Adsorption and Desorption

Physical adsorption

1. Weak force, e.g., van der Waals force
2. Reversible
3. Equilibrium attained rapidly
4. Q=1~10 kcal/mol
5. Accommodation coefficient (α) =1
6. Residence time on surface (τ) =10^{-12}~10^{-7} sec
   vs. 10^{-13} sec molecular vibration time
7. Taking place at low temperatures
8. Not limited to monolayer

Chemical adsorption

1. Q=20~40 kcal/mol
2. Bonding force $\approx$ valence bond
3. τ =10^2~10^{17} sec
4. Taking place at all temperatures
5. Monolayer adsorption
6. Not always reversible

Adsorption Isotherms: Describing the equilibrium course of surface adsorption as a function of pressure at a given temperature.
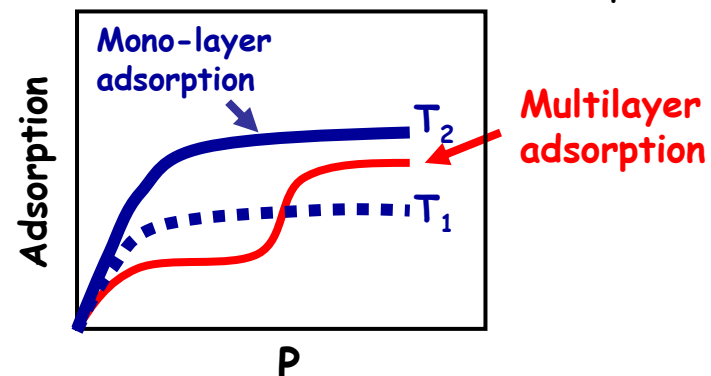
Langmuir Evaporation and Condensation

Dynamic equilibrium between adsorption and desorption

Assumptions:
1. The adsorbed molecule or atom is held at definite, localized sites
2. Each site can accommodate only one molecule or atom
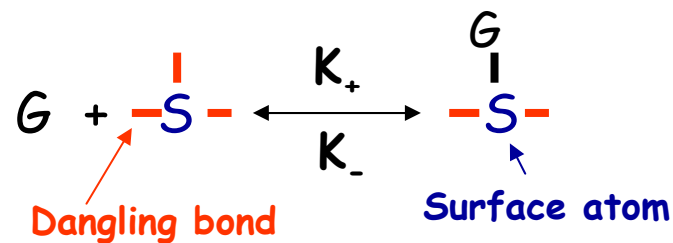3. The energy of adsorption is constant over all sites, and there is no interaction between neighboring adsorption.

(I) Adsorption without dissociation

Let **N** surface sites all with same power for adsorption if **n** of **N** sites are occupied and the fraction of surface sites occupied is

$$\theta \equiv \frac{n}{N}$$

$$G + -\overset{\mid}{S}- \underset{K_-}{\overset{K_+}{\longleftrightarrow}} -\overset{\overset{G}{\mid}}{S}-$$

Dangling bond   **Surface atom**

$$\boxed{\begin{array}{l} A + B \to \text{Products} \\ -r_A = -\dfrac{dC_A}{dt} = -\dfrac{dC_B}{dt} = kC_A C_B \end{array}}$$

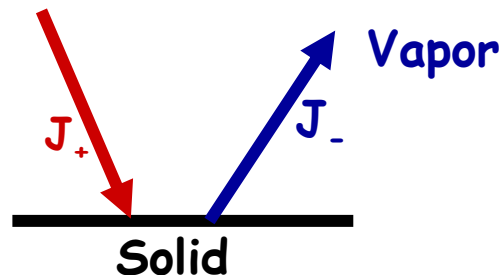$$J_+ = K_+ P(1-\theta) = \alpha \nu(1-\theta)$$

where ν is the collision frequency of gas molecules striking the surface, and α is an accommodation or sticking coefficient

$$\nu = C_{gas} \text{v}_+$$

$$C_{gas} = \frac{n \, (moles)}{\text{V (volume)}} = \frac{P}{kT} \quad \text{in vapor phase}$$

v$_+$: velocity of gas atom onto surface

$$= \sqrt{\frac{kT}{2\pi M}} \quad \text{(Gas kinetics)} \quad \text{(M:molecular weight)}$$

Vapor

$$J_+ \qquad J_-$$

Solid

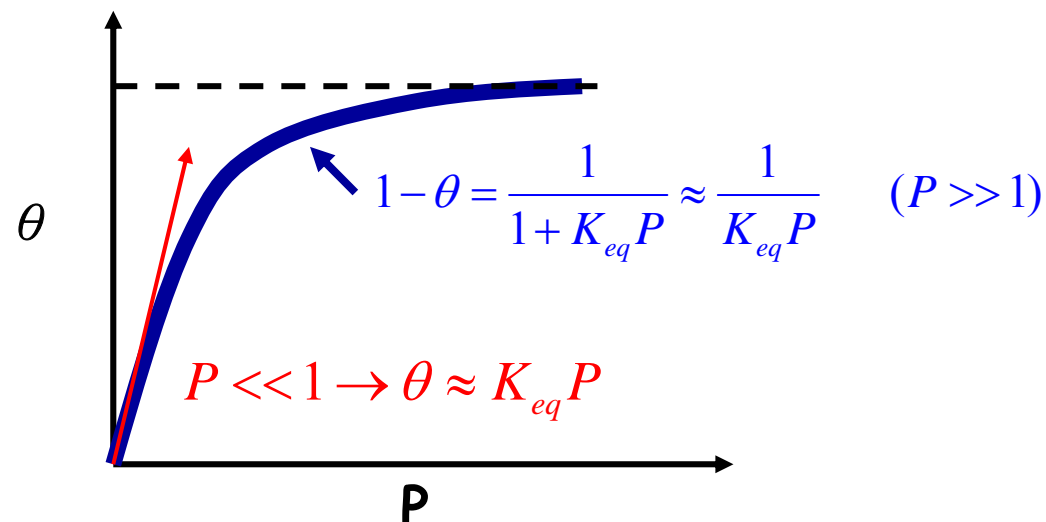Adsorption rate: $J_+ = \alpha \dfrac{P}{kT} \sqrt{\dfrac{kT}{2\pi M}} (1-\theta) = \dfrac{\alpha}{\sqrt{2\pi MkT}} P(1-\theta) = K_+ P(1-\theta)$

Desorption rate: $J_- = K_- \theta = \dfrac{K_+}{K_{eq}} \theta = \dfrac{\alpha / \sqrt{2\pi MkT}}{K_{eq}} \theta$

$J_{net} = J_+ - J_- = \dfrac{\alpha P(1-\theta)}{\sqrt{2\pi MkT}} - \dfrac{\alpha\theta}{K_{eq}\sqrt{2\pi MkT}} = \dfrac{\alpha}{\sqrt{2\pi MkT}}\left[P(1-\theta) - \dfrac{\theta}{K_{eq}}\right]$

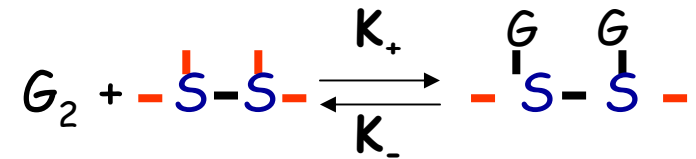At equilibrium $J_{net} = 0 \Rightarrow \theta = \dfrac{K_{eq}P}{1+K_{eq}P}$ or $1-\theta = \dfrac{1}{1+K_{eq}P}$

Note: K_+, K_- and K_{eq} vary with sticking coefficient and system temperature.

$1-\theta = \dfrac{1}{1+K_{eq}P} \approx \dfrac{1}{K_{eq}P}$ $(P \gg 1)$

$P \ll 1 \rightarrow \theta \approx K_{eq}P$

(II) Adsorption with dissociation

Assuming monolayer adsorption and a molecule will adsorb and occupy two adjacent sites on surface

$$G_2 + -S-S- \underset{K_-}{\overset{K_+}{\rightleftharpoons}} -\overset{G}{S}-\overset{G}{S}-$$

$$Adsorption \ \ Rate: J_+ = K_+ P(1-\theta)^2 = \frac{\alpha}{\sqrt{2\pi MkT}} P(1-\theta)^2$$

$$Desorption \ \ Rate: J_- = K_- \theta^2$$

$$J_{net} = J_+ - J_- = \frac{\alpha}{\sqrt{2\pi MkT}} [P(1-\theta)^2 - \frac{\theta^2}{K_{eq}}]$$

At equilibrium $J_{net} = 0 \Rightarrow \theta = \dfrac{\sqrt{K_{eq}P}}{1+\sqrt{K_{eq}P}}$ and $K_{eq} = \dfrac{K_+}{K_-}$

(III) Evaporation with constant concentration at surface

e.g., evaporation of metals

$$J_+ = \frac{\alpha P}{\sqrt{2\pi MkT}} \quad \text{(maximum adsorption rate assuming } \theta \approx 0 \text{)}$$

$$J_{net} = J_+ - J_-$$

$$= \frac{\alpha P}{\sqrt{2\pi MkT}} - J_-$$

At equilibrium $\quad J_{net} = 0 \rightarrow J_- = \dfrac{\alpha P^{eq}}{\sqrt{2\pi MkT}}$

Nonequilibrium $\quad J_{net} = J_+ - J_- = \dfrac{\alpha P}{\sqrt{2\pi MkT}} - \dfrac{\alpha P^{eq}}{\sqrt{2\pi MkT}}$

$$= \frac{\alpha(P - P^{eq})}{\sqrt{2\pi MkT}}$$

Special case: $\alpha = 1$ **and evaporation in the vacuum (P=0)**

$$J_{net} = \frac{-P^{eq}}{\sqrt{2\pi MkT}}$$

Example: The accommodation coefficient for the deposition atoms or molecules is the ratio of the number of atoms that stick to the surface to number that strike it. It is zero if none stick; it is one (unity) if all that hit stick. If the accommodation coefficient is one, then at a pressure of 10⁻¹⁰ atm, a monolayer will be formed in about 37 sec. If we require the surface to be kept clean for one hour, the pressure required would be about 10⁻¹² atm.

$$J = \frac{N*}{A \cdot \tau} = \frac{\alpha P}{\sqrt{2\pi M k_B T}} = \frac{P(atm) \cdot 1.013 \times 10^5}{\sqrt{2\pi \dfrac{M \cdot 10^{-3}}{6 \times 10^{23}} \cdot 1.38 \times 10^{-23} \cdot T}} \cdot 10^{-4} (cm^2/m^2)$$

$$= \frac{\#particles}{cm^2 sec}$$

M: g/mol=32g/mol for O_2

Assuming monolayer adsorption$=10^{15}/cm^2 = \dfrac{N*}{A}$

$$\frac{N*}{A \cdot \tau} = 2.72 \times 10^{23} \cdot P = \frac{10^{15}}{\tau}$$

$$if \ \alpha = 1$$

$$P=10^{-10} atm \Rightarrow \tau = 37\,sec$$

$$P=10^{-12} atm \Rightarrow \tau = 3600\,sec$$

Example: Vapor Pressure Measurement

When liquid aluminum is held in a stable, inert container suspended in a vacuum furnace (P=0), the mass loss through a hole with a cross-sectional area of 2×10^{-3} cm² is 1.7×10^{-9} g/s at a temperature of 1250 K. The molecular weight of aluminum is 27 g/mol, and the vapor is monatomic.

T=1250K

P⁰=? → A   P=0

Al
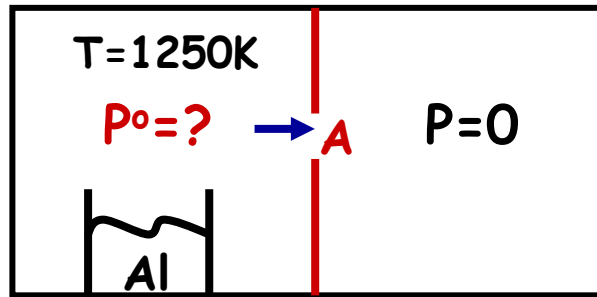
$$A = 2\mathrm{x}10^{-3} \text{ cm}^2$$

$$M = 27 \text{ g/mol}$$

$$\frac{N^*}{\tau} = 1.7\mathrm{x}10^{-9} \text{ g/sec}$$

$$P^o = \frac{N^*}{A\tau}\sqrt{2\pi M k_B T}$$

$$\frac{N^*}{A \cdot \tau} = \frac{1.7\mathrm{x}10^{-9}}{27} \cdot 6\mathrm{x}10^{23} \cdot \frac{1}{2\mathrm{x}10^{-7}} \text{ m}^{-2}\text{sec}^{-1}$$

$$P^o = \frac{N^*}{A\tau}(2\pi \frac{27\mathrm{x}10^{-3}}{6\mathrm{x}10^{23}} \cdot 1.38\mathrm{x}10^{-23} \cdot 1250)^{\frac{1}{2}}$$

$$= 1.32\mathrm{x}10^{-2} \text{ N/m}^2$$

$$= 1.3\mathrm{x}10^{-7} \text{ atm}$$

$$J = \frac{\alpha P}{\sqrt{2\pi M k_B T}}$$

	MKS	CGS
P	N/m^2	dyne/cm^2
M	kg/molecule	g/molecule
k_B	1.38x10^{-23} J/molecule.K	1.38x10^{-16} erg/molecule.K
J	molecule/m^{2}sec	molecule/cm^{2}sec

Fe:
ρ =7.8 g/cm^3
M=56/(6x10^{23})=9.3x10^{-23} g/molecule
ρ /M=7.8/(9.3x10^{-23})=8.35x10^{22} molecule/cm^3

Stagnant Layer (Boundary Layer)

