

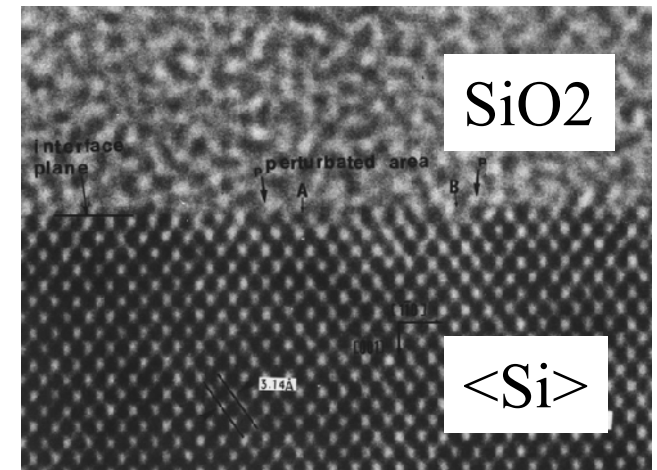
Thermal Oxidation of Si

- General Properties of SiO_2
- Applications of thermal SiO_2
- Deal-Grove Model of Oxidation

Thermal SiO_2 is **amorphous**.

Weight Density = 2.20 gm/cm^3

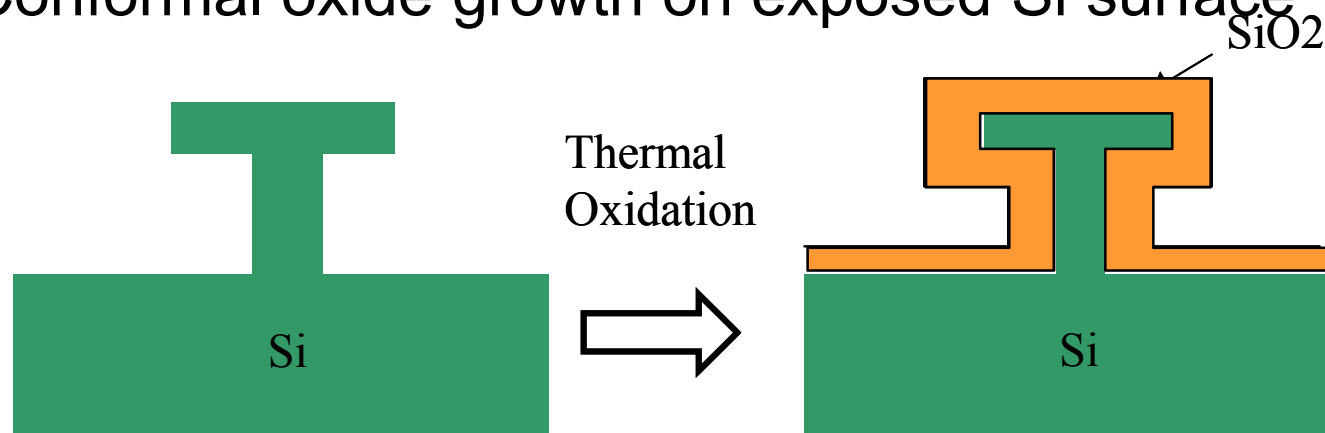
Molecular Density = $2.3\text{E}22 \text{ molecules/cm}^3$



Crystalline SiO_2 [Quartz] = 2.65 gm/cm^3

Thermal SiO₂ Properties

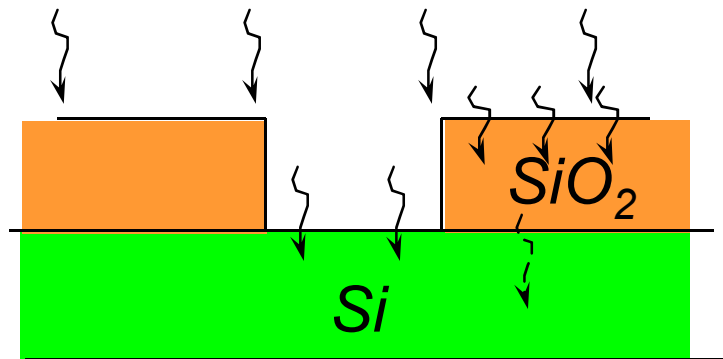
- (1) Excellent Electrical Insulator
Resistivity > 1E20 ohm-cm Energy Gap ~ 9 eV
- (2) High Breakdown Electric Field
> 10MV/cm
- (3) Stable and Reproducible Si/SiO₂ Interface
- (4) Conformal oxide growth on exposed Si surface



Thermal SiO₂ Properties – cont.

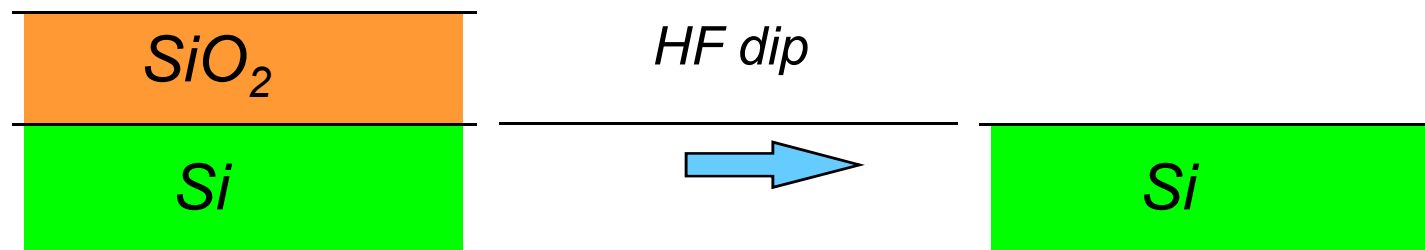
(5) SiO₂ is a good diffusion mask for common dopants

