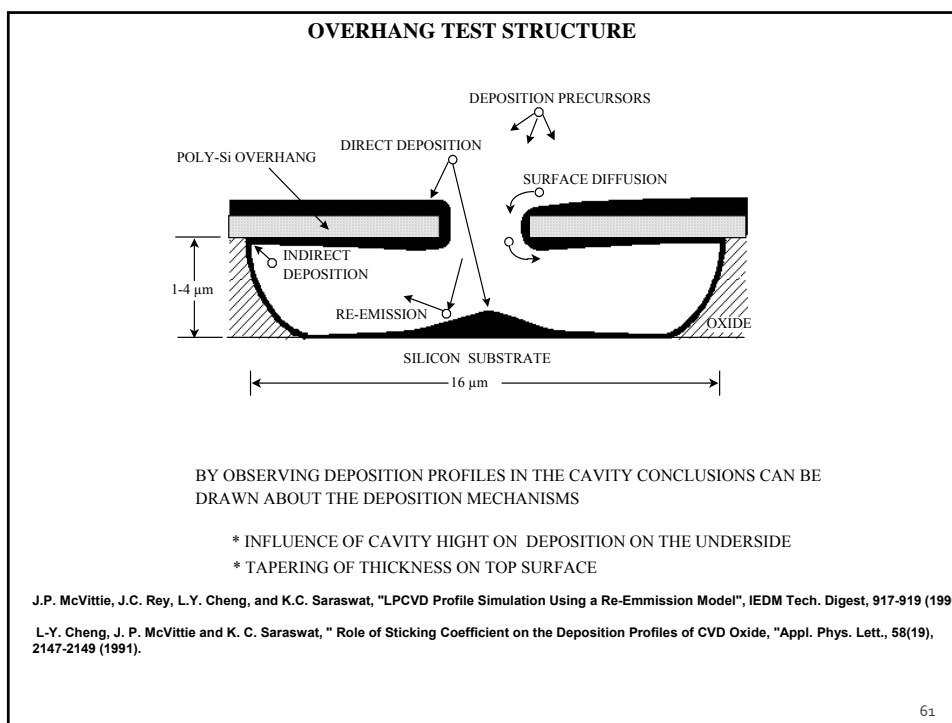L-Y. Cheng, J. P. McVittie and K. C. Saraswat, " Role of Sticking Coefficient on the Deposition Profiles of CVD Oxide, "Appl. Phys. Lett., 58(19), 2147-2149 (1991).

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Parameter Values for Specific Systems

	n (exponent in cosine arrival angle distribution)	S_C (sticking coefficient)
Sputter deposition		
-standard	~ 1 - 4	~1
-ionized or collimated	8 - 80	~1
Evaporation	3 - 80	~1
LPCVD silicon dioxide		
- silane	1	0.2 - 0.4
-TEOS	1	0.05 - 0.1
LPCVD tungsten	1	0.01 or less
LPCVD polysilicon	1	0.001 or less

- PVD systems - more vertical arrival angle distribution (low pressure line of sight or ε field driven ions). $\therefore$ n > 1 typically.
- CVD systems provide isotropic arrival angle distributions (higher pressure, gas phase collisions, mostly neutral molecules). $\therefore$ n ≈ 1 typically.
- PVD systems usually provide S_c of 1. Little surface chemistry involved. Atoms arrive and stick.
- CVD systems involve surface chemistry and S_c <<1. Molecules often reemit and redeposit elsewhere before reacting.

$\therefore$ CVD systems provide more conformal deposition.

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Summary of Key Ideas

- **Thin film deposition is a key technology in modern IC fabrication.**
- **Topography coverage issues and filling issues are very important, especially as geometries continue to decrease.**
- **CVD and PVD are the two principal deposition techniques.**
- **CVD systems generally operate at elevated temperatures and depend on chemical reactions.**
- **In general either mass transport of reactants to the surface or surface reactions can limit the deposition rate in CVD systems.**
- **In low pressure CVD systems, mass transport is usually not rate limiting.**
- **However even in low pressure systems, shadowing by surface topography can be important.**
- **A wide variety of systems are used in manufacturing for depositing specific thin films.**
- **Advanced simulation tools are becoming available, which are very useful in predicting topographic issues.**
- **Generally these simulators are based on physical models of mass transport and surface reactions and utilize parameters like arrival angle and sticking coefficients from direct and indirect fluxes to model local deposition rates.**

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Electroplated Cu:
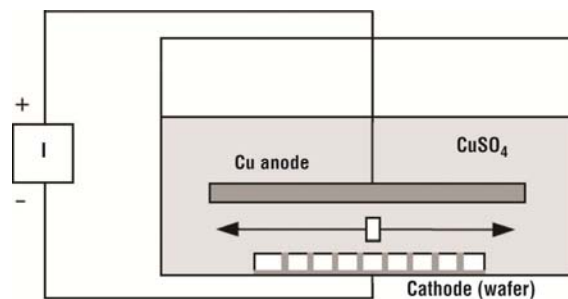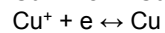
$$Cu^{2+} + e \leftrightarrow Cu^+$$
$$Cu^+ + e \leftrightarrow Cu$$
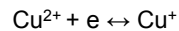
Figure 13.26 Basic electroplating setup.

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Cu requires barrier layer (diffusion)

e.g. TaN, TiN

Adhesion may require metal underlayer (Ta/TaN, Ti/TiN)
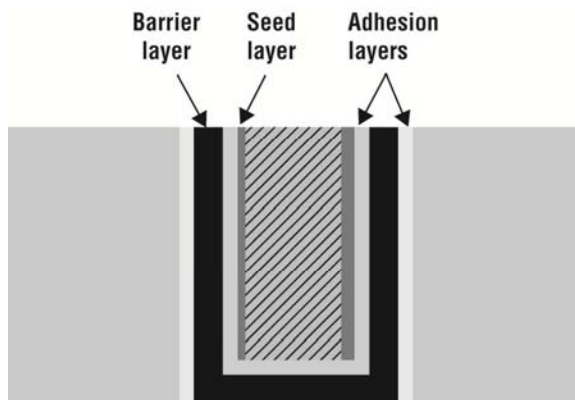
Figure 13.27 Most extreme stack in a contact, showing all of the needed layers. The crosshatched area is electroplated Cu.