Gas Flow →

δ_s
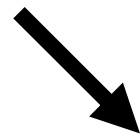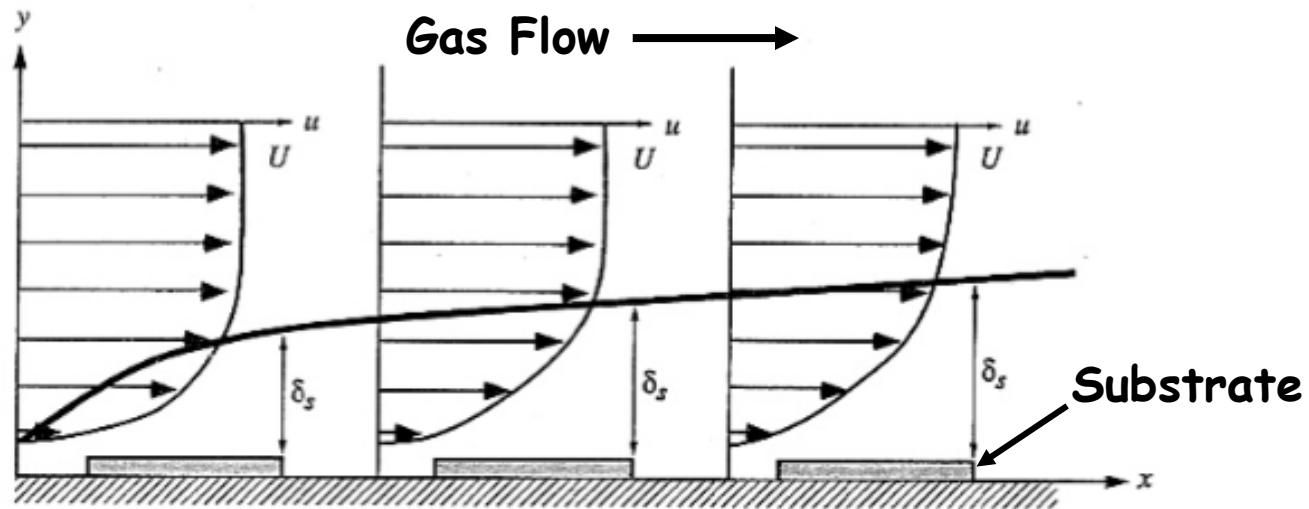
Substrate

Tilted CVD Substrates

Model of Mass-transfer Coefficient

I C_A^o II C_A^∞

δ_{eff}

Boundary Layer
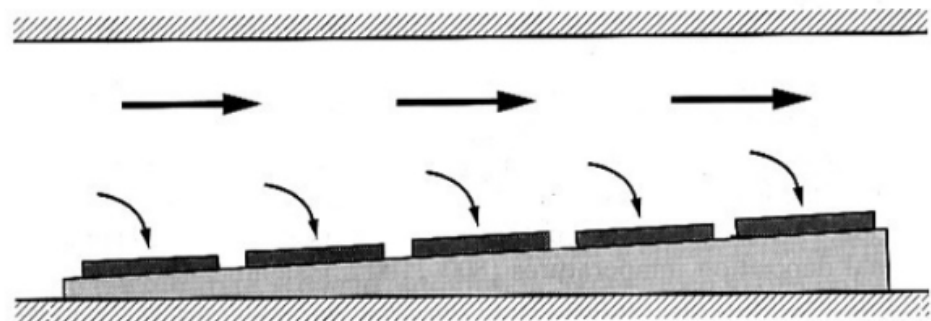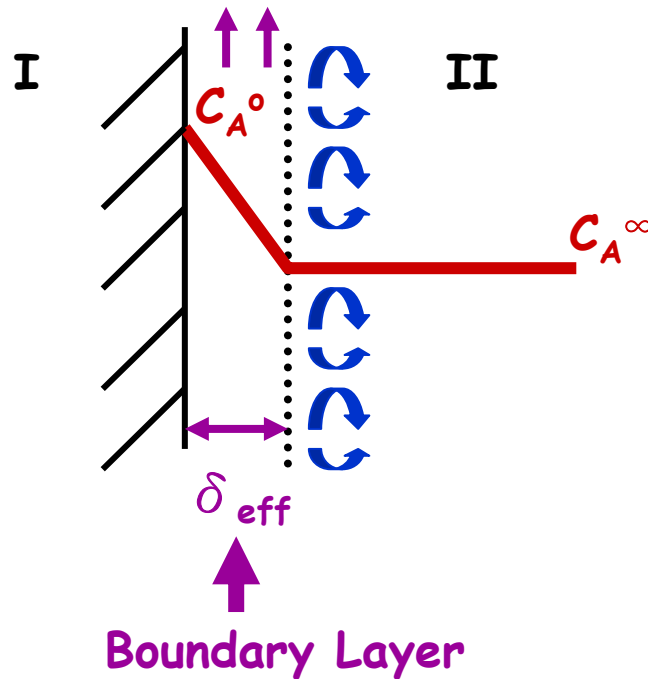
Approximation

- Unmixed layer or film in the fluid next to the actual interface
- Devoid of any fluid motion and offer resistance to the transfer of component A from the interface into the bulk solution
- Transfer takes place purely by atomic or molecular diffusion through the film
- Assuming a steady-state diffusion manner

$$J_A = K_M(C_A^\circ - C_A^\infty)$$

$$c.f. \quad J_A = -D\frac{\partial C_A}{\partial x} = D(\frac{C_A^\circ - C_A^\infty}{\delta_{eff}})$$

$$K_M \equiv \frac{D}{\delta_{eff}}$$

Mass Transfer with Vaporization

- Vacuum annealing **without melting**
- Elements (e.g. Zn, Pb) evaporate during annealing
- Several steps might take place
    1. Transport of volatile species to the surface of the condensed phase
    2. Formation of volatile compounds at the surface
    3. Evaporation from the surface into the gas or vacuum
    4. Transport away from the surface into the gas or vacuum
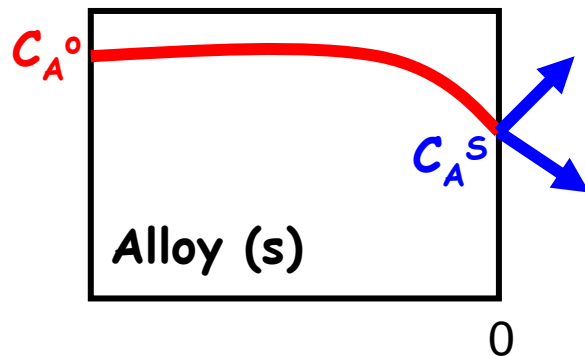
* If no boundary layer exists, evaporation takes place at the surface

C_A^o

C_A^s

Alloy (s)

0

$$J_D = (-)(-)D \frac{\partial C_A}{\partial x}\Big|_{x=0}$$

$$= \frac{\alpha(P_A^{External} - P_A^s)}{\sqrt{2\pi MkT}}\Big|_{x=0}$$

$$P_A^s = \gamma_A X_A P_A^\circ$$

P_A° : the vapor pressure of the pure component at a given temperature

$\gamma_A = 1 \rightarrow ideal\ gas$

$X_A = \dfrac{C_A^s}{\rho}$ (ρ : molar density of the alloy)

$$J_- = \frac{-\alpha P_s^{eq}}{\sqrt{2\pi MkT}} \ (Desorption)$$

$$J_+ = \frac{\alpha P^{ext}}{\sqrt{2\pi MkT}} \ (Adsorption)$$

$$J_{net} = J_+ + J_-$$

$$= \frac{\alpha(P^{ext} - P_s^{eq})}{\sqrt{2\pi MkT}}$$

$$J = -D\frac{\partial C}{\partial x} : \text{Positive}$$

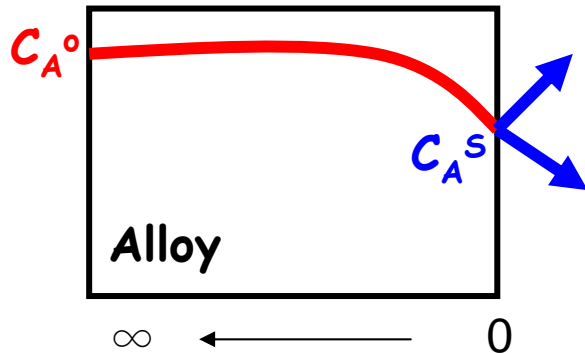$(-)$:from high to low concentration

$$J_- = (-)(-D\frac{\partial C}{\partial x}): \text{Flux out}$$

$$In \quad vacuum \quad P_A^{External} = 0$$

$$D \left. \frac{\partial C_A}{\partial x} \right|_{x=0} = \frac{-\alpha C_A^s P_A^\circ}{\rho \sqrt{2\pi MkT}}$$

If we consider the alloy as a semi-infinite solid

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2}$$

$$I.C.: C_A(x,0) = C_A^\circ$$

$$B.C.: C_A(\infty,t) = C_A^\circ$$

$$D \frac{\partial C_A(0,t)}{\partial x} = \frac{-\alpha P_A^\circ C_A(0,t)}{\rho \sqrt{2\pi MkT}}$$

$$\frac{\partial C_A(0,t)}{\partial x} = \frac{-\alpha P_A^\circ C_A(0,t)}{D\rho \sqrt{2\pi MkT}} = YC_A(0,t)$$

$$\frac{C_A}{C_A^\circ} = erf\left(\frac{x}{2\sqrt{Dt}}\right) + \exp(Yx + Y^2 Dt) erfc\left[\frac{x}{2\sqrt{Dt}} + Y\sqrt{Dt}\right]$$

$$x = 0 \Rightarrow \frac{C_A^s}{C_A^\circ} = \exp(Y^2 Dt) \cdot erfc(Y\sqrt{Dt})$$

Ref: Carslaw and Jaeger p.71

$$Note: C_A(0,t) = C_A^S$$

C_A°

C_A^s

Alloy

$\infty \longleftarrow \quad 0$

Alloy Vaporization during Melting

Steps:
(1) Mass transfer to the free surface
(2) Mass transfer in the boundary layer (B.L.)
(3) Vaporization from the B.L. into the vacuum
** No fluid motion is assumed.

δ=B.L.

C_A^∞

C_A^{S1}

melt

C_A^{S2}

0

Boundary
Layer
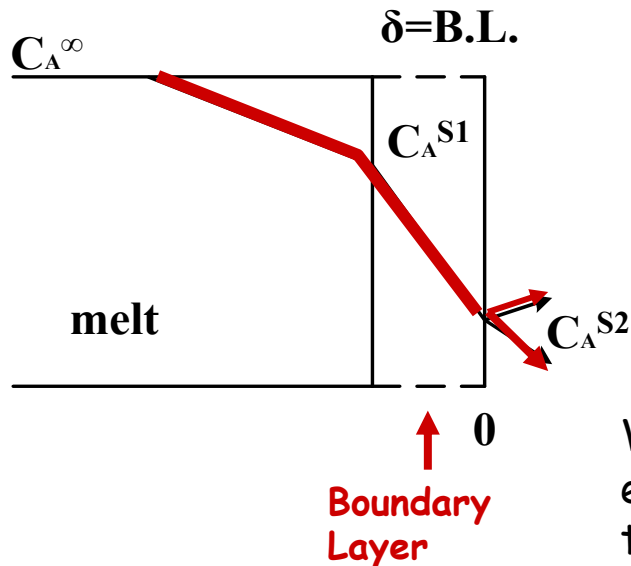
$$t = 0 \Rightarrow C_A^\infty = C_A^\circ$$

Mass transfer coefficient

$$K_{M.L} = 2\sqrt{\frac{D}{\pi\theta}} \quad (cm/\sec)$$

Where θ is the "lifetime" of a surface element which is equal to the average distance from the center of the melt to the edge of the crucible divided by the average velocity of the melt at the surface. In the induction melting case, "θ" is of the order of 1 sec or less.

Flux to the surface from the Bulk

$$J_A = -K_{M.L}(C_A^\infty - C_A^{s1})$$

Flux out

Mass Transfer Coefficient in the Melt

$$K_{M.L} = 2\sqrt{\frac{D}{\pi\theta}}$$

$$= \frac{2}{\sqrt{\pi}}\sqrt{\frac{D}{\theta}}\sqrt{\frac{D}{D}} = \frac{2}{\sqrt{\pi}}\frac{D}{\sqrt{D\theta}}$$

$$= \frac{2}{\sqrt{\pi}}\frac{D}{\delta_L}$$

δ_L: Diffusion layer or mass transfer layer thickness in the melt

Mass transfer coefficient in the B.L. $\quad K_{M.g} = \dfrac{D^g}{\delta} \quad (cm/sec)$

δ=B.L.