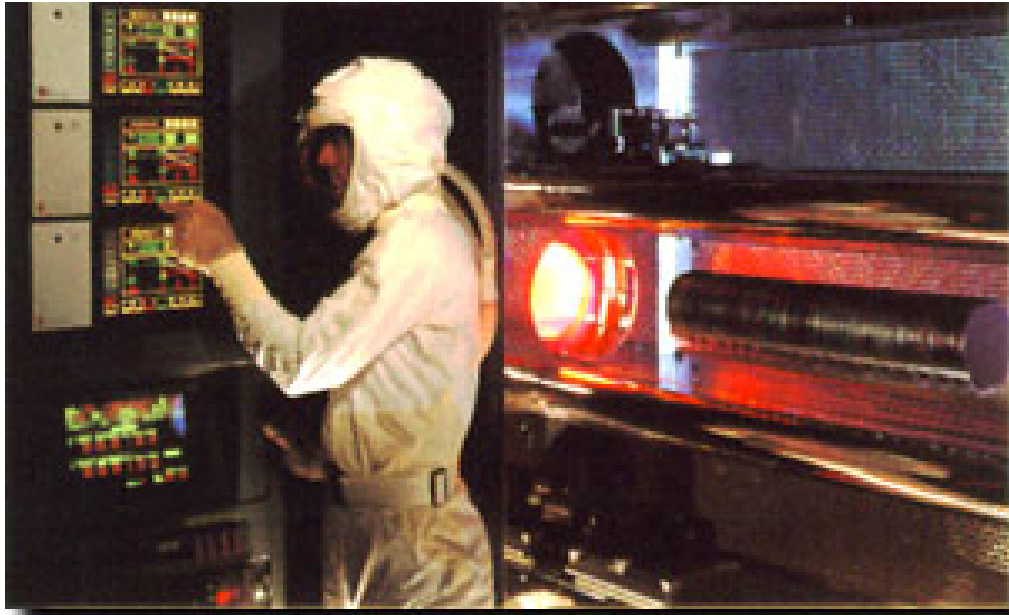
$$D_{\text{SiO}_2} \ll D_{\text{Si}} \quad \text{e.g. B, P, As, Sb.}$$



*exceptions are Ga (a p-type dopant) and some metals, e.g. Cu, Au

(6) Very good etching selectivity between Si and SiO₂.

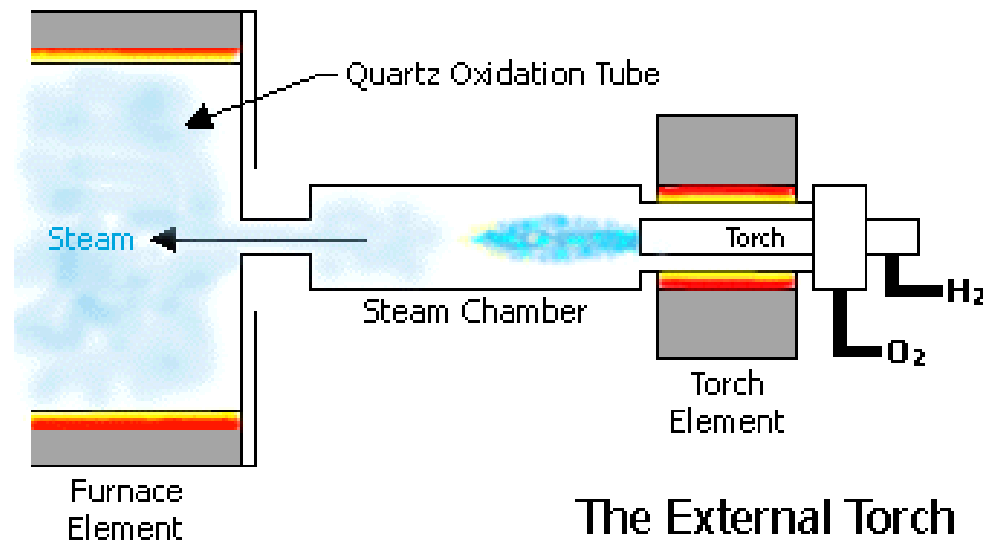




Oxidation Furnace
(Silicon Valley Group - Thermco Systems)

Thermal Oxidation Equipment

Steam generation
for wet oxidation



Volume change due to thermal oxidation

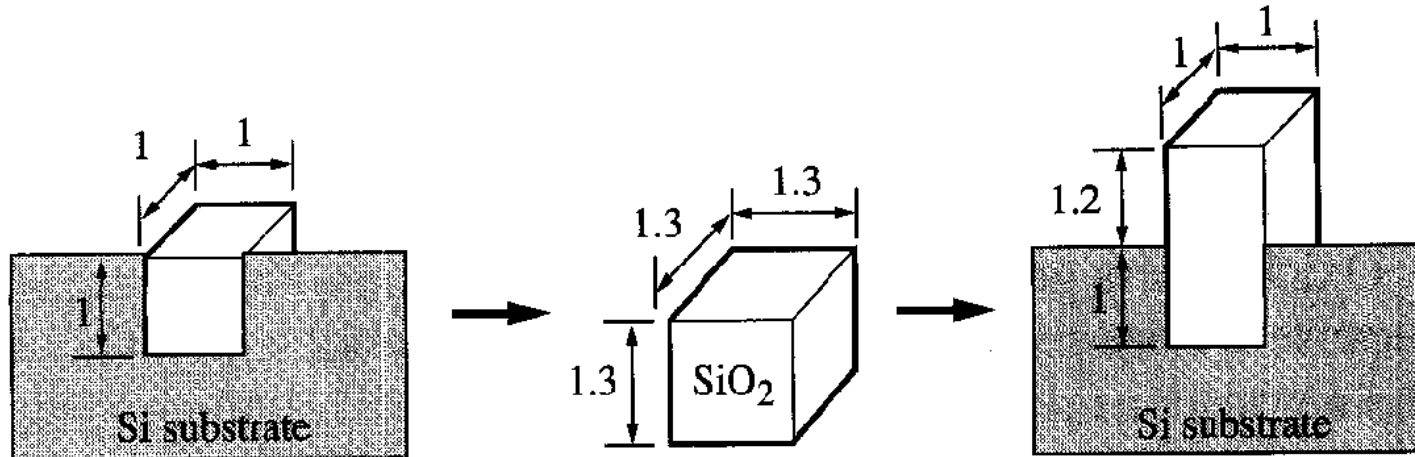


Figure 6-3 Volume expansion that occurs during silicon oxidation. A unit volume of silicon on the left is transformed into SiO₂. In the middle the volume expansion is unconstrained; on the right the substrate restricts the expansion to one dimension.