Seed layer PVD Cu
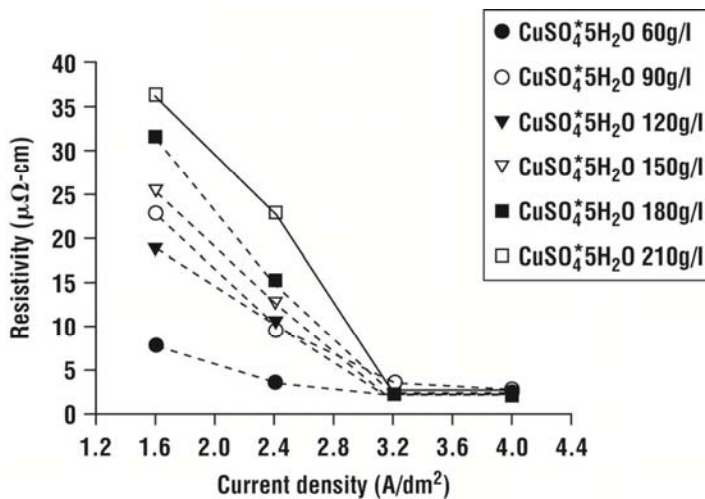
Figure 13.28 Copper resistivity as a function of the current density for various bath concentrations *(After Gau, et al., reprinted with permission from Journal of Vacuum Science and Technology. Copyright 2000 IOP Publishing).*

Chapter 14

**Epitaxial Growth**
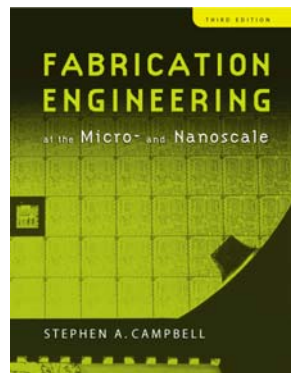
Lecture Topics & Objectives

Topics
Introduction
        VPE/MBE/LPE
Lattice mismatch
Thickness measurement
VPE chemistry
Selective epi-growth
Defects
Autodoping
MBE
LPE

Objectives

Be familiar with the
    principles and applications
    of VPE, MBE, & LPE

Able to calculate epi-layer
    doping profiles

Can calculate VPE and LPE
    growth rates.

"Single" Crystal & Epitaxial Growth

- "Single" Crystal Growth
- Thermal CVD/VPE (vapor phase epitaxy)
- MOCVD (metallorganic CVD)
- Rapid thermal VPE (RTCVD)
- Molecular beam epitaxy (MBE)

- Epitaxial Growth
- Underlying (substrate) crystal structure continued into thin film layer.
- In practice, many devices fabricated entirely within epi-layer (BJT)
- Some MOS systems on the basic Si slice, but for VLSI: better to be within the epi-layer for better control.
- Homoepitaxy and heteroepitaxy

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Epitaxial Growth: Homo/hetero, combinations

- Auto/homoepitaxy:
    grow SAME crystal structure on substrate
        - (e.g Si on Si)
- Heteroepitaxy:
    grow DIFFERENT crystal (or crystal orientation) on substrate
        - (e.g. tetrahedral/diamond Si on hexagonal Al_2o_3)
    (Usually hetero-systems use same crystal orientations)
- Inert substrate:
    -clean, doesn't grow other unwanted films
    -damage-free surface
- Substrate/layer:
    -no interdiffusion, chemical compound, etc.
    -match thermal expansion
    -match lattice parameters

Deposition Techniques

- MBE: molecular beam epitaxy
  - -UHV, molecular flow
  - -thermal evaporation, very slow
- VPE: vapor phase epitaxy
  - -CVD, MOCVD, etc.
  - -laminar, viscous flow
- LPE: liquid phase epitaxy
- Need to build surface layer atom by atom at correct sites
  - -surface adsorption
  - -surface diffusion to site
  - -nucleation in vapor or on dust, etc.
    - -> polycrystals, defects

Lattice Mismatch
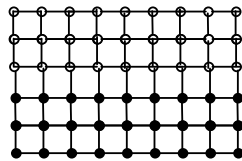
commensurate
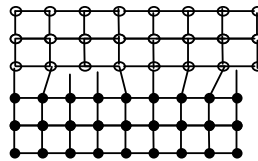
Strain relaxed incommensurate

Pseudomorphic

5/21/2012

Si on Sapphire

Basic VPE system

Figure 14.1 A simple VPE system. The susceptor in this chamber is inductively heated using RF power in the external coil.

Thermal → drive crystal growth reactions (typically 1000°C)
  → impurity diffusion, so must minimize impurities
  → high vacuum, load locks, etc