C_A^∞

C_A^{S1}

melt

C_A^{S2}

0

Boundary Layer
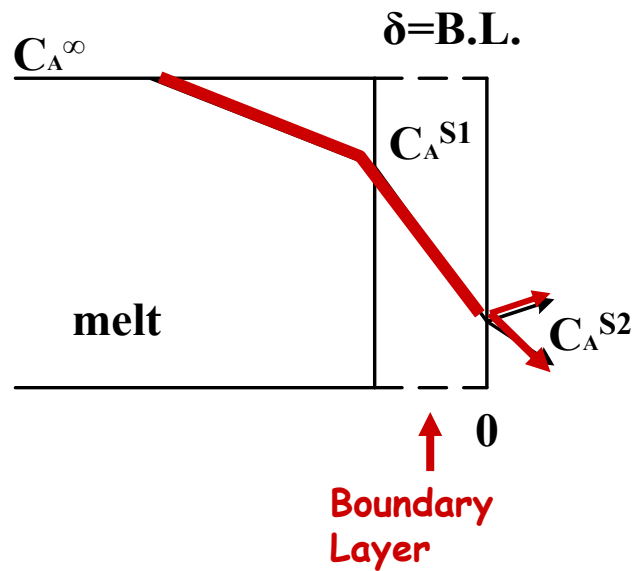
Flux in the B.L. $\quad J_A^1 = -K_{M.g}(C_A^{s1} - C_A^{s2})$

Vaporization at the B.L. $\quad J_A^2 = -\dfrac{\alpha P_A^\circ C_A^{s2}}{\rho \sqrt{2\pi M k T}} = -K_{M.e} \cdot C_A^{s2}$

$Steady \quad State: \quad J_A = J_A^1 = J_A^2$

$$J_A = \dfrac{-C_A^\infty}{\dfrac{1}{K_{M.L}} + \dfrac{1}{K_{M.g}} + \dfrac{1}{K_{M.e}}} = \dfrac{-C_A^\infty}{\dfrac{1}{K_{total}}}$$

$$\dfrac{1}{K_{total}} = \dfrac{1}{K_{M.L}} + \dfrac{1}{K_{M.g}} + \dfrac{1}{K_{M.e}}$$

: total kinetic resistance

Kinetic Processes in Series
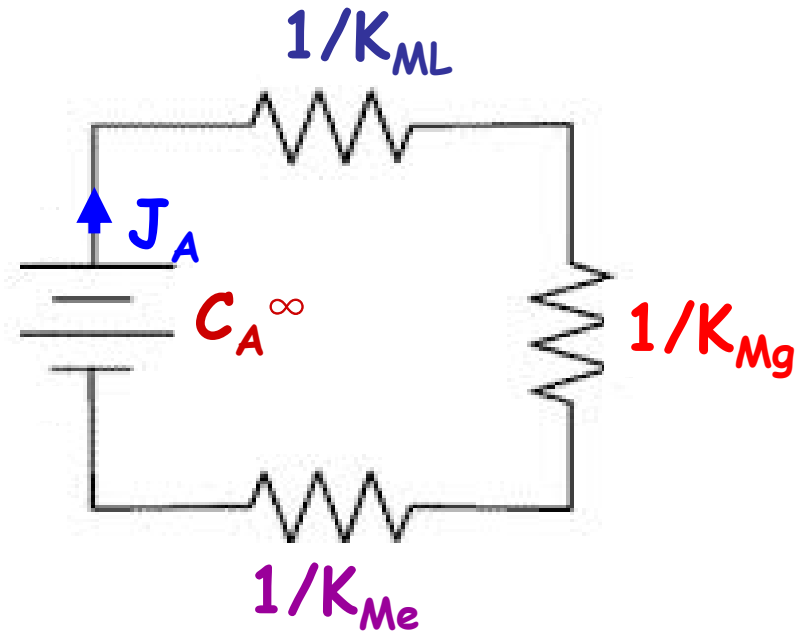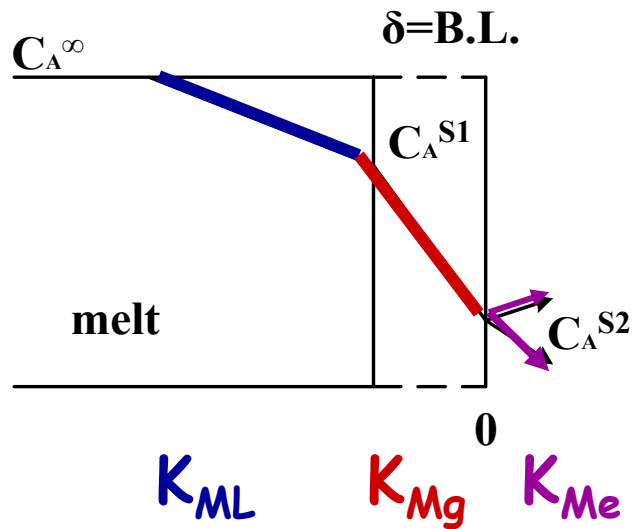
$$J_A = \frac{-C_A^\infty}{1/K_{total}} = -K_{total}C_A^\infty$$

$$\frac{1}{K_{total}} = \frac{1}{K_{ML}} + \frac{1}{K_{Mg}} + \frac{1}{K_{Me}}$$

(1) $K_{M.g} \gg K_{M.L}$ and $K_{M.e}$

* $C_A^{s1} = C_A^{s2}$

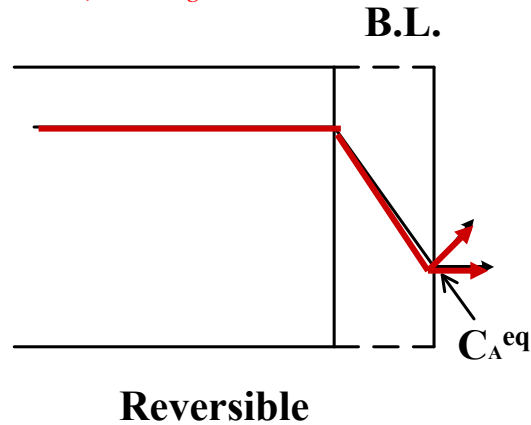* $\dfrac{1}{K_{total}} = \dfrac{1}{K_{M.L}} + \dfrac{1}{K_{M.e}}$
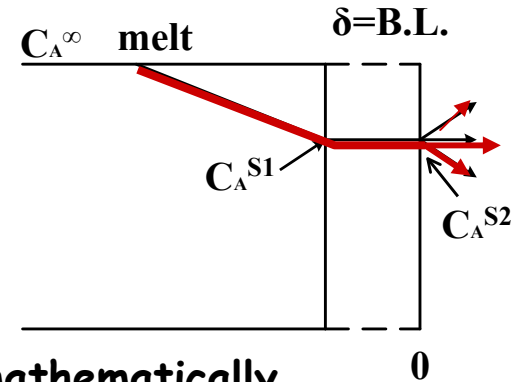
* Flux in the B.L. is not accessible mathematically

C_A^∞ melt   δ=B.L.

C_A^{S1}

C_A^{S2}

0

(2) $K_{M.e,}\ K_{M.g} \ll K_{M.L}$ $K_{M.g} \ll K_{M.L}$ and $K_{M.e}$

B.L.

C_A^{eq}

Reversible

B.L.

$C_A = 0$
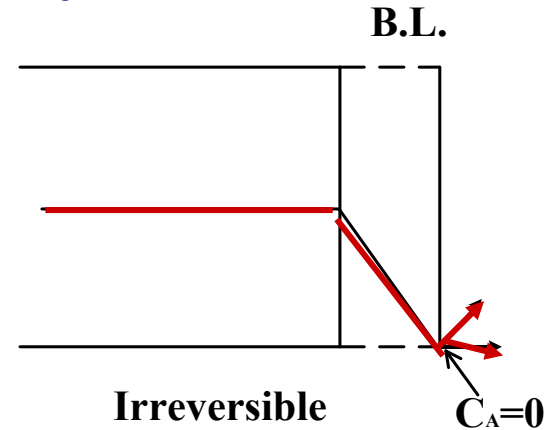
Irreversible

- **B.L. control**
- **Fluxes of diffusion in the melt and vaporization are not accessible mathematically (Irreversible)**
- **Reversible:**

$$J_e = -\frac{\alpha P_A^\circ C_A^{eq}}{\rho \sqrt{2\pi M k T}}$$

**Rate of decrease of solute A in melt
= mass flow of A from surface**

$$V \frac{dC_A^\infty}{dt} = -A_s J_A = -A_s K_{total} C_A^\infty$$

where A_s and V are the surface area of melt exposed to the vacuum and volume of the melt, respectively.

$$\int_{C_A^\infty}^{C_A^\circ} \frac{dC_A^\infty}{C_A^\infty} = \frac{A_s}{V} K_{total} \int_0^t dt \quad (t=0, C_A^\infty = C_A^\circ)$$

$$\ln(\frac{C_A^\circ}{C_A^\infty}) = \frac{A_s}{V} K_{total} \cdot t$$

(c.f.: the 1st order chemical reaction) ➡

*Overall evaporation constants for Fe-base melts at 1600℃

K_{total}(m/s)

Mn	$8.4*10^{-5}$
Cu	$4.8*10^{-5}$
Sn	$2.3*10^{-5}$
Cr	$2.1*10^{-6}$
S	$7.0*10^{-6}$

$$A \rightarrow \text{Products}$$

$$-r_A = -\frac{dC_A}{dt} = kC_A$$

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

$$-\ln(\frac{C_A}{C_{Ao}}) = kt$$

$$\ln\left(\frac{C_A^{\circ}}{C_A^{\infty}}\right) = \frac{A_s}{V} K_{total} \cdot t$$
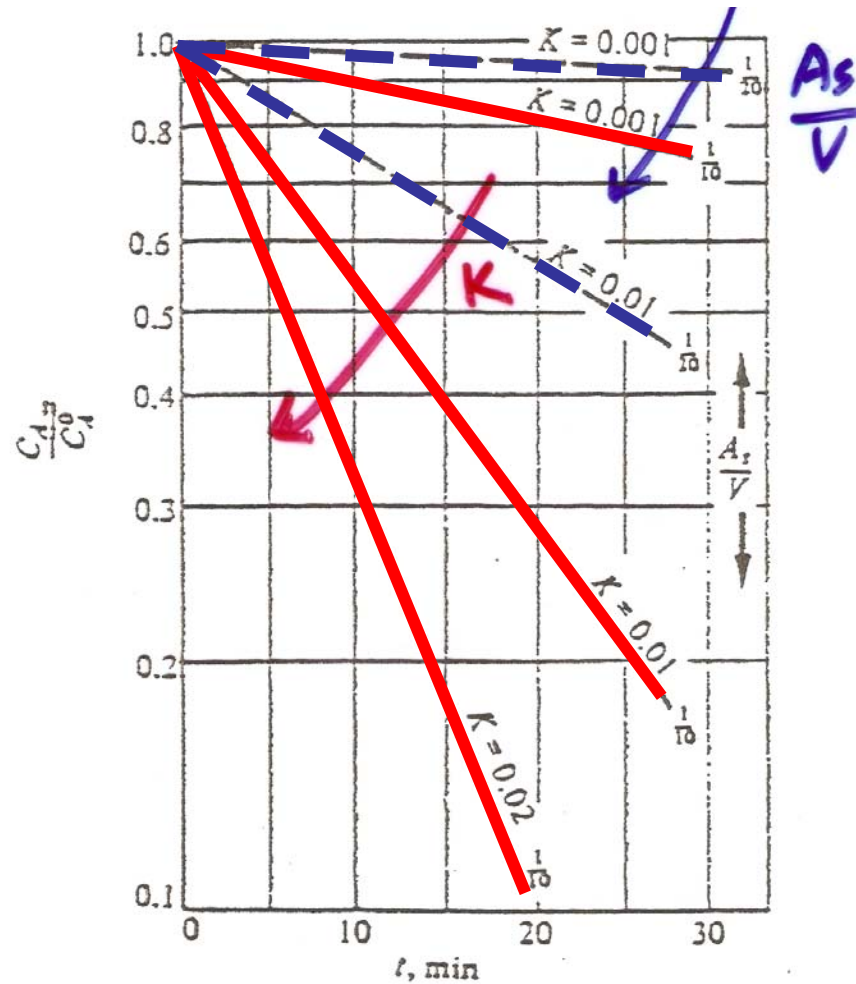
5.3 Decrease in concentration of alloying element as a function of mass transfer coefficient and A_s/V ratio. Units of K are cm s^{-1}, and units of A_s/V are ft^{-1}.

$$* \quad \frac{1}{K_{total}} = \frac{1}{K_{M.g}}$$

$$* \quad K_{M.g} \quad \alpha \quad P^{-1}_{(total\ pressure)}$$

($K_{M.L}$ and $K_{M.e}$ are relatively independent of external pressure)
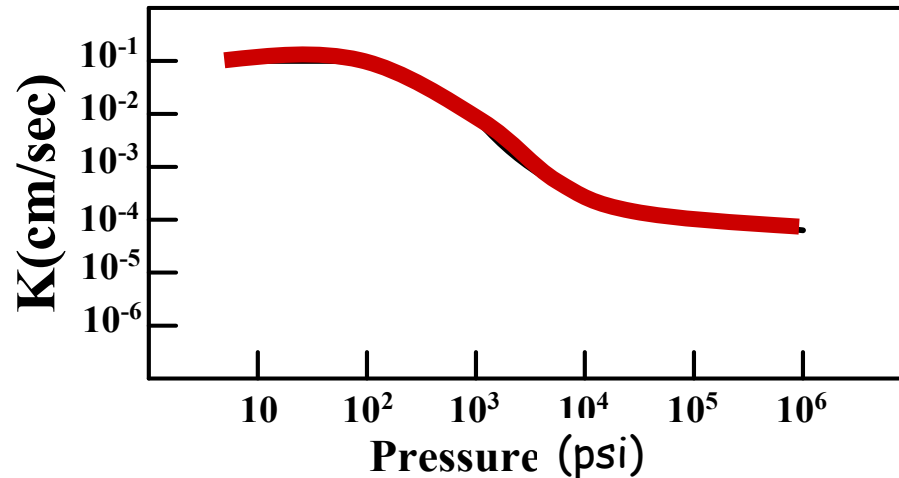
Mn vaporization from 0.25%C steel at 1580℃ as a function of Ar pressure over the melt

* **As Ar pressure increases, K decreases → minimize the vaporization of Mn**
* **Laser welding to reduce the vaporization**