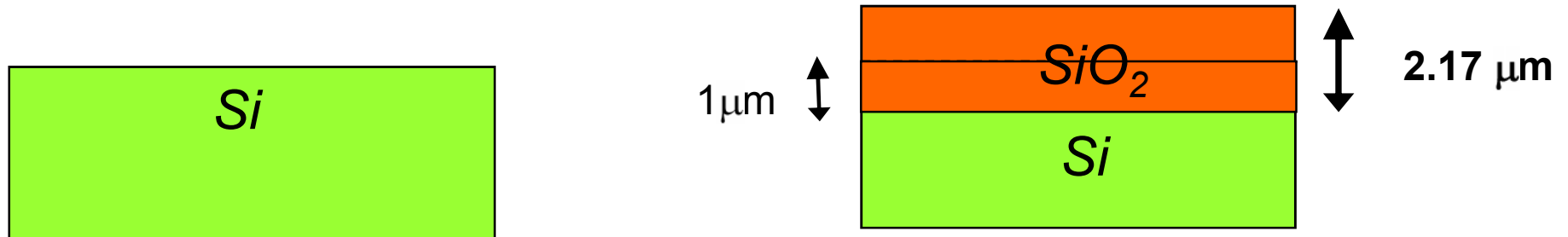
Molecular Density of SiO₂ = 2.3E22 molecules / cm³

Atomic Density of Si = 5.0E22 atoms / cm³

∴ Volume of SiO₂ = 2.16 × Volume of Si consumed

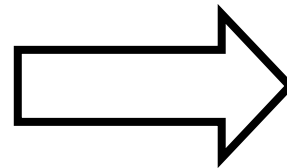
Mechanical stress will be generated with confined oxidation

One-dimensional planar oxide growth



•Roughly half of oxide grown is under original Si surface

$1\ \mu\text{m}$ Si oxidized



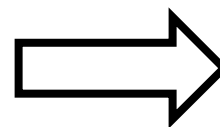
$2.17\ \mu\text{m}$ SiO_2

Suggested exercise:

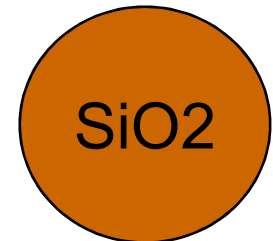
$1\ \mu\text{m}$ diameter
Si *sphere*



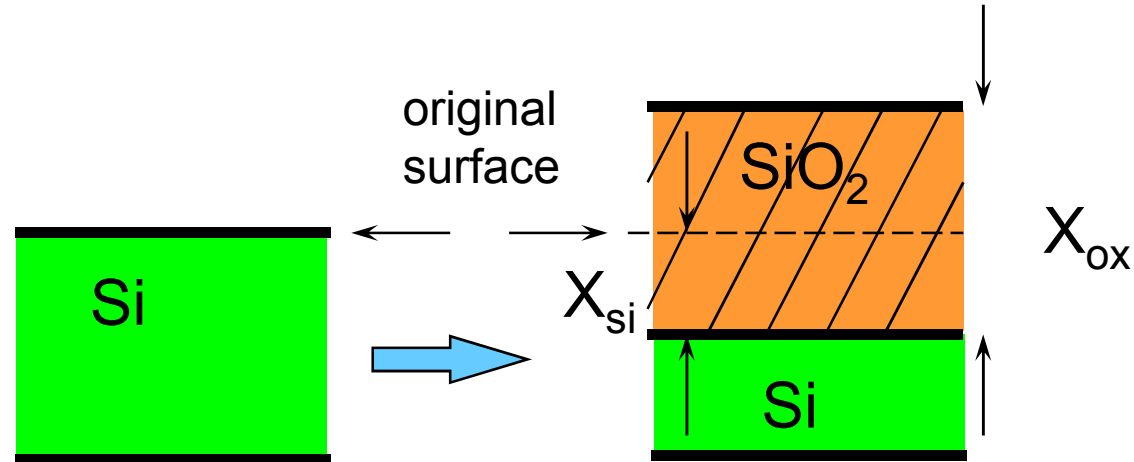
completely
oxidized



$1.3\ \mu\text{m}$
diameter
 SiO_2 *sphere*



Thickness of Si consumed (planar oxidation)