Use for compound semiconductors; concentrate on Si first
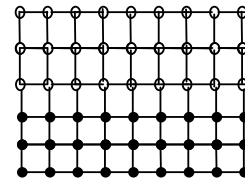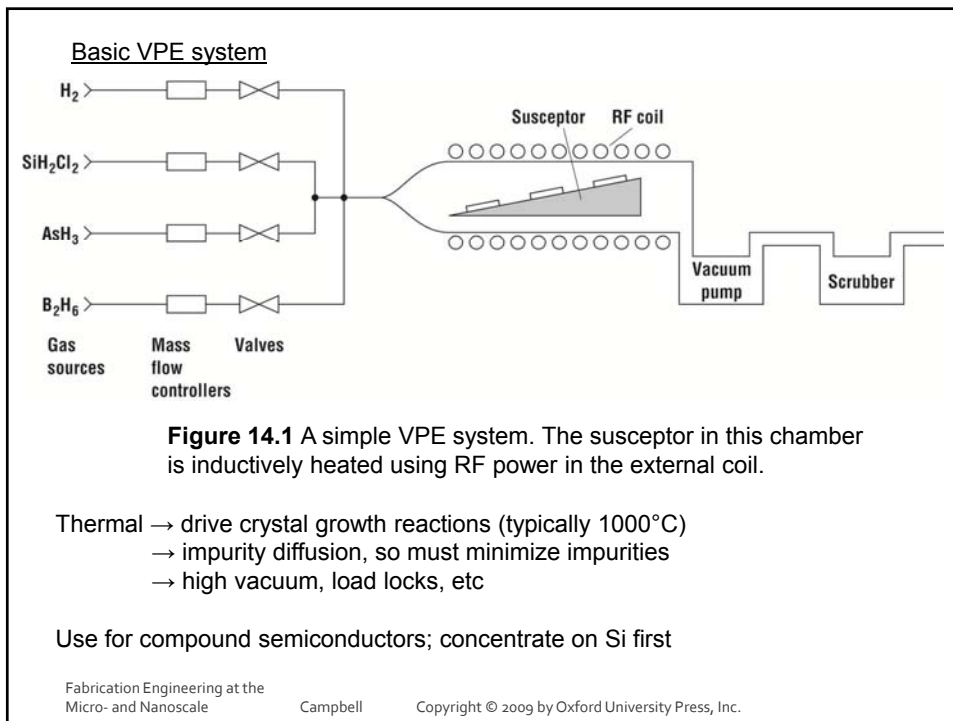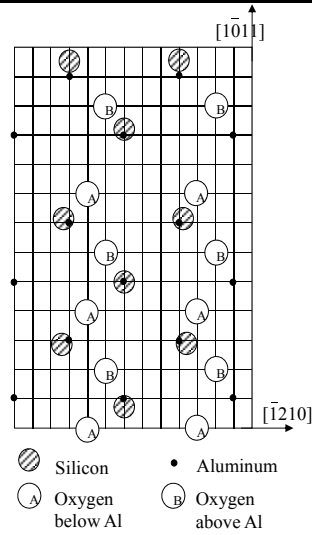
VPE: Endothermic

- See back to CVD
  for endothermic growth reaction

- In practice: epi-growth at high T,
  i.e. mass transfer rate limited.
  ∴ growth controlled by gas flow,
  rather than by surface conditions, etc.

Endothermic/Exothermic Reactions

- Endothermic growth reactions

- Exothermic growth reactions

  *Actually reaction rate limited by the ability to remove heat of reaction.

Growth rate

Reaction limited
$k \propto \exp\text{-}\Delta E/kT$

Diffusion limited
$D \propto \exp\text{-}\Delta E_D/kT$

1/T

Growth rate

Reaction limited
$k \propto \exp\text{-}\Delta E/kT$

*

1/T
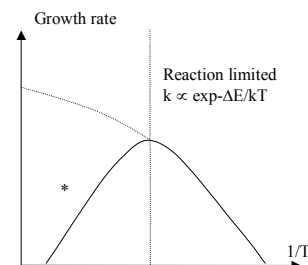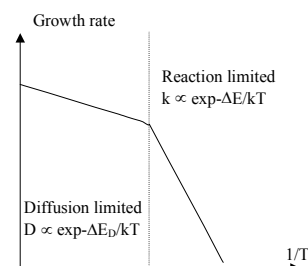
VPE Chemistry:Chlorosilanes

Si deposition (μm/min)

6

4

1270 °C
1 1 /min H$_2$

Polycrystal

2

Single crystal

0

ETCH

-2

0   .1   .2   .3   .4   .5

Mole fraction SiCl$_4$ in H$_2$

SiCl$_4$, SiHCl$_3$, SiH$_2$Cl$_2$ -> H$_2$, HCl, SiCl$_2$
in vapor phase at >1000°C.

Basic reaction (1050-1200°C):
$$2SiCl_2 <=> Si + 4HCl$$
which may <u>deposit</u> or <u>etch</u> Si.
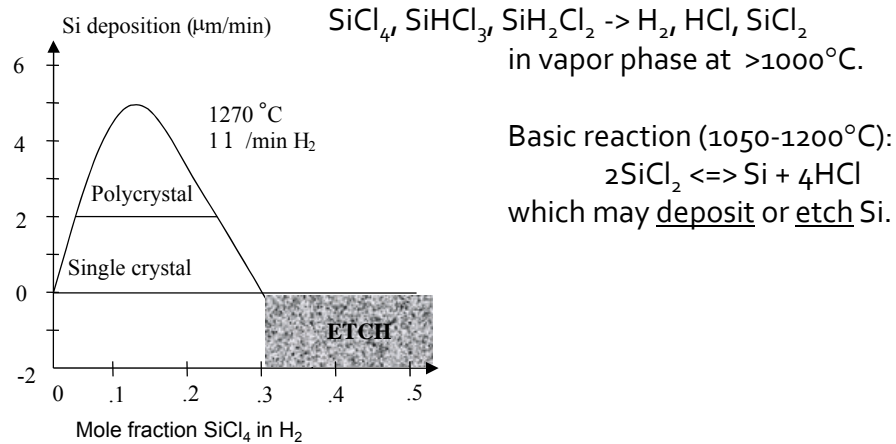
See back to CVD for thermodynamics of chlorosilane concentrations.