Epitaxial Growth

- Deposition of a layer on a substrate which has a similar crystalline order to that of deposited layer
- Homoepitaxy – Si/Si
- Heteroepitaxy – GaAs/Si
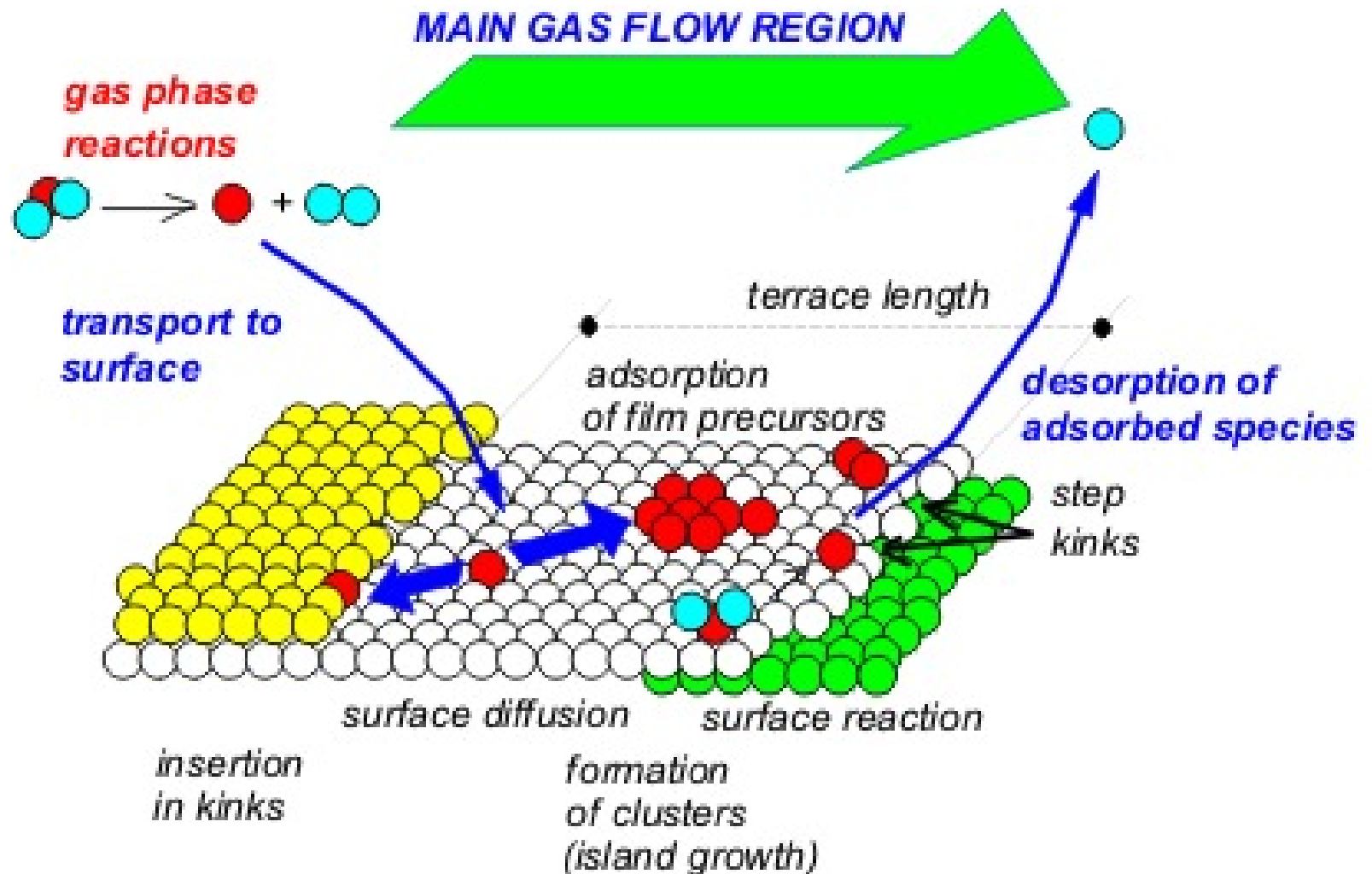
Silicon Epitaxial Growth
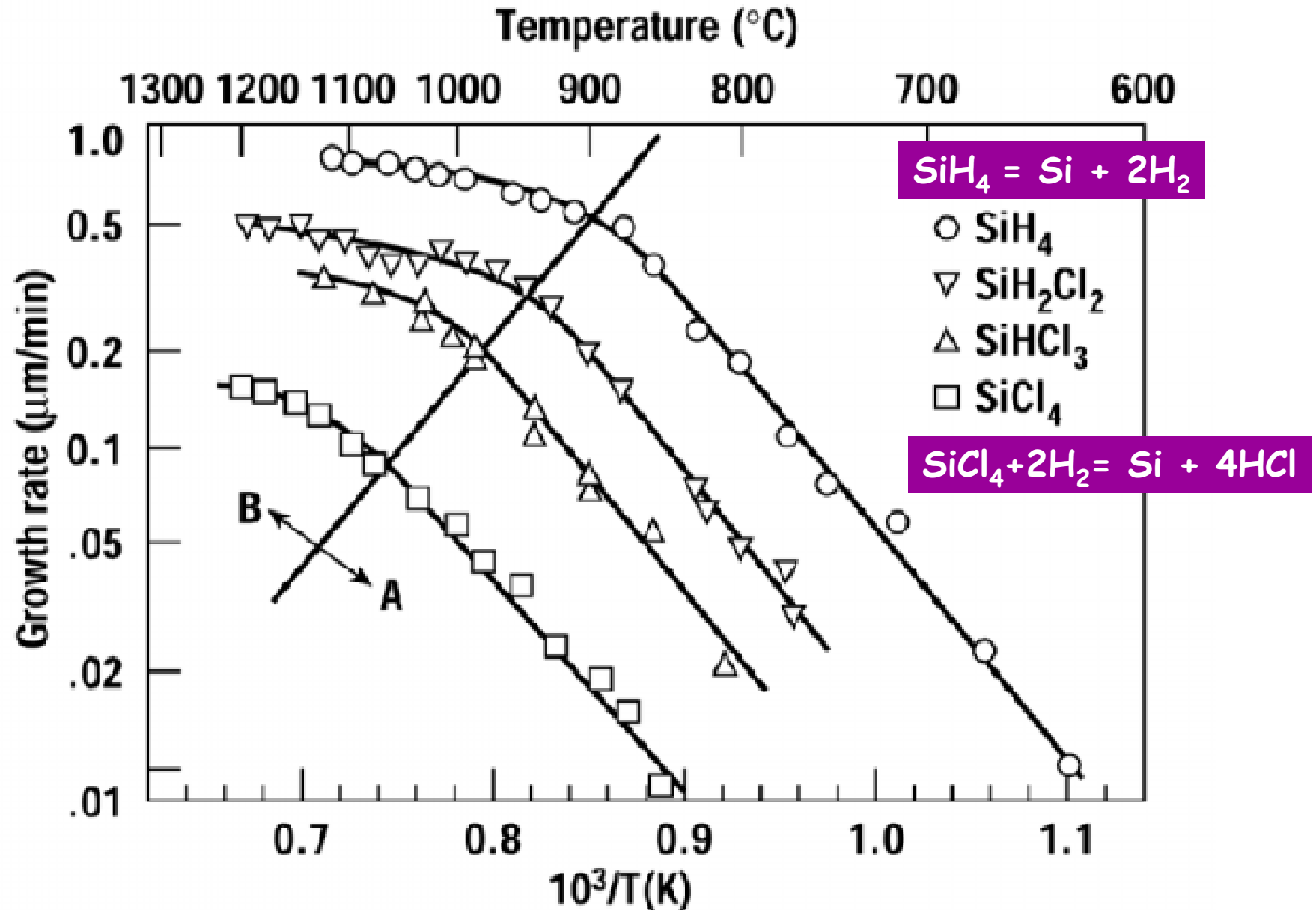
Arrhenius Analysis

$$Rate = K_o \exp\left(-\frac{Q}{RT}\right)$$

$$\ln(Rate) = -\frac{Q}{RT} + \ln(K_o)$$

$-Q_S/R$

$-Q_M/R$

ln(Growth Rate)

Mass Transfer

Surface Reaction

$1/T_o$

T

$Q_{total} = S\%Q_s + (1-S\%)Q_M$

$$A + B \leftrightarrow C$$

$$\text{e.g., } Si + 2H_2 \leftrightarrow SiH_4$$

$$\Delta G_f = -RT \ln(K_{eq})$$

$$\Delta G_f > 0 \Rightarrow \ln(K_{eq}) < 0 \rightarrow C \text{ is unstable}$$
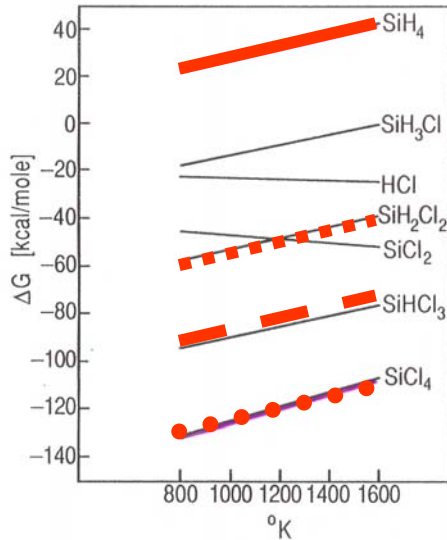
$$\Delta G_f < 0 \Rightarrow \ln(K_{eq}) > 0 \rightarrow C \text{ is stable}$$

Figure 4-4. Free energies of formation of important gaseous species in the Si–Cl–H system in the temperature range 800–1600 K. (Reprinted by permission of the publisher, The Electrochemical Society, Inc. from Ref. 14).
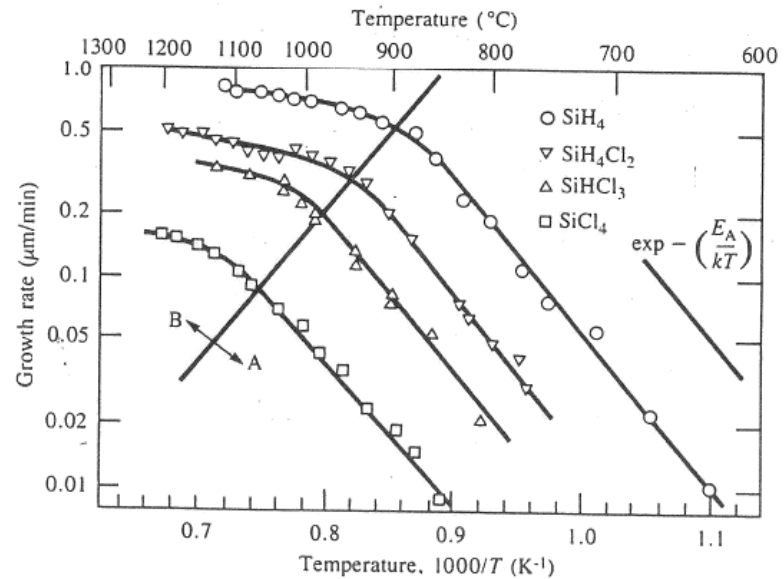
Fig. 6.10 Temperature dependence of the silicon epitaxial growth process for four different sources. The growth rate is surface-reaction-limited in region A and is mass-transfer-limited in region B. Reprinted with permission from Philips Journal of Research from ref. [3].

Vapor-phase Epitaxy

Silicon epitaxial layers are commonly grown with silicon deposited from the gas phase
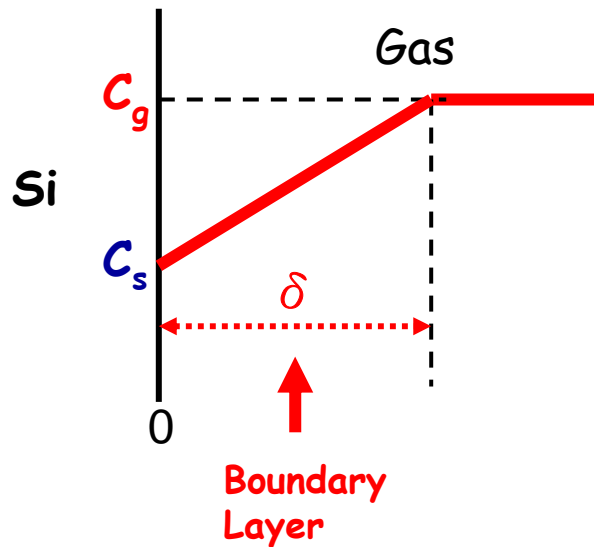
$$J_g = \frac{D_g}{\delta}(C_g - C_s)$$ **(B.L. Mass transfer)**

$$J_s = K_s C_s$$ **(1st order chemical reaction)**

:flux at the surface

K_s: surface reaction rate constant

$at \quad X = 0 \quad J_s = J_g$ **(Assuming Steady State)**

$$K_s C_s = \frac{D_g}{\delta}(C_g - C_s)$$ **($K_{Mg} = D_g/\delta$)**

$$C_s = \frac{\dfrac{D_g}{\delta}C_g}{K_s + \dfrac{D_g}{\delta}}$$

$$J_g = \frac{D_g}{\delta}\left(C_g - \frac{\dfrac{D_g}{\delta}C_g}{K_s + \dfrac{D_g}{\delta}}\right)$$

$$= \frac{C_g}{\dfrac{1}{K_s} + \dfrac{1}{\dfrac{D_g}{\delta}}} = K_{total}C_g$$ **(in-series kinetic processes)**

($1/K_{total} = 1/K_s + 1/K_{Mg}$)
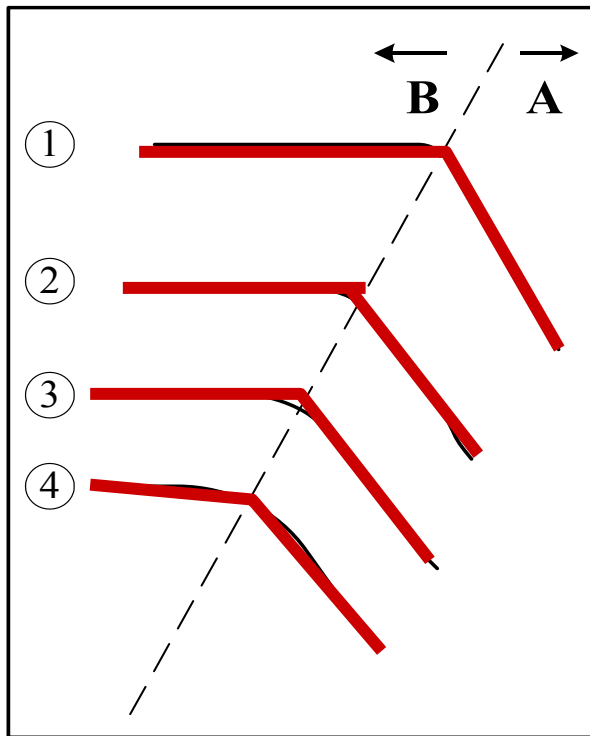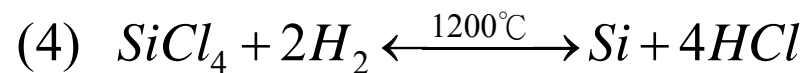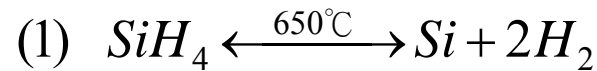
$$\frac{1}{K_{total}} = \frac{1}{K_s} + \frac{1}{D_g/\delta} \qquad \left(\frac{1}{K_{total}} = \frac{1}{K_s} + \frac{1}{K_{Mg}}\right)$$

$$J_g = v_{growth\ rate}\left(\frac{cm}{sec}\right) \cdot N\left(\frac{\#Si}{cm^3}\right)$$