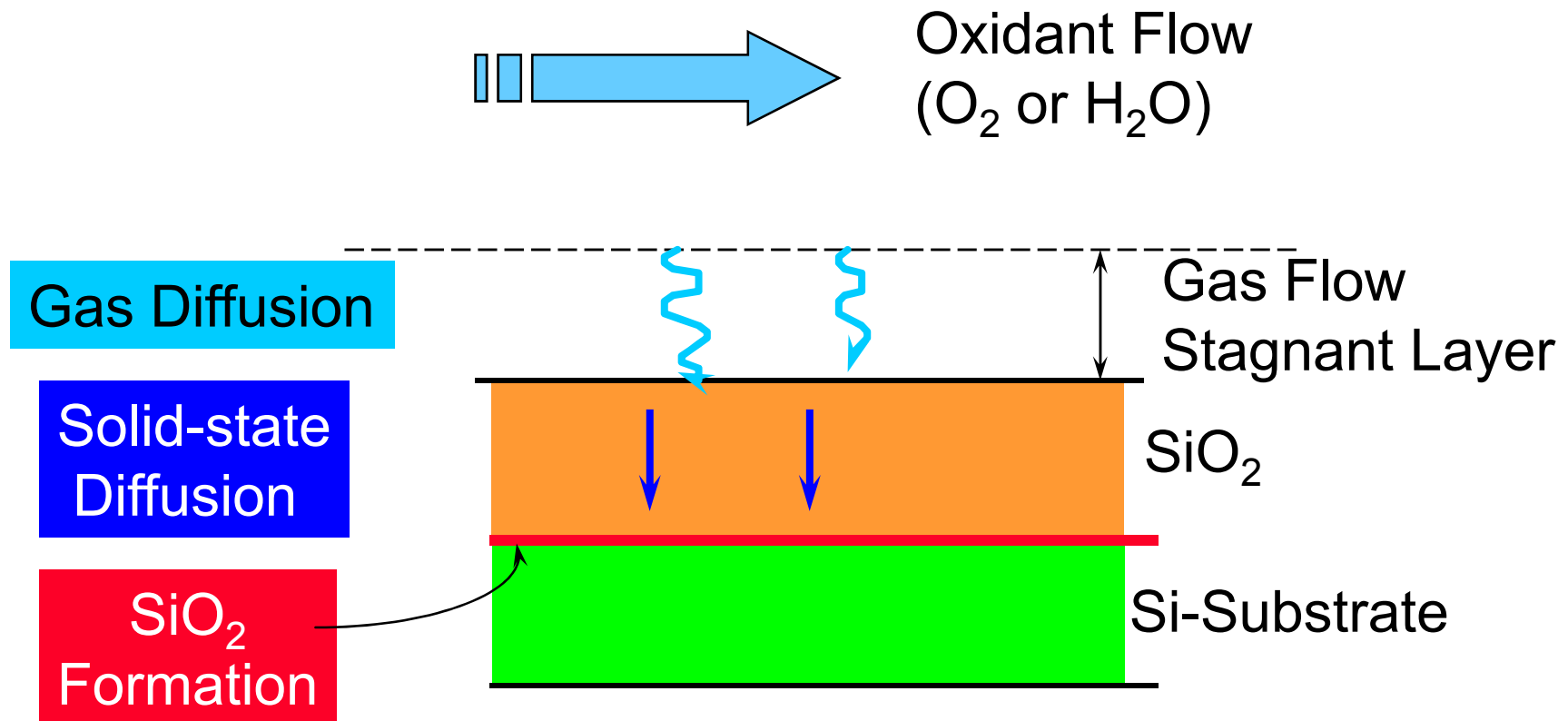


$$X_{si} = X_{ox} \cdot \frac{N_{ox}}{N_{si}}$$

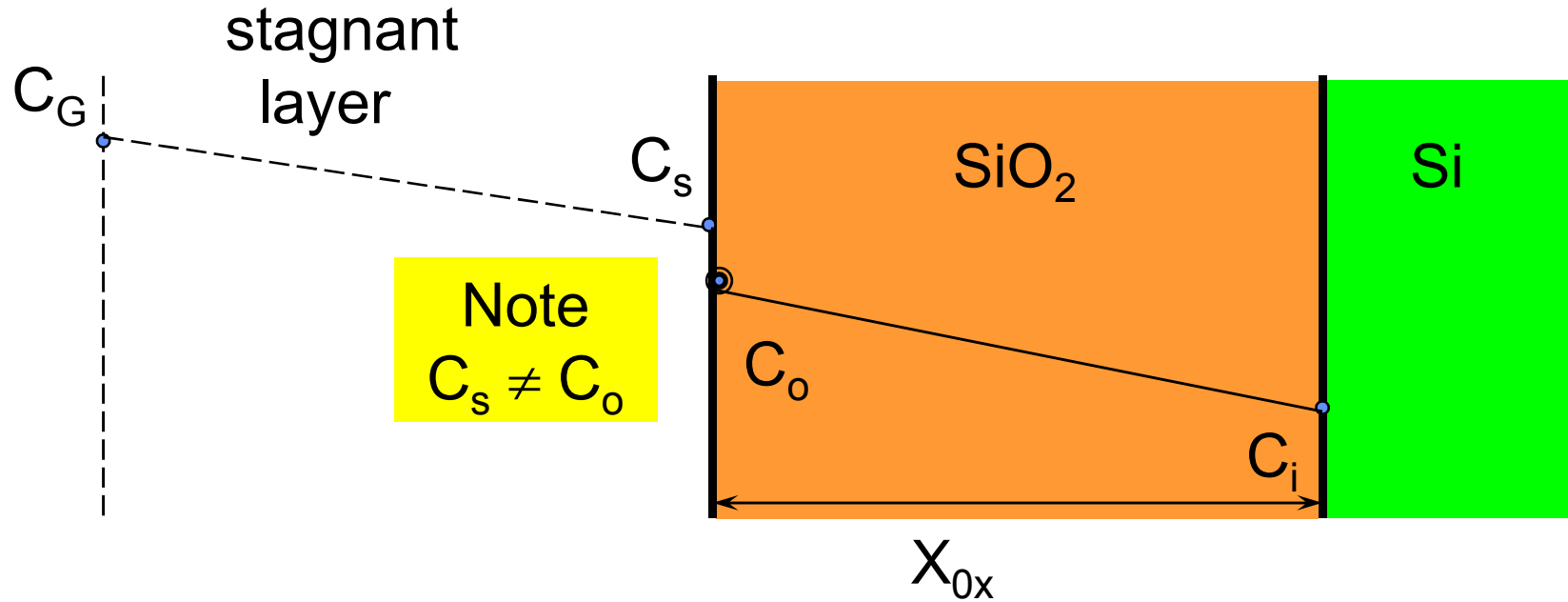
N_{ox} ← molecular density of SiO₂
 N_{si} ← atomic density of Si

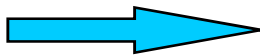
$$= X_{ox} \cdot \frac{2.3 \times 10^{22} \text{ molecules} / \text{cm}^3}{5 \times 10^{22} \text{ atoms} / \text{cm}^3} = 0.46 X_{ox}$$

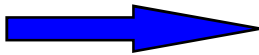
Kinetics of SiO_2 Growth




Deal-Grove Model



F_1 
 gas
 transport
 flux

F_2 
 diffusion
 flux
 through SiO₂

F_3 
 reaction
 flux
 at interface

$$F_1 = h_G(C_G - C_S)$$

Mass transfer coefficient [cm/sec].

$$F_2 = -D \frac{\partial C}{\partial x} \quad \text{“Fick’s Law of Solid-state Diffusion”}$$

$$\cong D \cdot \left(\frac{C_o - C_i}{X_{ox}} \right)$$

Diffusivity [cm²/sec]

$$F_3 = k_s \cdot C_i$$

Surface reaction rate constant [cm/sec]

Comment: The derivation used in Jaeger textbook assumes F_1 is large (not a rate-limiting factor for growth rate). Hence, the algebra looks simpler. However, the lecture notes derivation includes gas transport effect and can be directly applied to the CVD growth rate model which will be discussed in later weeks.

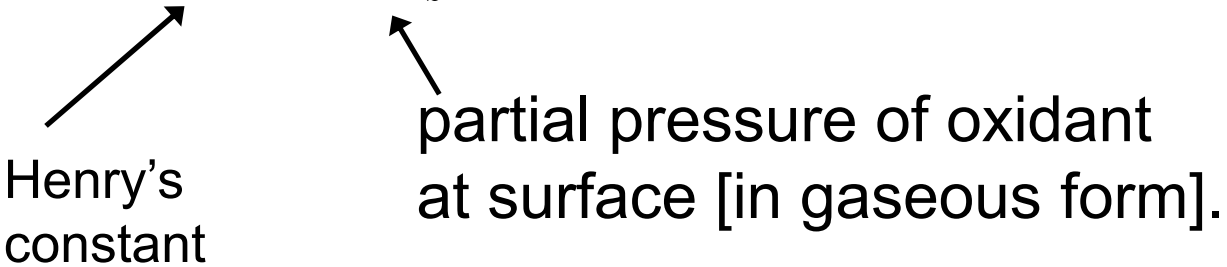
How to solve the oxidant concentrations?