VPE Chemistry:
Silane & Pre-etch

- Silane:
  $$SiH_4 \text{ ---500°C---> } Si + 2H_2$$
  - Difficult to avoid homogenous nucleation in the gas phase -> polycrystals
  - Susceptible to oxidation (SiO$_2$ dust)
- Pre-etching
  $$4Si(s) + 6SF_6(g) -> SiS_2(g) + 3SiF_4(g)$$
  - Sulphur-hexafluoride:
    non-toxic, non-corrosive
  - Irreversible reaction at 1060°C

Wafer cleaning:

Sequential surface cleaning steps (e.g. oxides, organics)
Organic removal → oxidation, then HF to remove SiO_2
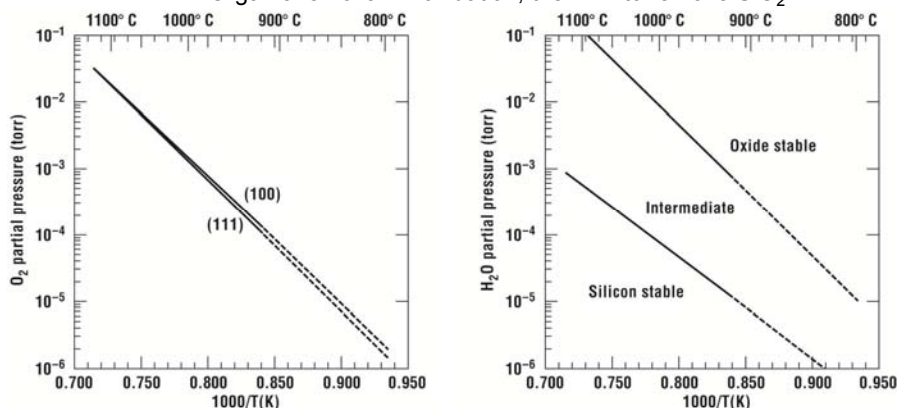
Figure 14.2 Stability diagram for the surface of silicon and silicon dioxide as functions of the temperature and the partial pressure of oxygen and water vapor. The curve for water vapor has an intermediate region where both surfaces can coexist *(redrawn using data from Ghidini and Smith, and Smith and Ghidini).*

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Vapor phase growth

Feed gas composition complex
(multiple Si constituents)

Basic:
Silane $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

(e.g poly-Si deposition 600°C
& epi-Si 600-800°C)
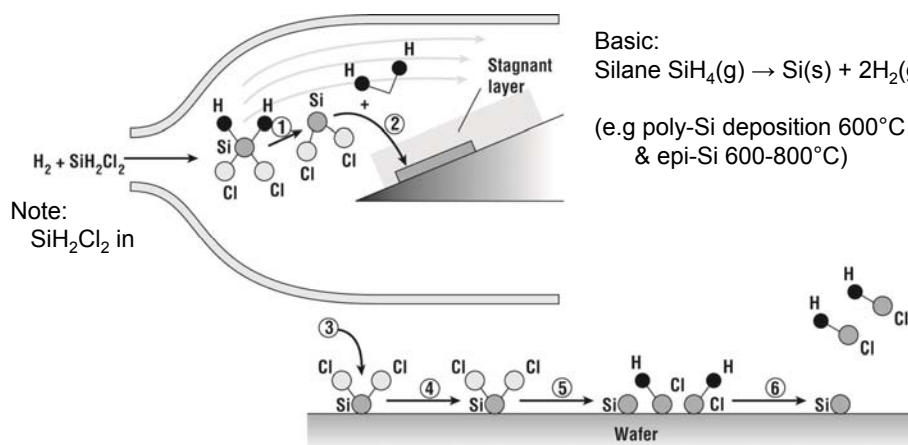
Note:
SiH_2Cl_2 in

Figure 14.4 VPE steps include (1) gas phase decomposition and (2) transport to the surface of the wafer. At the surface the growth species must (3) adsorb, (4) diffuse, and (5) decompose; and (6) the reaction by-products must desorb.

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Vapor phase growth

Flux $\quad F = h_g(C_g - C_s) = k_s C_s$

where h_g = mass transport coefficient
k_s = surface reaction rate
C_g = gas concentration of reactant
C_s = surface concentration of reactant

Growth rate

$$R = \frac{k_s h_g}{k_s + h_g} \frac{C_g}{N} \text{ where } N = \frac{Si\ density\,(\,5x10^{22}\,/\,cc)}{Number\ Si\ atoms/growth\ molecule}$$

Homogeneous nucleation in the gas phase limits SiH_4 pressure in
Critical nucleus:

$$r^* = \frac{2.U.V}{kT.\ln \sigma_0} \text{ where saturation ratio } \sigma_0 = \frac{Pressure\ of\ growth\ species}{Equilibrium\ pressure\ of\ growth\ species} = \frac{N\downarrow}{N\uparrow}$$

$$U = surface\ energy,\ V = atomic\ volume$$

In practice, use chlorosilanes: SiH_xCl_{4-x}
$\qquad\qquad\qquad$ x=0, 1, 2, or 3

Increase x, decreases required T
$\qquad SiCl_4 \rightarrow 1150°$
DCS now common
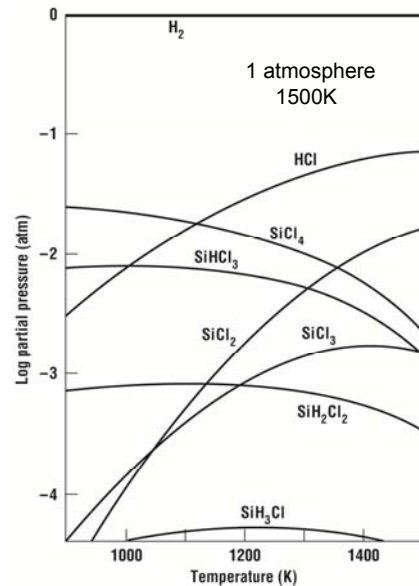
Figure 14.5 Equilibrium partial pressures in the Si–Cl–H system at 1 atm and a Cl: H ratio of 0.06 *(after Bloem and Claasen, reprinted by permission, Philips).*

Reactive species primarily $SiCl_2$

$$Si(s) + 2HCl(g) \leftrightarrow SiCl_2(g) + H_2(g)$$

Deposition:
$$SiCl_2(g) + H_2(g) \rightarrow Si(s) + 2HCl(g)$$
Etching:
$$Si(s) + 2HCl(g) \rightarrow SiCl_2(g) + H_2(g)$$