(1) $SiH_4 \xleftrightarrow{\ 650°C\ } Si + 2H_2$

(2) SiH_2Cl_2

(3) $SiHCl_3$

(4) $SiCl_4 + 2H_2 \xleftrightarrow{\ 1200°C\ } Si + 4HCl$

- At low temp (A regime), chemical reaction on surface tends to follow Arrhenius relation with an activation energy of 1.5eV/mol.
  Ref: Si-Si (1.83 eV/mol)

- At high temp (B regime), the reaction becomes rapid and controlling step shifts to mass transfer. The growth rate shows relatively independent of temperature, and that is the area of interest from manufacturing viewpoint.

$$SiCl_{4(g)} + 2H_{2(g)} \xleftrightarrow{1200^{\circ}C} Si_{(solid)} + 4HCl_{(g)}$$
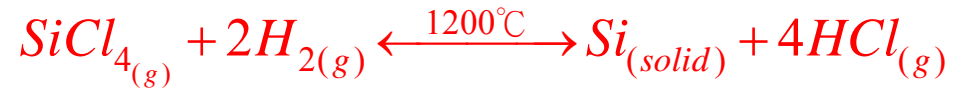
- Reversible
- T~1200℃
- HCl could etch the surface of Si
→cleaning before epitaxy

$$SiCl_{4(g)} + Si_{(s)} \rightarrow 2SiCl_{2(g)}$$

→also etch the surface
- Etching and growing Si layer take place competitively
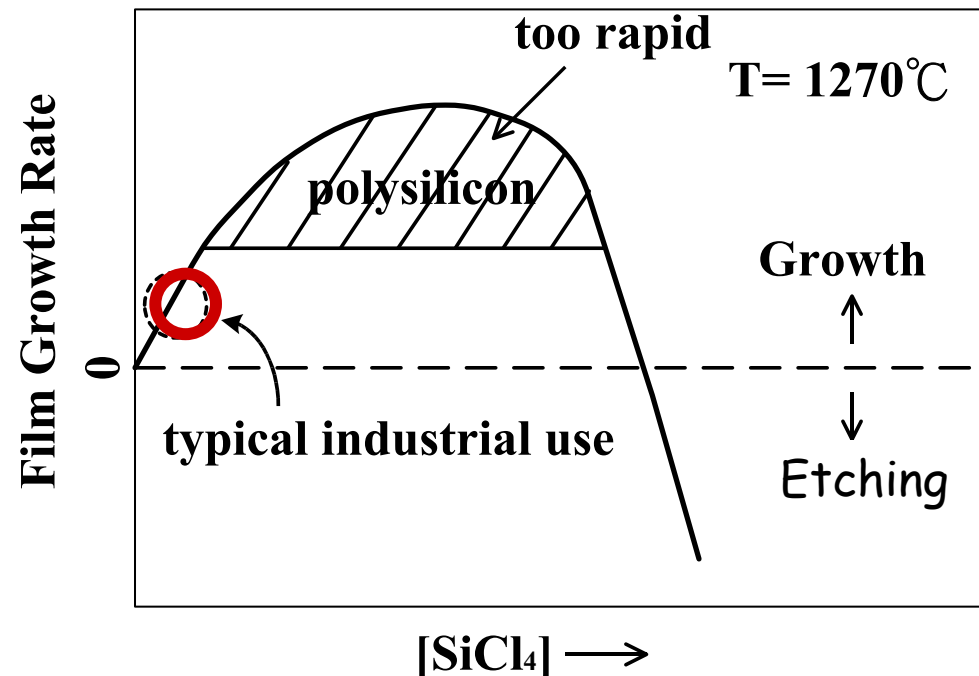
Deposited SiO$_2$ Properties

(1) Excellent electrical insulator
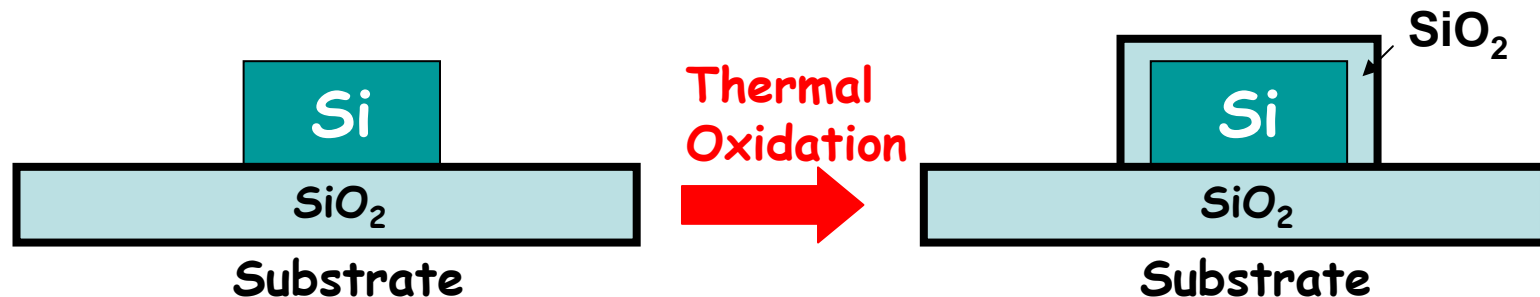   * Resistivity >10^{20} ohm-cm
   * Energy Gap ~ 9eV

(2) High breakdown strength
   * >10^6V/cm

(3) Stable and reproducible Si/SiO$_2$ interface

(4) Conformal oxide growth on exposed Si surface

(5) Excellent diffusion mask for common dopants
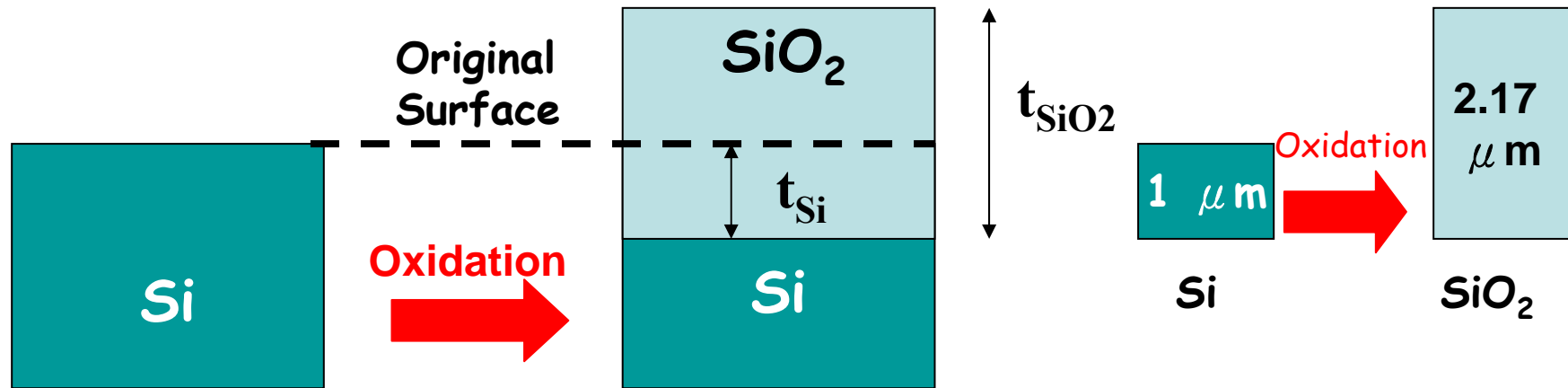   * Diffusivity of B,P,As and Sb in SiO_2 << Si
   * Exceptions including Ga, Cu and Au
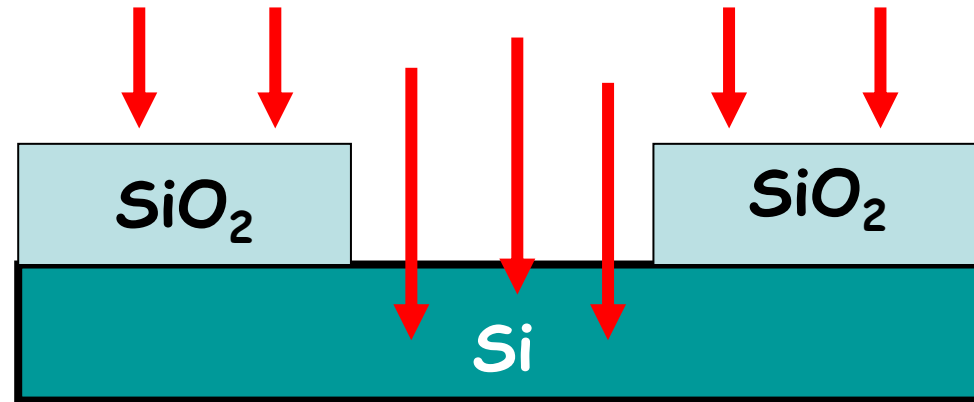
(6) Excellent etching selectivity between SiO_2 and Si
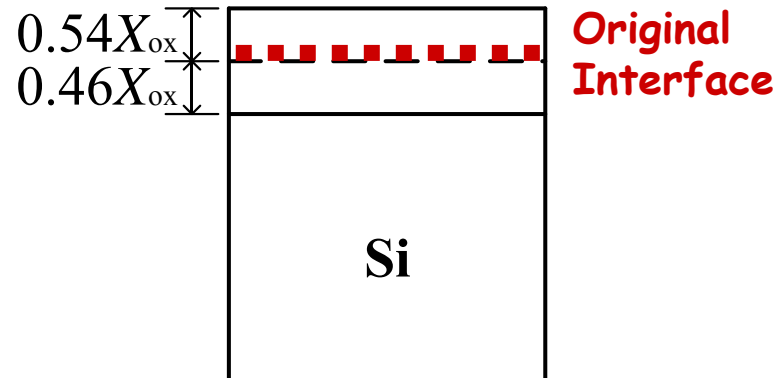
Thickness of Si Consumed during Oxidation

$$t_{Si} = t_{SiO_2} \frac{density_{SiO_2}}{density_{Si}}$$

$$= t_{SiO_2} \frac{2.3 \times 10^{22} \text{ molecules/cm}^3}{5 \times 10^{22} \text{ atoms/cm}^3} = 0.46 t_{SiO_2}$$
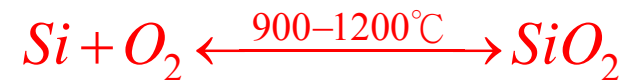
Example of mixed control

Thermal oxidation of Silicon

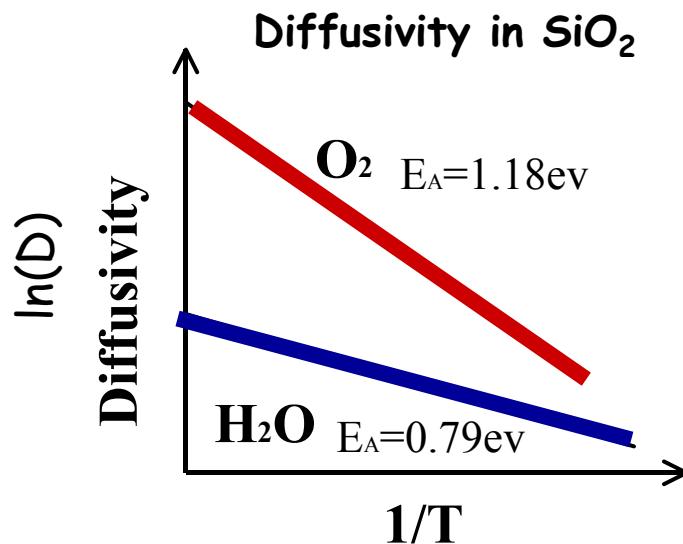Ref:(1)"Introduction to Microelectronic Fabrication" vol.4. R.C. Jaeger, 1988, Chap.3
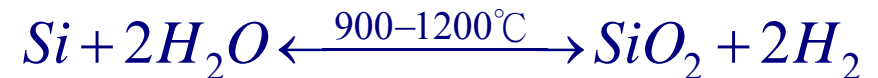(2)"Transport Phenomena in Materials Processing". D.R. Poirier and G.H. Geiger, 1994, Chap. 15
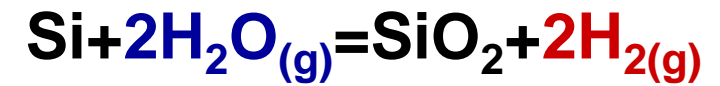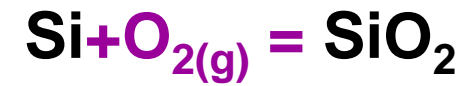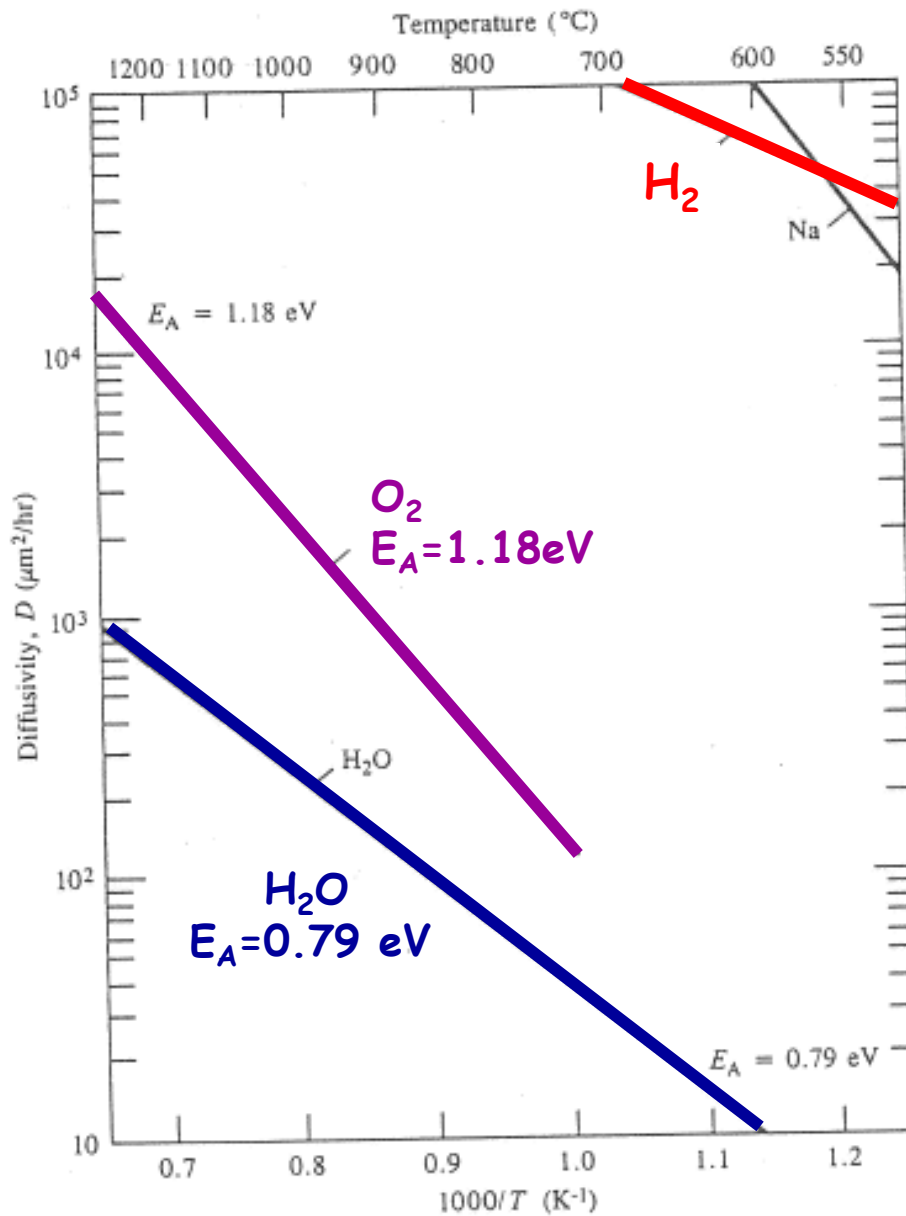
$0.54 X_{ox}$
$0.46 X_{ox}$