- C_s and C_o are related by Henry's Law
- C_G is a controlled process variable (proportional to the input oxidant gas pressure)

Only C_o and C_i are the 2 unknown variables which can be solved from the steady-state condition:
$$F_1 = F_2 = F_3 \text{ (2 equations)}$$

Derivation of Oxidation Growth Rate

$$C_o = H \cdot P_s \quad \text{Henry's Law}$$



$$= H \cdot (kT \cdot C_s) \quad \text{from ideal gas law } PV = NkT$$

$$\therefore C_s = \frac{C_o}{HkT}$$

Derivation of Oxidation Growth Rate – cont.

Define $C_A \equiv (HkT \cdot C_G)$ This is a control process variable. For a given oxidant pressure, C_A is known.

F_1 can be re-written as:

$$F_1 = \frac{h_G}{HkT} (C_A - C_o)$$

$\equiv h$

Using the steady-state condition:

Conservation of mass flux

$$F_1 = F_2 = F_3$$

① ②

2 equations to solve the 2 unknowns: C_o & C_i

Derivation of Oxidation Growth Rate – cont.

Therefore

$$C_i = \frac{C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}}$$

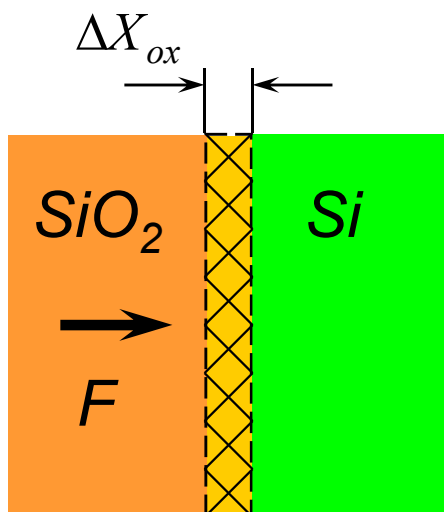
$$C_o = C_i \cdot \left(1 + \frac{k_s X_{ox}}{D} \right)$$

$$\boxed{\mathbf{F}} \quad (= \mathbf{F}_1 = \mathbf{F}_2 = \mathbf{F}_3) = \mathbf{k}_s \cdot \mathbf{C}_i = \boxed{\frac{\mathbf{k}_s \mathbf{C}_A}{1 + \frac{\mathbf{k}_s}{\mathbf{h}} + \frac{\mathbf{k}_s \mathbf{X}_{ox}}{\mathbf{D}}}}$$

Now, convert Flux F into Oxide Thickness Growth Rate

$$F = N_1 \cdot \left(\frac{dX_{ox}}{dt} \right)$$

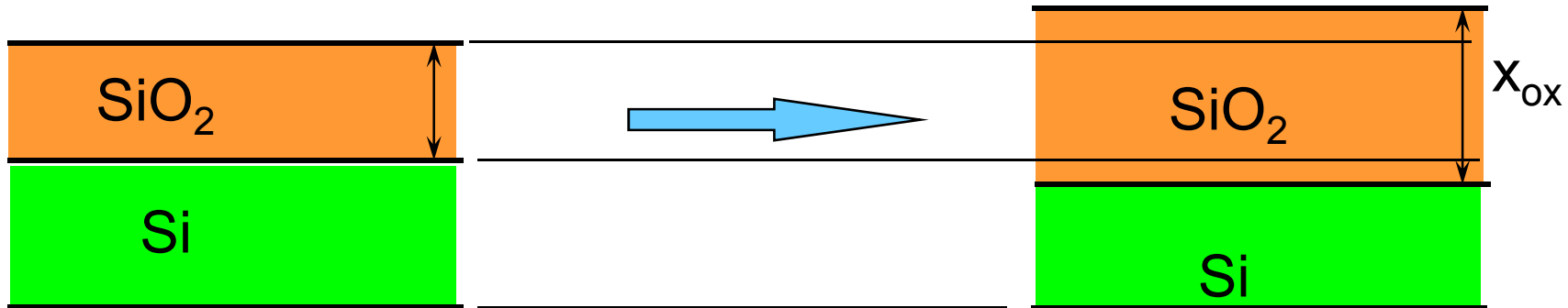
Oxidant molecules/unit volume required to form a unit volume of SiO_2 .



Therefore, we have the oxide growth rate eqn:

$$N_1 \cdot \frac{dX_{ox}}{dt} = \left[\frac{k_s C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}} \right]$$