Add HCl to slow deposition, increase etching

Reaction rate:
$$R = c_1 p_{SiCl_2} - c_2 p_{HCl}^2$$

for reaction rate limited

where c_1 & c_2 are thermally activated

Figure 14.6 Growth rate as a function of the $SiCl_4$ flow. At high concentrations, the chlorine in the chamber leads to etching *(after Theuerer, reprinted by permission of the publisher, The Electrochemical Society).*

Supersaturation

$$\sigma = \left[\frac{p_{Si}}{p_{Cl}} \right]_{feed} - \left[\frac{p_{Si}}{p_{Cl}} \right]_{equil}$$

Equilibrium ratios
(functions of T)

Find [Cl/H] at chamber T:
If $\sigma > 0$,
vapor supersaturated
$\rightarrow$ growth
If $\sigma < 0$,
vapor undersaturated
$\rightarrow$ etching

Figure 14.7 The equilibrium ratio of silicon to chlorine at 1 atm *(after Arizumi, reprinted by permission, Elsevier Science).*

Need 2D growth at terrace edge for single crystal. If deposition rate too high, get 3D island nucleation (Stranski-Krastanov) of new crystal.

Figure 14.32 A microscopic view of a semiconductor surface during MBE growth or evaporation.

Surface reactions (SiCl$_2$ primary for all, so dominates reaction rate constants)
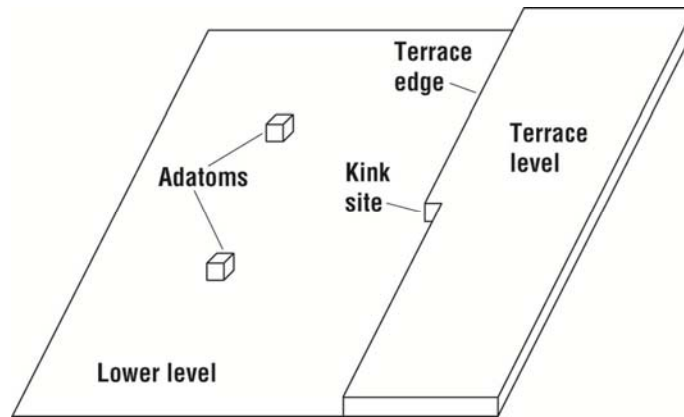
Primarily H, Cl, & SiCl$_2$ on surface (see Table 14.2). Si Cl$_2$ physisorbed.

Assume θ_x of possible absorption sites occupied. $\theta_x \propto p_x \propto flow_x$

Reaction rate

$$R = k_1 \frac{p_{H_2} p_{siCl_2}}{1 + k_2 p_{H_2}} \theta - k_3 \frac{p_{HCl}^2}{p_{H_2}}$$

deposit   etch

where free sites $\theta = \dfrac{1}{1 + k_4 p_{SiCl_2} + k_5 \dfrac{p_{HCl}}{p_{H_2}^2} + k_6 p_{H_2}^2}$
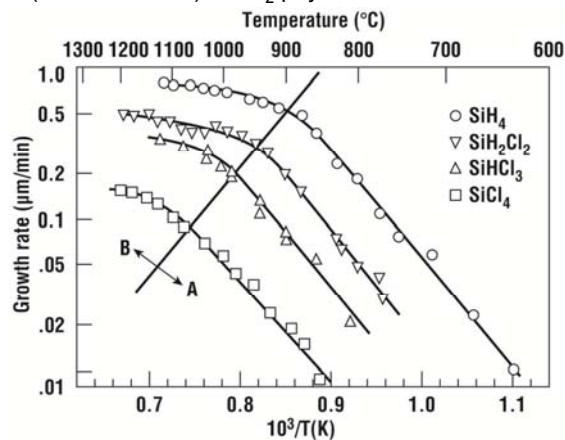

Figure 14.8 Arrhenius behavior of a variety of silicon-containing growth species *(after Eversteyn, reprinted by permission, Philips).*

Doping

Unintended from substrate, gas, etc

If growth rate $R > \sqrt{\dfrac{D}{t}}$, erfc impurity distribution
(D impurity diffusivity)

Gas phase autodoping $\rightarrow$ C(x) = f.N_{os}exp-x/x_m
(where f = trapping density, N_{os} = surface trapping sites,
& x_m = characteristic transition depth)

Intended doping B_2H_6, PH_3, AsH_3, (typically H_2 diluted)

VPE/LPE:Auto-doping

- Impurity Redistribution during growth
- Ideally:
    Have substrate doping density N_S
    Growth epi-layer with doping density N_E
- In Practice:
    Interdiffusion operates during growth and all
                                subsequent processing
- Si & dopant removed from substrate
                        by evaporation &/or etching
    -diffuse through boundary layer & change effective
    doping density of epi-source gas
    -time dependent until equilibrium reached.

Auto-Doping Theory: Simple (n on n⁺)

- Assume substrate as sink
- Substrate doped N_S & epi-layer ideally intrinsic ($N_E = 0$)
$$\therefore N_E(x) = N_S \exp - \phi x$$
- Intrinsic substrate & epi-layer ideally doped
  ($N_S = 0$ & $N_E = N_{E\infty}$) $\therefore N_E(x) = N_{E\infty}(1 - \exp - \phi x)$
- In practice:
  Lightly doped epi-layer on heavily doped substrate.
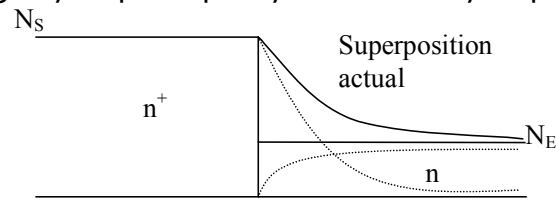
Auto-Doping Theory : (n on p)
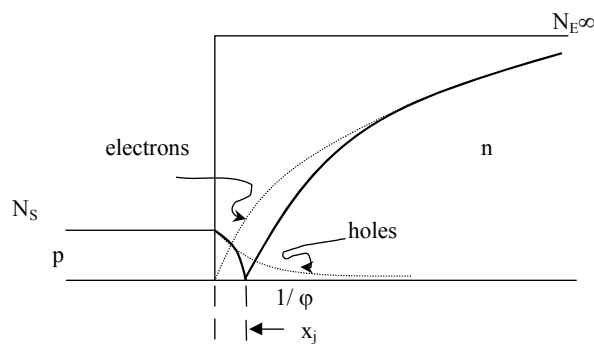
- Junction lag, i.e. p - n junction not at surface as assumed.
  - Reduce x_j by increasing ϕ --- i.e. increase T