Original Interface

Si

Diffusivity in SiO$_2$

$\ln(D)$ / **Diffusivity**

O$_2$ $E_A = 1.18ev$

H$_2$O $E_A = 0.79ev$

$1/T$

Dry Oxidation :

$$Si + O_2 \xleftrightarrow{\quad 900-1200^\circ C \quad} SiO_2$$

Wet Oxidation :

$$Si + 2H_2O \xleftrightarrow{\quad 900-1200^\circ C \quad} SiO_2 + 2H_2$$

Fig. 3.1 Diffusivities of hydrogen, oxygen, sodium, and water vapor in silicon glass. Copyright John Wiley & Sons, Inc. Reprinted with permission from ref. [2].

Plot labels and annotations:

Temperature (°C) — axis values: 1200 1100 1000 900 800 700 600 550

Diffusivity, D ($\mu m^2/hr$) — y-axis: 10^5, 10^4, 10^3, 10^2, 10

$1000/T$ (K^{-1}) — x-axis: 0.7 0.8 0.9 1.0 1.1 1.2

H_2

Na

$E_A = 1.18$ eV

O_2 $E_A = 1.18$ eV

H_2O

H_2O $E_A = 0.79$ eV

$E_A = 0.79$ eV

$Si + O_{2(g)} = SiO_2$

$Si + 2H_2O_{(g)} = SiO_2 + 2H_{2(g)}$

$D_{H2O} \ll D_{H2}$

-> Controlling step: Diffusion of H_2O
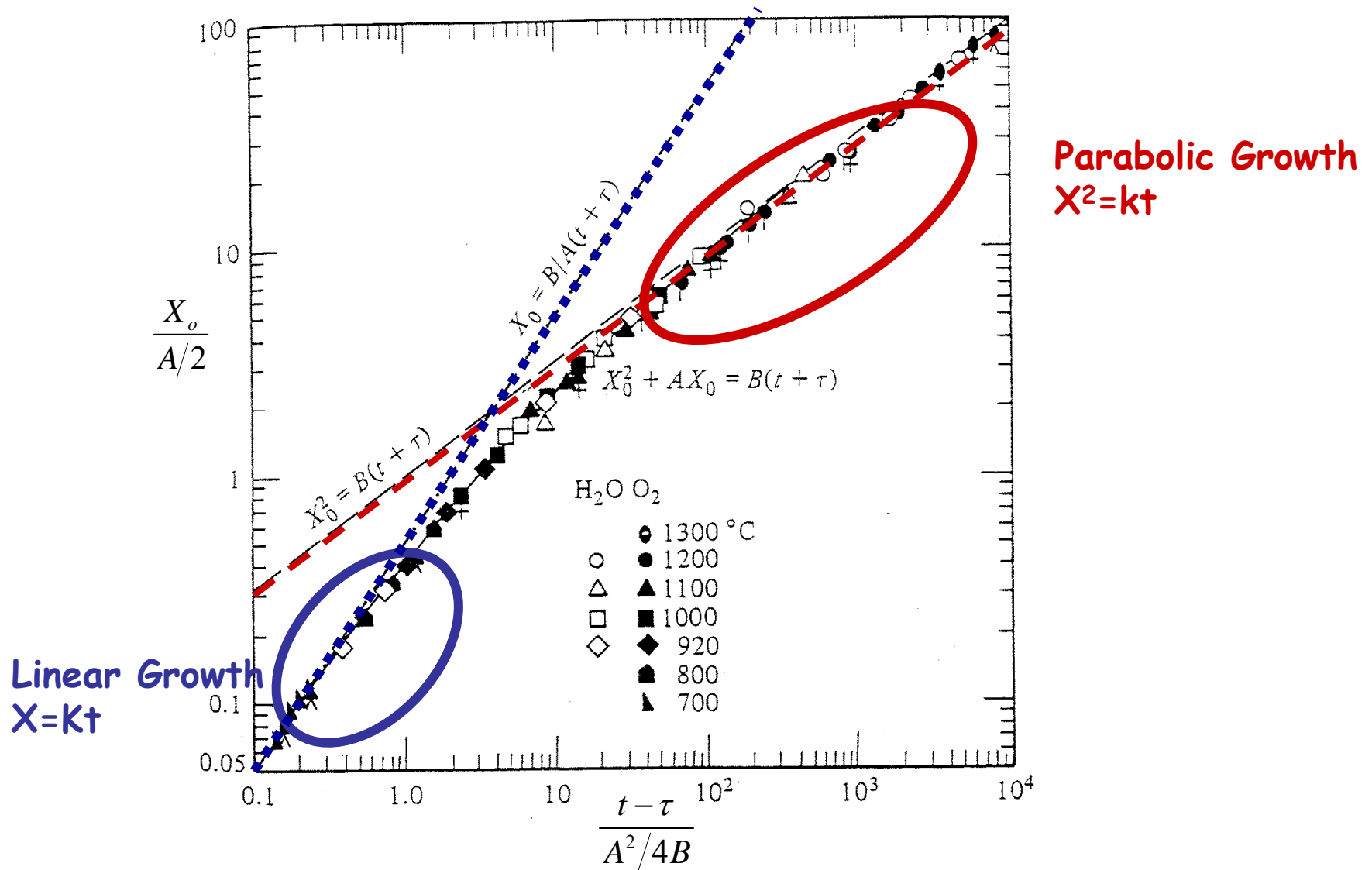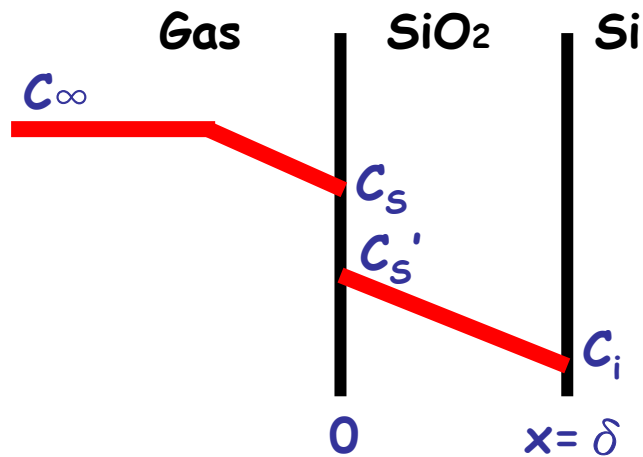
Thermal Oxidation of Si

Figure shows general thermal oxidation behavior of Si. The solid line represents the general relationship, and the dashed and chain lines, two limiting forms. The values of t correspond to $X_i=0$ and 200 Å for wet and dry O respectively. (From Deal and Grove.[5])

Modeling - Oxidation

Gas | **SiO₂** | **Si**

C_∞

C_s

C_s'

C_i

0   **x= δ**

The overall mass transfer of oxygen includes
(1) Mass transfer in the gas
(2) Diffusion through the SiO_2
(3) Reaction at the SiO_2-Si interface

If the oxidation rate is low enough, the fluxes through the above steps are equal. Assuming that the concentration of the diffusion species in the oxide layer is linear

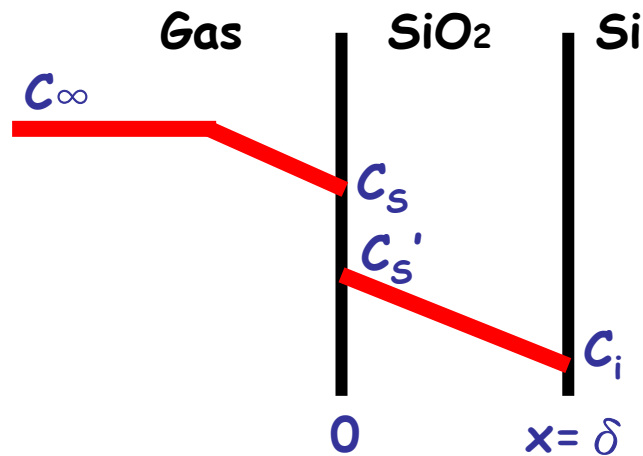$$J = J_G = J_o = J_R$$

$$J_G = K_M (C_\infty - C_s)$$

$$J_o = \frac{D}{\delta}(C_s' - C_i) = K_D(C_s' - C_i)$$

$$J_R = K_R C_i$$

Since the chemical reaction at x=0 is fast enough to establish equilibrium (oxidation rate is low), no interfacial resistance exists.

$$\frac{C_s'}{C_s} = k \text{ (constant)}$$

The concentration of O_2 in the gas

$$C_\infty = \frac{P_{O_2}^\infty}{k_B T}$$

$$C_S = \frac{P_{O_2}^S}{k_B T}$$

At the gas-oxide interface, C_S and C_S' are at equilibrium

$$C_S' = K P_{O_2}^S \quad (K\text{:equilibrium constant})$$

The same to the oxide-Si interface where

$$C_i = K P_{O_2}^i \quad (K\text{:equilibrium constant})$$

$$\therefore K_M(C_\infty - C_s) = K_D(C_s' - C_i) = K_R C_i$$

$$J_{O_2} = \cfrac{C_\infty}{\cfrac{1}{kK_R} + \cfrac{1}{kK_D} + \cfrac{1}{K_M}} \quad (1)$$

m: mass per molecular O_2 **(J=Cv)**

$$J_{O_2} = \frac{\rho_{SiO_2}}{m}\frac{d\delta_{SiO_2}}{dt} \quad (2) \qquad (J_{O_2} = \frac{32}{60}\frac{\rho_{SiO_2}}{m}\frac{d\delta_{SiO_2}}{dt} \approx J_{O_2} = \frac{\rho_{SiO_2}}{2m}\frac{d\delta_{SiO_2}}{dt})$$

$Eq.(1) = (2),\ K_D = \dfrac{D}{\delta}$ and $\delta = \delta_i$ at $t = 0$ (Initial thickness of oxide layer)
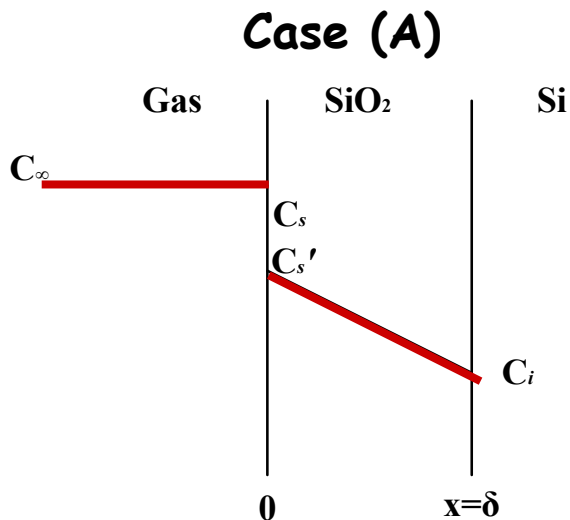
$$\frac{\delta^2 - \delta_i^2}{2Dt} + [\frac{1}{K_R} + \frac{k}{K_M}](\frac{\delta - \delta_i}{t}) - \frac{mkC_\infty}{\rho} = 0$$

$$(\frac{\delta^2 - \delta_i^2}{2Dt} + [\frac{1}{K_R} + \frac{k}{K_M}](\frac{\delta - \delta_i}{t}) - \frac{2mkC_\infty}{\rho} = 0)$$