Initial Condition: At $t = 0$, $X_{ox} = X_i$



Solution $X_{ox}^2 + AX_{ox} = B(t + \tau)$

$$A \equiv 2D \left(\frac{1}{k_s} + \frac{1}{h} \right)$$

Note: $h \gg k_s$ for typical oxidation condition

$$B \equiv \frac{2DC_A}{N_1}$$

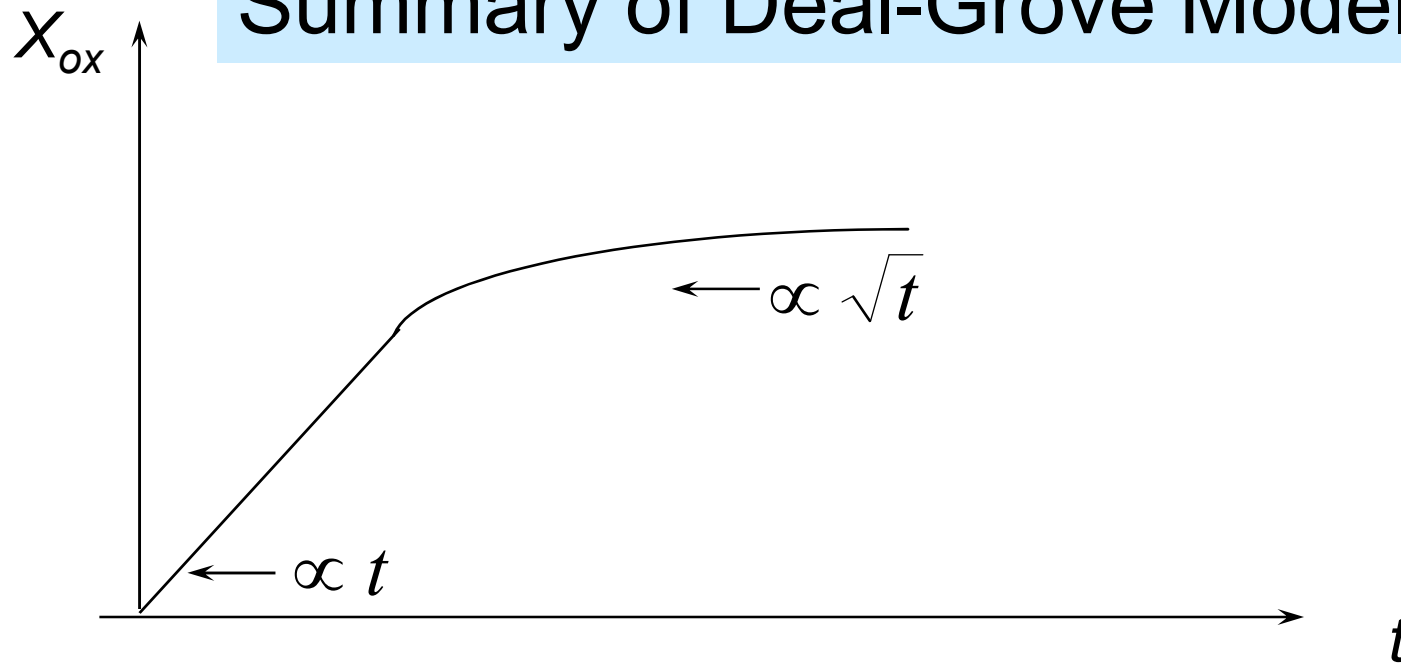
$$\tau = \frac{X_i^2 + AX_i}{B}$$

Note : “dry” and “wet” oxidation have different N_1 factors

$$N_1 = 2.3 \times 10^{22} / \text{cm}^3 \quad \text{for } O_2 \text{ as oxidant}$$
$$Si + O_2 \rightarrow SiO_2$$

$$N_1 = 4.6 \times 10^{22} / \text{cm}^3 \quad \text{for } H_2O \text{ as oxidant}$$
$$Si + 2H_2O \rightarrow SiO_2 + 2H_2 \uparrow$$

Summary of Deal-Grove Model



$$X_{ox}^2 + AX_{ox} = B(t + \tau)$$

$$2X_{ox} \frac{dx_{ox}}{dt} + A \frac{dx_{ox}}{dt} = B$$

$$\therefore \frac{dx_{ox}}{dt} = \frac{B}{A + 2X_{ox}}$$

Oxide Growth Rate slows down with increase of oxide thickness

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

(Case 1) Large t [large X_{ox}]

$$X_{ox} \rightarrow \sqrt{Bt}$$

(Case 2) Small t [Small X_{ox}]

$$X_{ox} \rightarrow \frac{B}{A} t$$

Deal-Grove Model Parameters

$$(1) \quad B \equiv \frac{2 D C_A}{N_1} \propto D$$

$$D \propto e^{-Q/kT}$$

$Q =$ activation energy
for diffusion

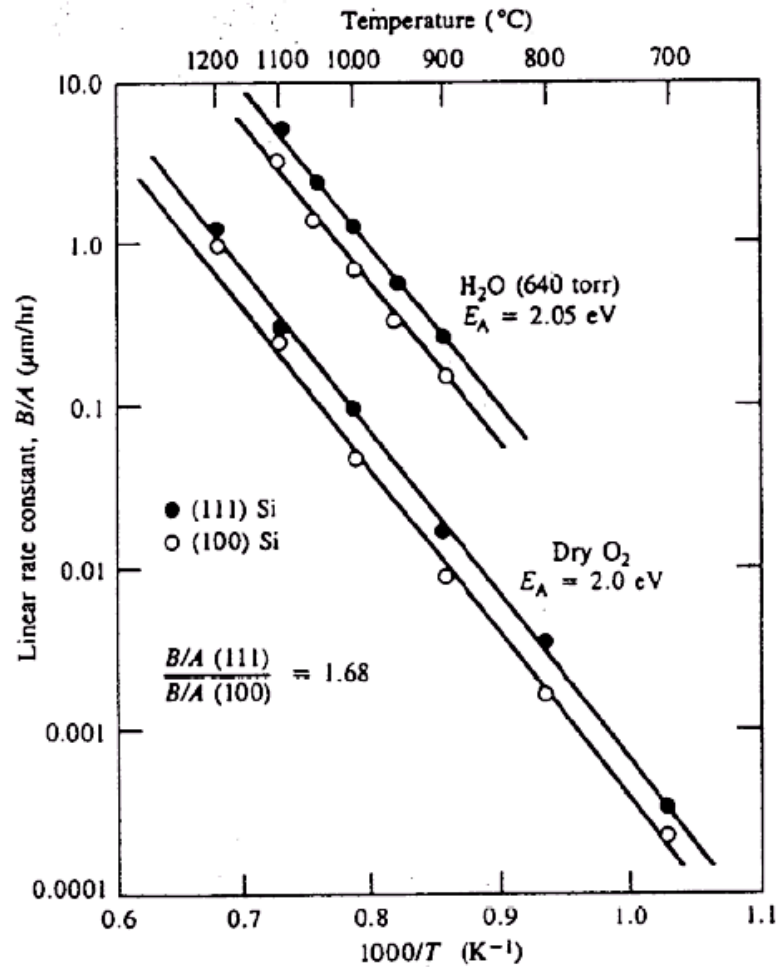
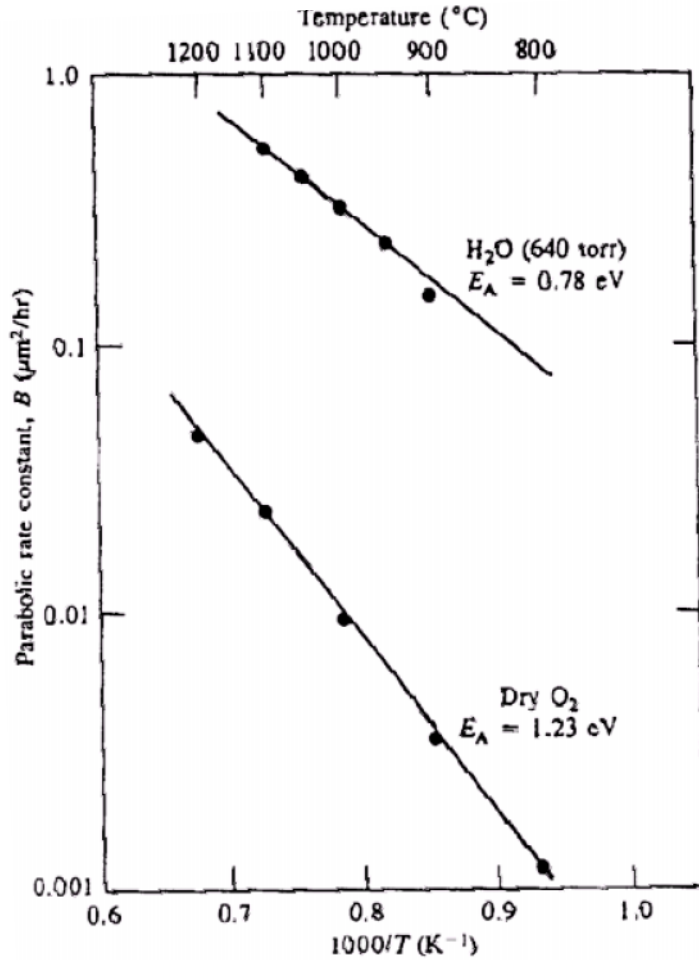
$$(2) \quad \frac{B}{A} = \frac{1}{\left(\frac{1}{h} + \frac{1}{k_s}\right)} \frac{C_A}{N_1}$$