Auto-Doping Theory: Diffusion

- Includes substrate effects close to boundary (i.e. substrate not infinite sink.)
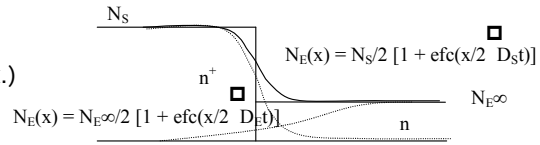
- Assume infinite epi-layer; (valid if growth rate >> diffusion rate.)

- D_S for substrate impurity
  D_E for epi-layer impurity

$N_E(x) = N_S/2 \ [1 + \text{efc}(x/2\ \sqrt{D_S t})]$

$N_E(x) = N_E\infty/2 \ [1 + \text{efc}(x/2\ \sqrt{D_E t})]$
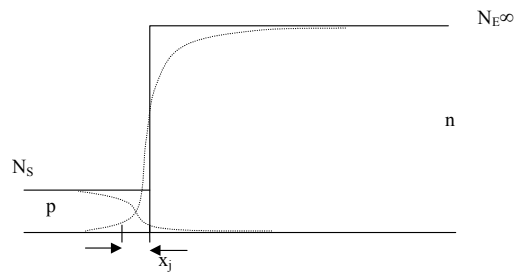
Advanced Si VPE techniques

$\sqrt{Dt} \rightarrow$ defect/dopant redistribution
Hence RTP
or UHV at low T

Figure 14.25 A typical time/temperature cycle for growing 1 μm of epitaxial silicon in a VPE reactor.

Pattern Shift

Epi — Pattern shifts; no distortion

Epi — Positive symmetrical distortion; no pattern shifts

Epi — Negative symmetrical distortion; no pattern shifts

x_1' c' x_2' — Pattern shift and asymmetrical distortion
t
x_1 c' x_2

Center of mark

As etched

Apparent shift

Epi

After growth

Figure 14.10 A schematic diagram of pattern shift. Alignment marks are etched into the wafer, but nonuniform growth rates cause the mark position to shift after growth.

Relative pattern shift
$$g = (c' - c)/t$$
$$= (x_1' + x_2')/2t - (x_1 + x_2)/2t$$
$$= [(x_1' - x_1) + (x_2' - x_2)] / 2t$$

Relative distortion,
$$S = [(x_2' - x_1') - (x_2 - x_1)] / t$$

Selective epi-growth (SEG)

Nucleation rates on SiO_2 < Si_3N_4 < Si

Etch holes in SiO_2 to grow Si

Epi   Oxide

Ideal SEG

Thickness variations   Silicon nodules   Facets

Actual SEG

Figure 14.12 A cross-sectional view of selective epitaxial growth.

Note: Extended lateral overgrowth if Si continues past SiO_2 thickness
→ defects (oxide interface, overgrowth interface)

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Selective Epitaxial Growth (SEG)

Actual   0   Si modules

facets

thickness variations

Heteroepitaxy

Figure 14.14 Temperature and pressure regimes of various epitaxial growth techniques.

Heteroepitaxial growth

Figure 14.15 Epitaxial growth processes can be divided into (A) commensurate, (B) strain relaxed incommensurate, and (C) incommensurate but pseudomorphic.

Possible heteroepitaxy pairs (vertical lines for similar lattice constants)

Figure 14.17 The bandgap and lattice parameter of a variety of semiconductor compounds and alloys.

e.g. GaAs   → AlP/InP $(Ga_xIn_{1-x}P)$
                   → AlAs $(Al_xGa_{1-x}As)$

Pseudomorphic Ge$_x$Si$_{1-x}$ on Si

Energy gap (eV) Ge$_x$Si$_{1-x}$

unstrained

1.1

1.0

0.9

0.8

coherently
strained

0.7

0.6

0   0.2   0.4   0.6   0.8   1.0   x

1µm

1000 Å

100 Å

10 Å

Misfit
dislocations

Ge$_x$Si$_{1-x}$ layer thickness

Metastable
strain

Stable strain

0.0   0.2   0.4   0.6   0.8   1.0

x for Ge$_x$Si$_{1-x}$ on Si

Figure 14.18 For pseudomorphic GeSi on Si there are three regions:
mechanically stable, metastable, and unstable *(after People and Bean).*

Also Ge on GeSi on Si substrate

Figure 14.20

MOCVD

 A typical OM (organometallic) source for
MOCVD includes valves that isolate and
bypass the bubbler during changeout,
allowing cycle purging of the process line
with nitrogen.