Case (A) $K_M \to \infty \quad C_\infty = C_s \quad but\ C_s \neq C_s'$

Gas   SiO₂   Si

C_∞

C_s
C_s'

C_i

0   x=δ

$$\frac{C_s'}{C_s} \neq k$$

C_s is not equal to equilibrium value. Interfacial resistance exists at x=0 and flux equals to $h(C_s - C_s')$

$$J = h(C_s - C_s') = \frac{D}{\delta}(C_s' - C_i) = K_R C_i \quad (K_D = D/\delta)$$

$$J = \frac{C_s(= C_\infty)}{\dfrac{1}{h} + \dfrac{1}{K_D} + \dfrac{1}{K_R}}$$

$$\frac{\delta^2 - \delta_i^2}{2Dt} + \left[\frac{1}{K_R} + \frac{1}{h}\right]\left(\frac{\delta - \delta_i}{t}\right) - \frac{mC_\infty}{\rho} = 0$$
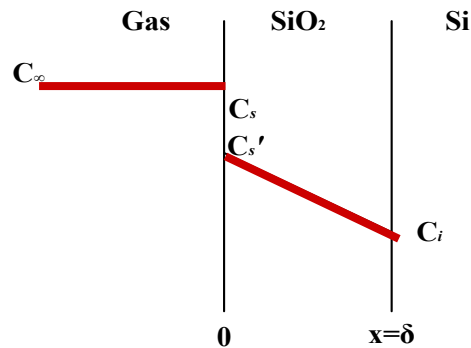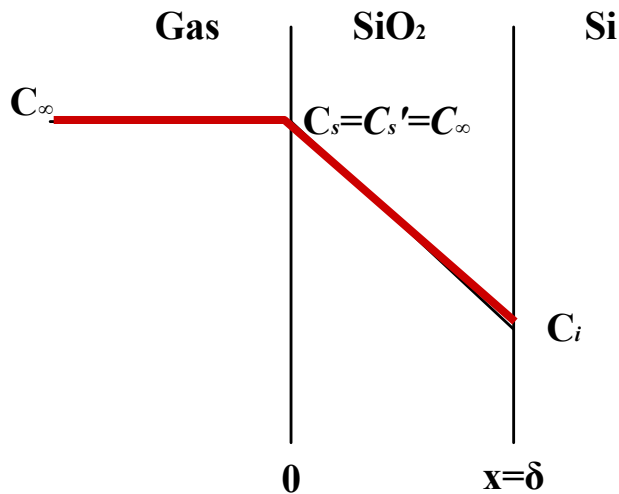
Case (B) $\quad K_M \to \infty \quad h \to \infty \Rightarrow C_\infty = C_s = C_s'$

*No interfacial resistance exists at x=0

$$*J = K_D(C_s' - C_i) = K_R C_i$$

$$*J = \frac{C_s(= C_\infty = C_s')}{\dfrac{1}{K_D} + \dfrac{1}{K_R}}$$

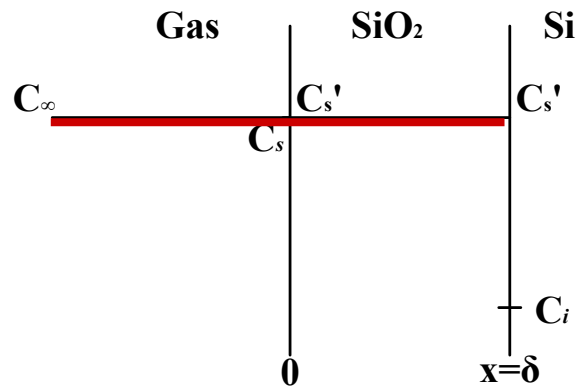$$\frac{\delta^2 - \delta_i^2}{2Dt} + \left[\frac{1}{K_R}\right]\left(\frac{\delta - \delta_i}{t}\right) - \frac{mC_\infty}{\rho} = 0$$

$$\delta = \frac{A}{2}\left\{\left(1 + \frac{4B(t+\tau)}{A^2}\right)^{1/2} - 1\right\}$$

where $\quad A = \dfrac{2D}{K_R}, \quad B = \dfrac{2DC_s' m}{\rho}$

$$\tau = \frac{\delta_i^2 + A\delta_i}{B}$$

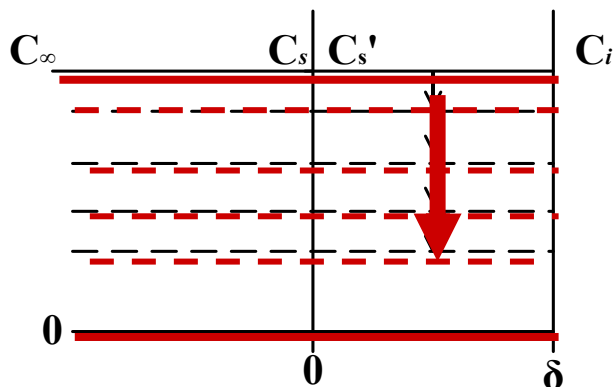## Case (C) $\quad K_M \to \infty \quad h \to \infty \quad K_D \to \infty$

*Interfacial resistance exists at $x = \delta$

$$J_I = h'(C_s' - C_i)$$

$$*J_R = K_R C_i$$

$$J = \frac{C_\infty}{\dfrac{1}{h'} + \dfrac{1}{K_R}}$$

Case (D) $\quad K_M \to \infty \quad h \to \infty \quad K_D \to \infty, \ h' \to \infty$

$$C_\infty = C_s = C_s' = C_i$$

$$J = K_R C_i = K_R C_\infty$$

$$*-V\frac{dC_\infty}{dt} = AK_R C_\infty$$

A: Area of interface at $x = \delta$

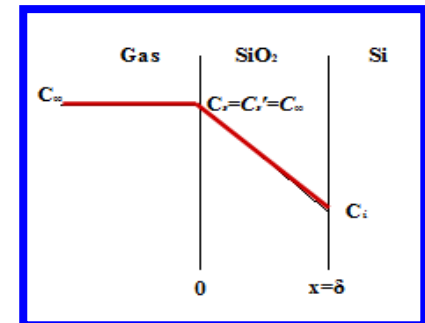$$K_D(C_s' - C_i) = K_R C_i \qquad \text{assuming } K_M = \infty; \ k=1$$

$$J_{O_2} = \frac{C_\infty}{\dfrac{1}{K_R} + \dfrac{1}{K_D}} = \frac{\rho_{SiO_2}}{m}\frac{d\delta_{SiO_2}}{dt} \quad \text{where } K_D = \frac{D}{\delta} \text{ and } \delta_i = 0 \text{ at } t = 0$$

$$\frac{C_\infty}{\dfrac{1}{K_R} + \dfrac{1}{\dfrac{D}{\delta}}} = \frac{\rho_{SiO_2}}{m}\frac{d\delta_{SiO_2}}{dt} \rightarrow \frac{mC_\infty}{\rho_{SiO_2}} = \left(\frac{1}{K_R} + \frac{\delta}{D}\right)\frac{d\delta_{SiO_2}}{dt}$$

$$\int_0^t \frac{mC_\infty}{\rho_{SiO_2}}\,dt = \int_0^\delta \left(\frac{1}{K_R} + \frac{\delta}{D}\right)d\delta_{SiO_2} \rightarrow \frac{mC_\infty}{\rho_{SiO_2}}t = \frac{\delta}{K_R} + \frac{\delta^2}{2D}$$
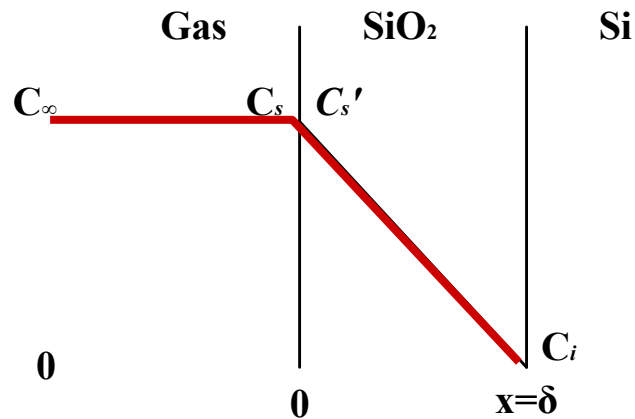

$$\delta^2 + \frac{2D}{K_R}\delta = \frac{2DmC_\infty}{\rho_{SiO_2}}t \rightarrow \delta^2 + A\delta = Bt$$

$$\delta = \frac{-A + \sqrt{A^2 + 4Bt}}{2} = \frac{-A + A\sqrt{1 + \dfrac{4Bt}{A^2}}}{2} = \frac{A}{2}\left(\sqrt{1 + \frac{4B}{A^2}t} - 1\right)$$

Case (E) $K_M \to \infty$ $h \to \infty$ $K_R \to \infty$, $h' \to \infty$

Gas   SiO₂   Si

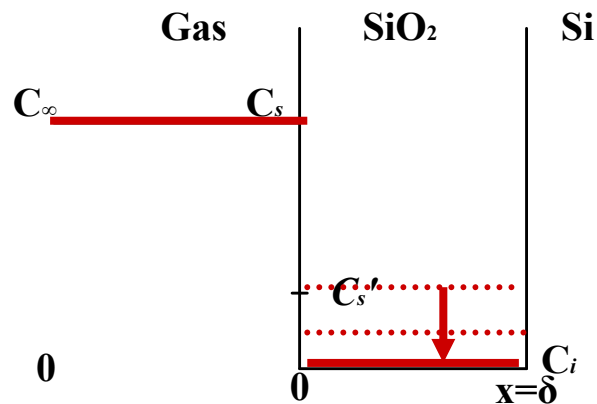C_∞ C_s $C_s{}'$

C_i

0

0   $x=\delta$

$$J = K_D(C'_s - C_i)$$
$$= K_D(C'_s - 0) \quad \text{(Irreversible)}$$
$$J = K_D(C'_s - C^{eq}) \quad \text{(Reversible)}$$

Case (F) $K_M \to \infty$ $K_D \to \infty$ $K_R \to \infty$, $h' \to \infty$

Gas   SiO₂   Si

C_∞ C_s

$C_s{}'$

C_i

0

0   $x=\delta$

$$J = h(C_s - C'_s)$$

(Interfacial resistance exists at x=0)

C_i=0 for irreversible reaction
C_i=C^{eq} for reversible reaction

Case (B) $K_M \to \infty \quad h \to \infty \quad h' \to \infty$

δ_i = the initial thickness of oxide on the surface
= 10-20 Å due to atmospheric oxidation

$Short\ Time\ \ t + \tau << \dfrac{A^2}{4B}$

$\delta(t) = \dfrac{B}{A}(t + \tau)$

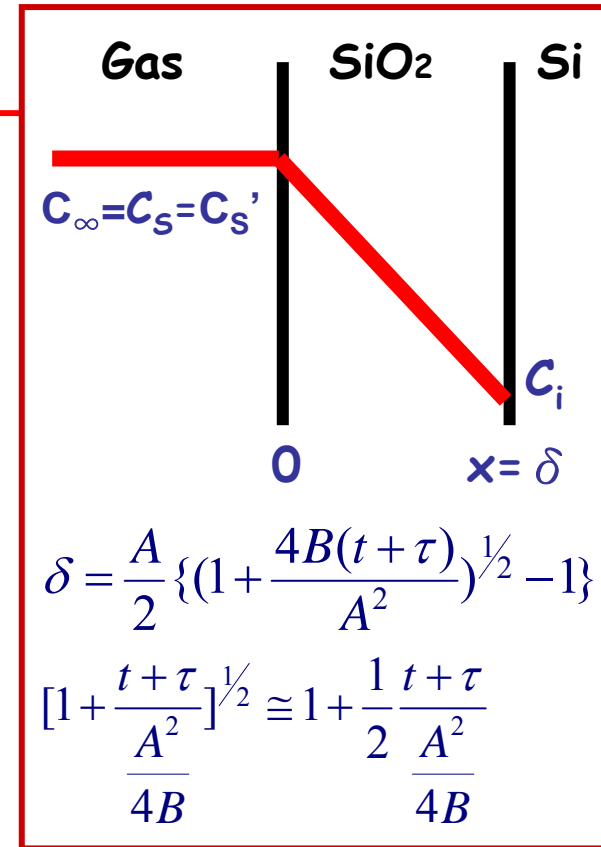$\dfrac{B}{A} = \dfrac{2DC_s' m / \rho}{2D / K_R} = \dfrac{C_s' m K_R}{\rho}$

* Linear growth period and the rate-controlling step is the reaction at the silicon surface

$Long\ Time\ \ t + \tau >> \dfrac{A^2}{4B} \quad (t > \tau)$

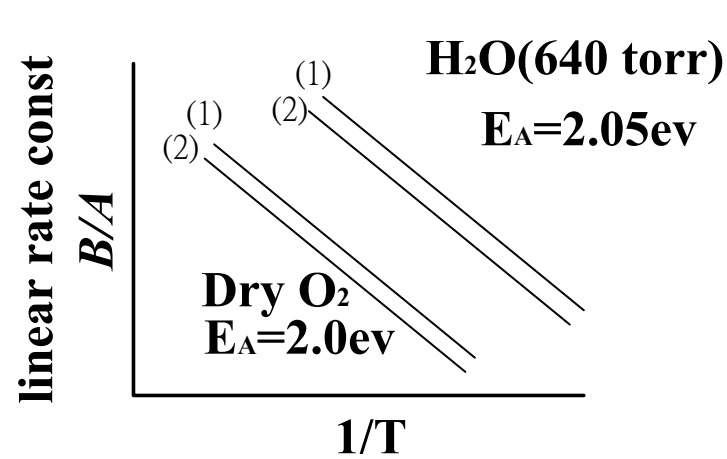$\delta(t) = \sqrt{Bt}$

$B = \dfrac{2DC_s' m}{\rho}$

- Parabolic growth period
- Diffusion controlling process

Gas | SiO₂ | Si

$C_\infty = C_s = C_s'$

C_i

0   x = δ

$\delta = \dfrac{A}{2}\{(1 + \dfrac{4B(t+\tau)}{A^2})^{1/2} - 1\}$

$[1 + \dfrac{t+\tau}{\frac{A^2}{4B}}]^{1/2} \cong 1 + \dfrac{1}{2}\dfrac{t+\tau}{\frac{A^2}{4B}}$