$$k_s \propto e^{-Q'/kT}$$

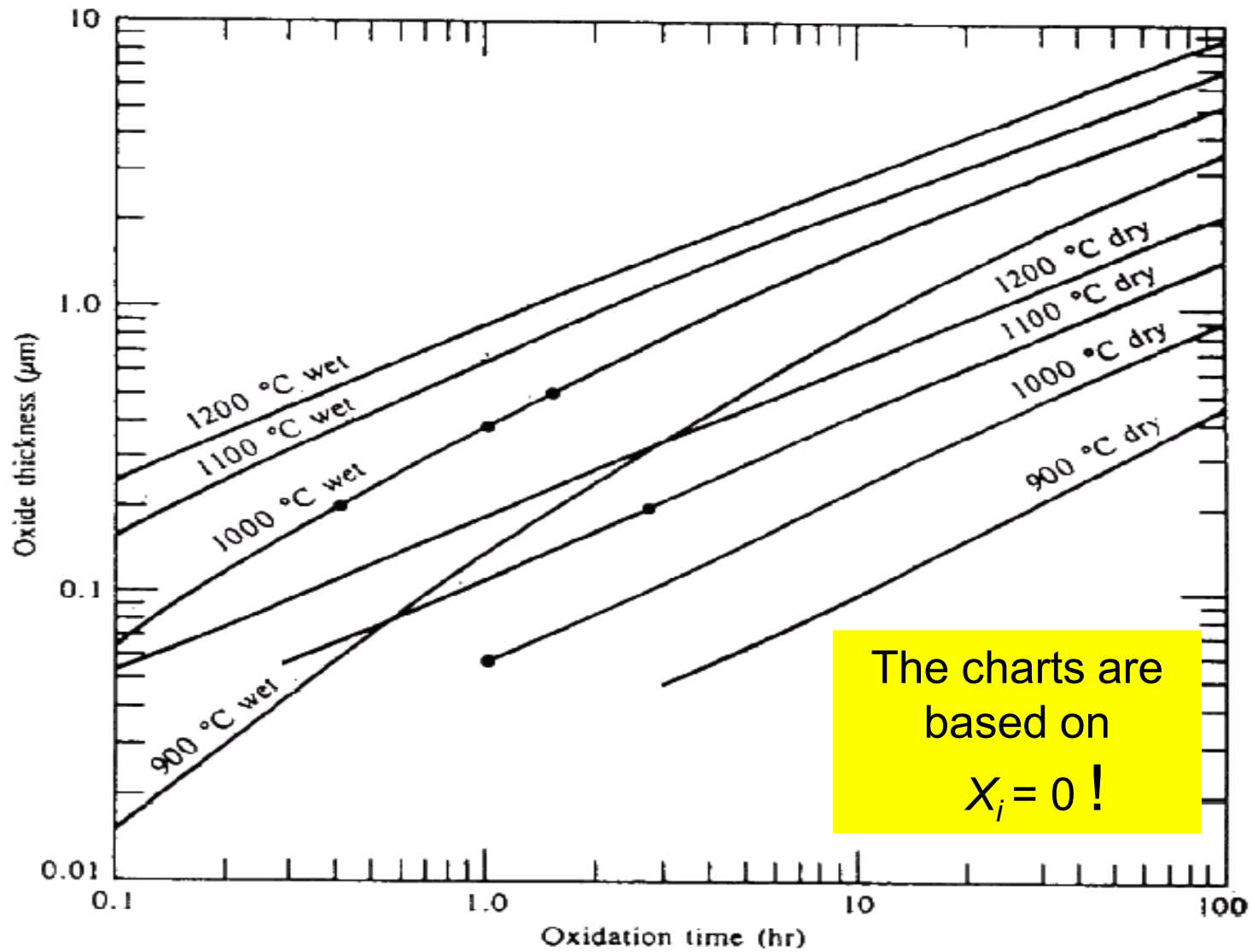
$Q' =$ activation energy
for interface reaction

For thermal oxidation of Si, h is typically $\gg k_s$
 B/A is $\propto k_s$ (i.e. F_1 is rarely the rate-limiting step)