To manifold

N2

H2

Back pressure
regulator

Mass flow controller

Gas PV

Process valve

Pressure Gauge

Purge gas valve

Bypass PV

Bubbler PVs

Vacuum valve

To pump

Bubbler valves

Bubbler

Outlet   Inlet

Bath

○ Hydrogen
● Carbon
● Metal

Figure 14.19
Examples of common organometallics used in
MOCVD include (from top to bottom):
trimethylgallium (TMG) Ga(CH$_3$)$_3$, tetrabutylarsine
(TBA)*, and triethylgallium (TEG).
        *Alternative to AsH$_3$ storage

Predominantly methyl-…….. & ethyl- …….
e.g. TMG, TEG, DMZ
(dimethyl zinc , a dopant)

TEX=triethyl-X
TMX=trimethyl-X

Figure 14.21 Vapor pressure curves for some common organometallics *(after Stringfellow).*

MBE

Pump
Cryo/turbo
LN2 molecular sieve
10-6 torr load-locks

Sources
Thermal (Knudsen) under
thermocouple/pyrometer control
Electron beam

Shutter
On/off deposition

Figure 14.28 Schematic and photograph of a molecular beam epitaxy growth system *(after Davies and Williams).*

MBE Growth Rate

Atom flux=I_n=J_nA= $A\sqrt{\dfrac{n^2 kT}{2\pi n}} = A\sqrt{\dfrac{P_e^2}{2\pi mkT}}$

Ex. 14.4. Deposit Al at 1150K from 25cm^2 cell. What are the atomic flux 0.5m away, directly above the source, and the growth rate?

$$J = A\sqrt{\dfrac{P_e^2}{2\pi mkT}}\ \dfrac{\cos\theta\cos\phi}{\pi r^2}$$ and $\theta = \varphi = 0$, $\cos\theta = 1$

P_e(Al) at ~ 10^{-6}torr at 1150K
M = 27 x 10^{-27}Kg
so J → 4.8 x 10^{14}/cm^{2}sec & R = J/N = 4.8 nm/min (N = 6x10^{22}/cc)
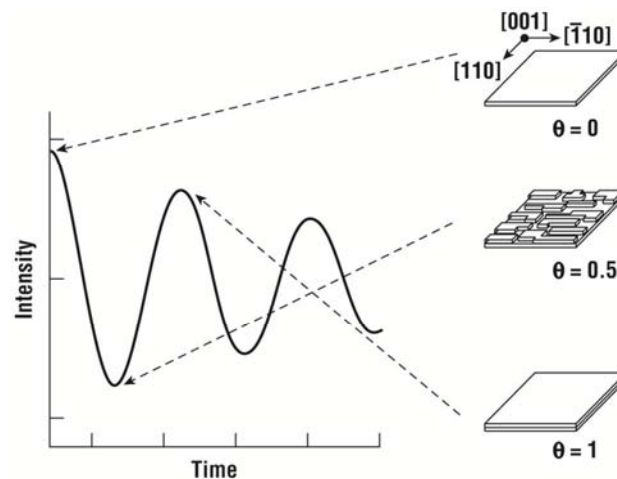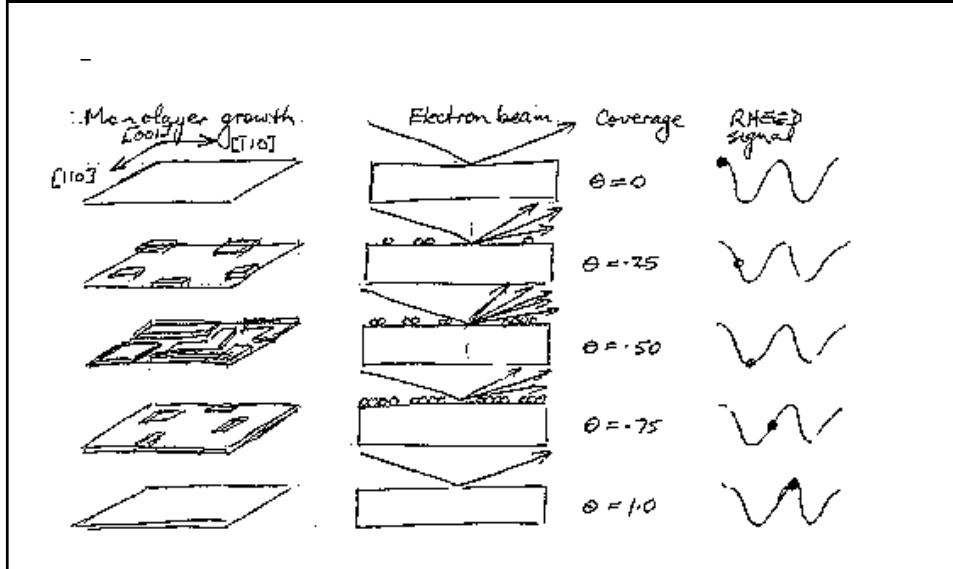
RHEED (Reflective high energy electron diffraction)

Figure 14.31 Electron diffraction oscillations during MBE growth. The peaks correspond to nearly complete layers.

MBE Deposition Thickness: in situ RHEED

BCF (Burton-Cabrera-Franks) theory:

Consider the opposite of growth, i.e. evaporation from kink site
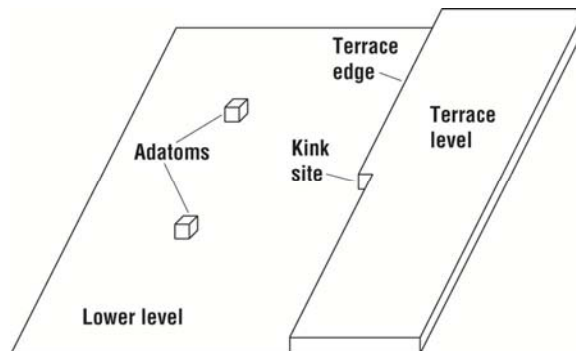
Atoms break off, diffuse across surface, evaporate

Figure 14.32 A microscopic view of a semiconductor surface during MBE growth or evaporation.