$\delta = \dfrac{A}{2}\{(1 + \dfrac{4B(t+\tau)}{A^2})^{1/2} - 1\}$

$\approx \dfrac{A}{2}(\dfrac{4Bt}{A^2})^{1/2} \approx (Bt)^{1/2}$

Short time

linear rate const B/A

(1)
(2)
(1)
(2)

Dry O₂
E_A=2.0ev

1/T

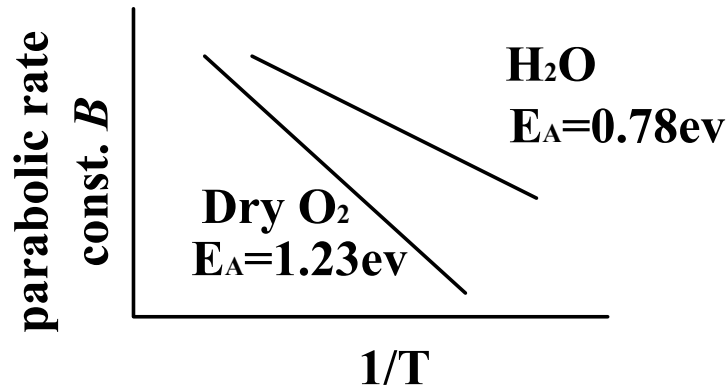H₂O(640 torr)
E_A=2.05ev

(1) (111)Si
(2) (100)Si

$$\frac{B/A(111)}{B/A(100)} = 1.68$$

E_A=2~2.05 eV close to the bonding energy of Si-Si (1.83 eV/mol)

Long time

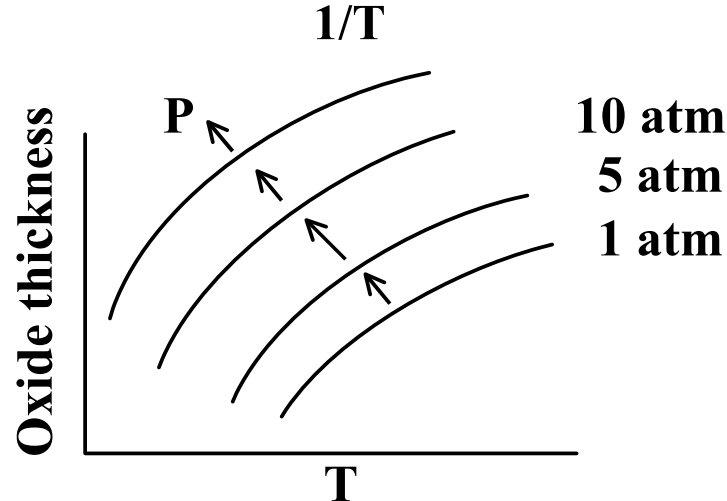**Oxidation Rate Wet >> Dry**

parabolic rate const. B

Dry O₂
E_A=1.23ev

1/T

H₂O
E_A=0.78ev

$$\because C'_S(H_2O) >> C'_S(O_2)$$

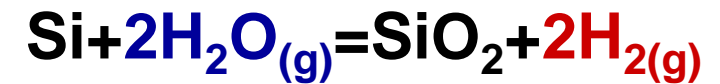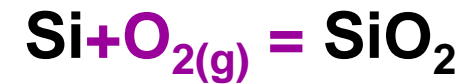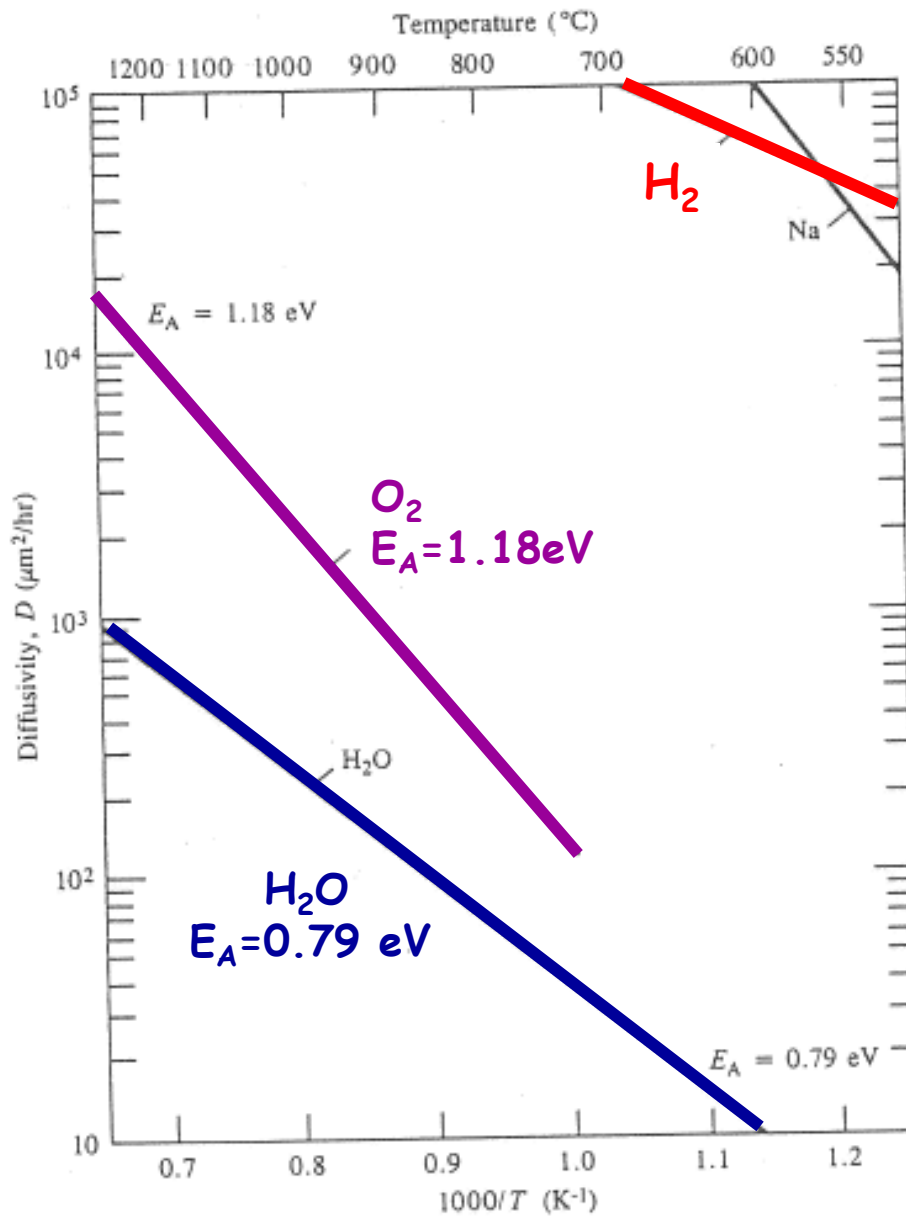**Pressure effect**

Oxide thickness

P

10 atm
5 atm
1 atm

T

$$B = \frac{DC'_S m}{\rho}$$

$$C'_S = C_\infty$$

α Pressure of reacting gas

Low temp. oxidation process for VLSI fabrication requires high pressure

Fig. 3.1 Diffusivities of hydrogen, oxygen, sodium, and water vapor in silicon glass. Copyright John Wiley & Sons, Inc. Reprinted with permission from ref. [2].

The figure is annotated with:

$Si + O_{2(g)} = SiO_2$

$Si + 2H_2O_{(g)} = SiO_2 + 2H_{2(g)}$

$D_{H2O} << D_{H2}$

->Controlling step: Diffusion of H_2O

Graph axes:
- Top axis: Temperature (°C) — 1200, 1100, 1000, 900, 800, 700, 600, 550
- Left axis: Diffusivity, D ($\mu m^2/hr$) — from 10 to 10^5
- Bottom axis: $1000/T$ (K^{-1}) — 0.7, 0.8, 0.9, 1.0, 1.1, 1.2

Curve labels:
- H_2
- Na
- O_2, $E_A = 1.18\,eV$
- H_2O, $E_A = 0.79\,eV$

$$Si + 2H_2O = SiO_2 + 2H_2$$
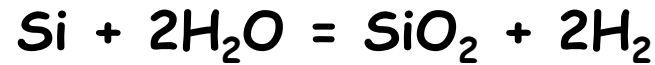
*Since D_{H2} in SiO_2 = $1000D_{H2O}$ in SiO_2
→H_2O diffusion control

*T=1273K
$C_S'(H_2O)$ = 3×10^{19} molecule/cm³
$C_S'(O_2)$ = 5×10^{16} molecule/cm³

$$\therefore C_S' \approx KP_{O_2}^S$$

$$K_{H_2O} >> K_{O_2}$$

→Oxidation rate in H_2O>>Dry O_2

Note: * Wet oxidation results in poor quality silica film with more dangling
bonds, larger leakage currents and lower dielectric strength.
   * Thick oxide film prepared by a dry-wet-dry cycle, i.e., a long
wet oxidation bracketed by short dry oxidation.

Diffusion-controlling process
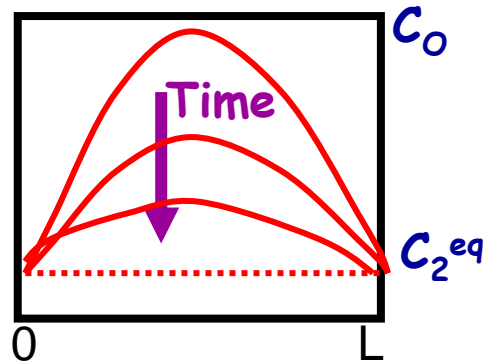
Reversible

$$J_D = -D\frac{\partial C}{\partial x} = J_{evap} \ \ at \ x = 0 \ and \ x = l$$

$$J_{evap} = \frac{\alpha(P_1 - P_2)}{\sqrt{2\pi MkT}}$$

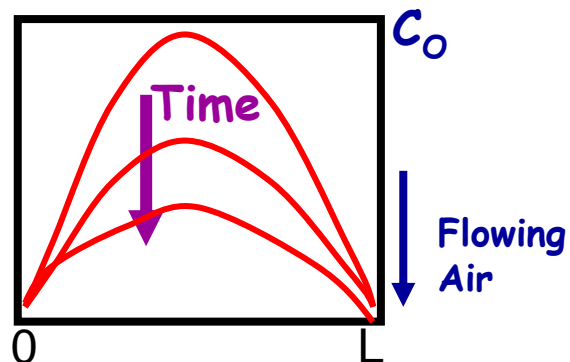$$if \ P_1 = 0 \ \text{in vacuum}$$

$$J_{evap} = \frac{-\alpha P_2^{eq}}{\sqrt{2\pi MkT}} = \frac{-\alpha C_S^{eq} P_2^o}{\rho\sqrt{2\pi MkT}}$$

P_2^o : pressure of pure component 2
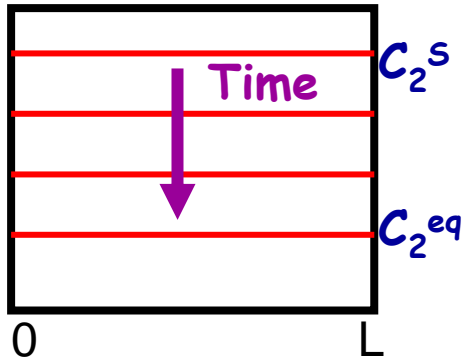
ρ : density of alloy

Irreversible

$$J_D = -D\frac{\partial C}{\partial x}$$

J_{evap} is too large to calculate directly.
C_2^S(surface)=0→ removed forcefully.
J_D has to be calculated directly.

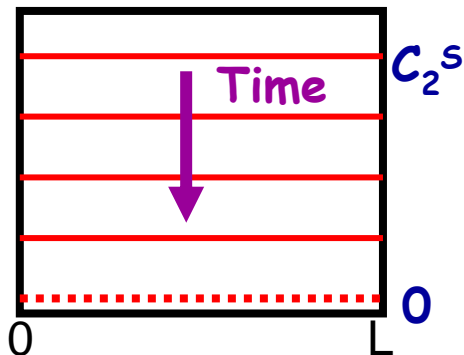# Reaction or Evaporation Controlling Process

Reversible

$$J_r = k(C_2^S - C_2^{eq})$$

:driving force for degassing

$$J_{evap} = \frac{\alpha(0 - P_2)}{\sqrt{2\pi M kT}} \ (in \ vacuum)$$

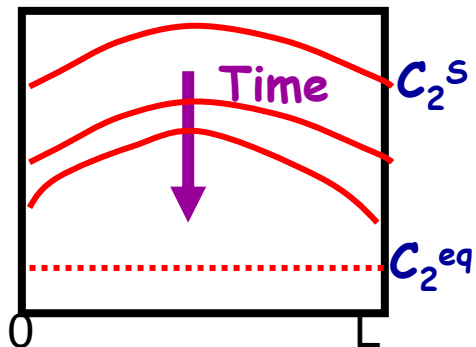$$= \frac{-\alpha C_2^S P_2^o}{\rho\sqrt{2\pi M kT}}$$

Irreversible

$$J_r = k(C_2^S - 0)$$

$$J_{evap} = \frac{-\alpha C_2^S P_2^o}{\rho\sqrt{2\pi M kT}}$$

Mixed Controlling Process

$$J_D = -D\frac{\partial C}{\partial x}$$

$$J_{evap} = \frac{-\alpha C_2^S P_2^o}{\rho\sqrt{2\pi M kT}}$$

$$J_D = J_{evap} \ at \ x = 0 \ and \ x = l$$