B = Parabolic Constant
B/A = Linear Constant



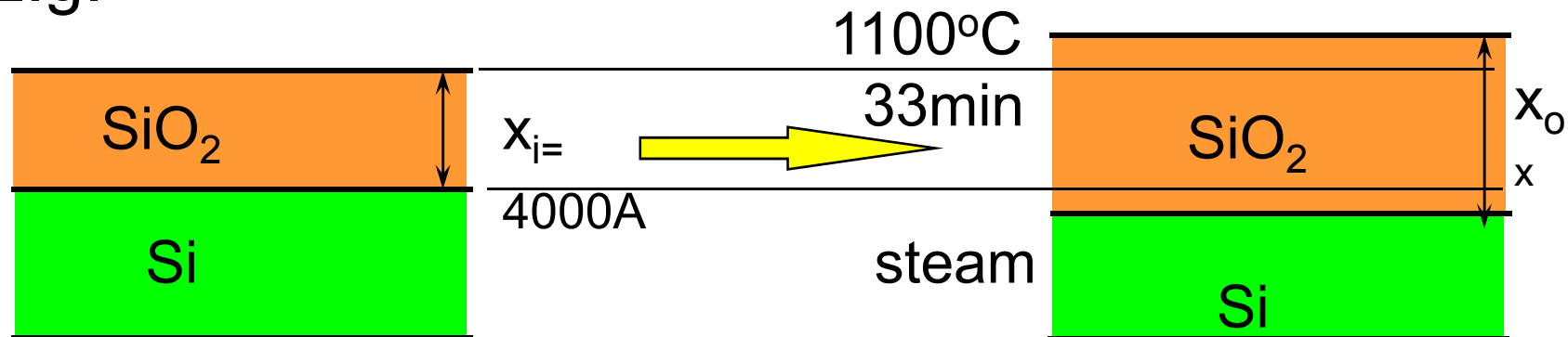
Oxidation Charts



Wet and dry silicon dioxide growth for (100) silicon

Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

E.g.

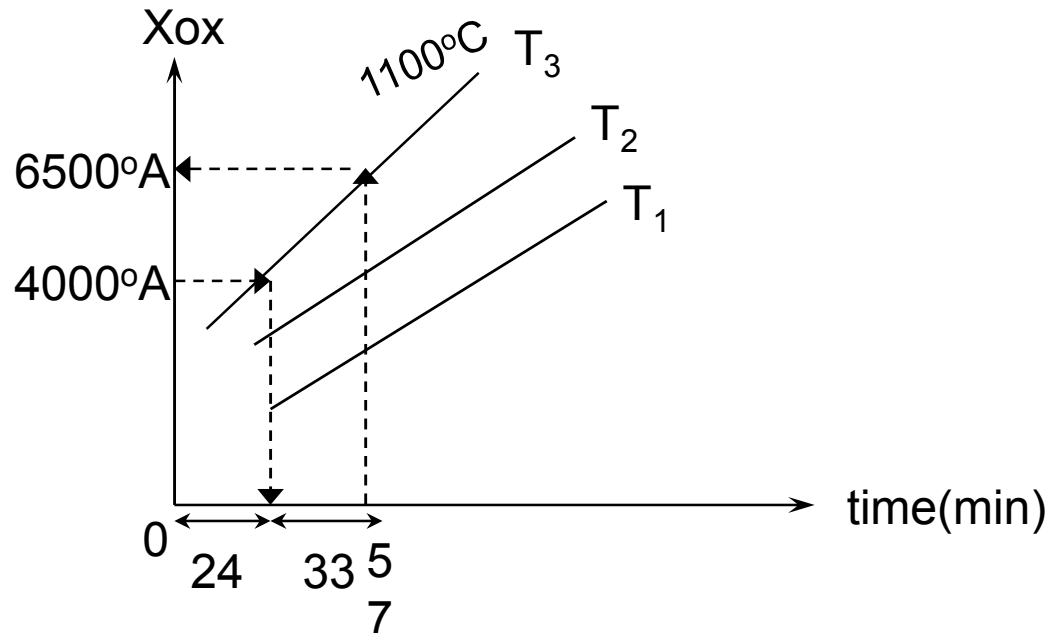


Method 1: Find B & B/A from Charts

$$\text{Solve } X_{ox}^2 + AX_{ox} = B(t + \tau)$$

Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

Method 2: Use Oxidation Charts



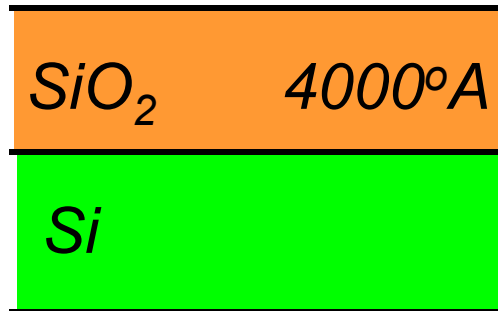
The charts are based on $X_i = 0$!

$X_i = 4000 \text{ Å} \Rightarrow \tau = 24 \text{ min}$ at 1100°C from chart

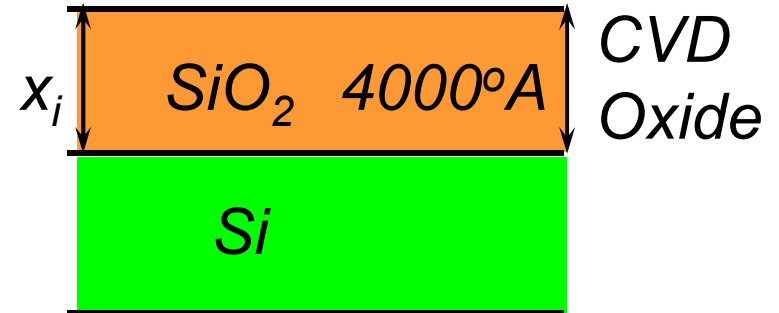
\therefore Total effective oxidation time

$(24 + 33) \text{ min} = 57 \text{ min}$ if start with $X_i = 0$

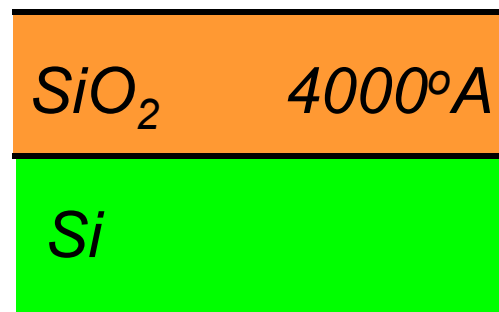
(1) Grown at 1000°C , 5hrs



(3) CVD Oxide



(2) Grown at 1100°C , 24min



For same X_i ,
 τ is the same for all three
 cases shown here