Energy to liberate kink site atom = W_s
Therefore, density of surface (adsorbed) atoms = $N_s \exp{-W_s/kT}$
(where N_s = surface site density)

Surface diffusivity $D_s = a^2 f.\exp{-U_s/kT}$ (where f = lattice vibration frequency,
a = distance between sites
(Usually, $U_s << W_s$)

Atom desorbs after time τ, so $1/τ = f' \exp{-E_d/kT}$
(where E_d = desorption energy, & $f' \approx f$ is "related to" f

Mean migration length before desorption $λ_s = \sqrt{D_s}\, τ \approx a\, \exp{(E_d - U_s)/2kT}$

Desorption flux $F_0 = n_{seq}/τ = N_s f/\exp{-(E_d + W_s)/kT}$

If terraces due to crystal misorientation Δθ, then terrace separation $L_0 = h/\sin{Δθ}$, where h = terrace step height. L_0 must be $< λ_s$ for 2D growth at the terrace edge.

Net flux of adatoms at the terrace edge $j_v = j_{inc} - n_s/τ$

Surface diffusion current density of adatoms $j_s = -D_s \nabla n_s$

For steady state, net growth flux = divergence of diffusion current
$$-\nabla \cdot j_s = j_n$$

Define supersaturation $\sigma = \dfrac{j_{inc}}{n_{sec}/\tau} - 1$

σ > 0, epitaxial layer grows, σ < 0, evaporates

Hence $\lambda_s^2 \nabla^2 n_s + n_s = n_{seq}(\sigma + 1)$

At terrace edge (y=0) $n_s = n_{seq}$, and $n = (1+\sigma)n_{seq}$ as y→∞
$$n_s = n_{seq}\left[1 + \sigma\left(1 - e^{-y/\lambda_s}\right)\right]$$

Surface supersaturation $\sigma_s = \dfrac{n_s}{n_{seq}} - 1$

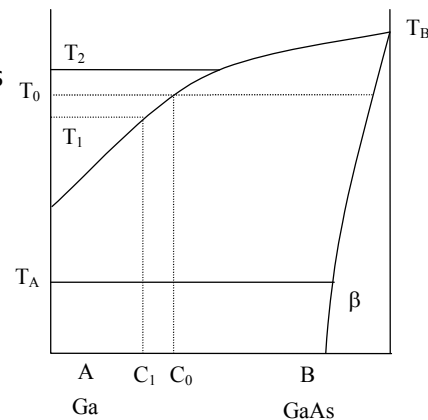and $\sigma_s = \sigma\left[1 - \dfrac{\cosh(y/\lambda_s)}{\cosh(L_0/2\lambda_s)}\right]$
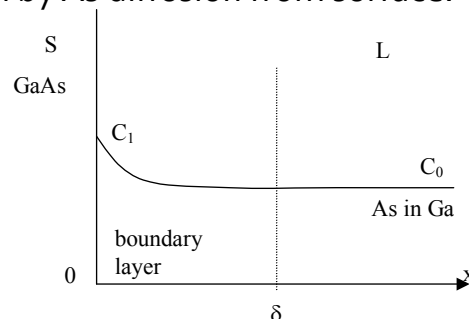
LPE: GaAs

- Instead of grow β crystal of B at T_B, grow epitaxially from melt C_o at $T_o \ll T_B$.
- Used for GaAs, AlGaAs, etc.
    - -High quality, slow growth
    - -Long minority carrier lifetimes
    - -Optical devices

- Not used for Si (high T process OK)

LPE Growth: Approx.

Approx: linear gradient --> Flux = j = $D(C_1 - C_o) / \delta$
   Note : Distribution coefficient of As in GaAs < 1.
Growth by As diffusion from surface.

Saturated solution of As in Ga; lower T $\rightarrow$ supersat!
   Restores equilib by decr As, ie by deposit GaAs

LPE Growth:Practical

Melt saturated at T_0
Lower Temperatures 5 - 20°C to T1
Supersaturation initiates growth
Supersaturation decreases as melt depleted.

$$\partial C/\partial t = D.\partial^2 C/\partial x^2 + v.\partial C/\partial x$$

If v = interface velocity ≈ 0, then $\partial C/\partial T \approx \partial^2 C/\partial x^2$
& deposition on substrate:
$$M_t / \text{unit area} = \int_0^t D(\partial C/\partial x)_{x=0}\, dt$$
& thickness $d=M_t/C_s$ \qquad (C_s= 0.5 for GaAs)

LPE Growth: Cooling

<u>Step Cooling:</u>
Boundary conditions: $C(x,0) =C_0$ \qquad $C(0,t) =C_1$
gives \qquad $(C - C_1)/(C_0 - C_1) = \text{erf}\,[x/2(Dt)^{1/2}]$
so \qquad $M_t = 2(C_0-C_1)(Dt/\pi)^{1/2}$ \quad & $d = 2[(T_0 - T_1)/C_s m](D/\pi)^{1/2}\, t^{1/2}$
where \qquad $m= dT/dC \approx (T_0-T_1)/(C_0 - C_1)$
so growth rate $\propto t^{-1/2}$

<u>Equilibrium Cooling</u>
Boundary Conditions: $C(x,0) = C_0$ \quad $C(0,t) = C_0 - (\alpha/m)t$
for linear decrease in T from T_0
$C(x,t) = C_0 - 4(\alpha t/m)\, i^2\, \text{erfc}[x/2(Dt)^{1/2}]$ \qquad where $i^2\, \text{erfc}\, x = \int_x^\infty \int_y^\infty \text{erfc}\, \xi\, .d\xi\, . dy$
gives $d=(4/3)(\alpha/C_s m)(d/\pi)^{1/2}\, t^{3/2}$
so growth rate $\propto t^{1/2}$

Summary

Homo/Hetero epitaxy
  Lattice mismatch; (lattice strain)
FTIR & RHEED monitoring
Endothermic/exothermic rates
VPE chlorosilane chemistry (revise CVD)
Pattern shift/defects
Autodoping
LPE for GaAs.

Assignment #7

- 13.2
- 13.5
- 13.6
- 13.7

- 15.4
- 15.7
- 15.10
- 15.11

- 14.1
- 14.4
- 14.7
- 14.11

- 20.1
- 20.2