

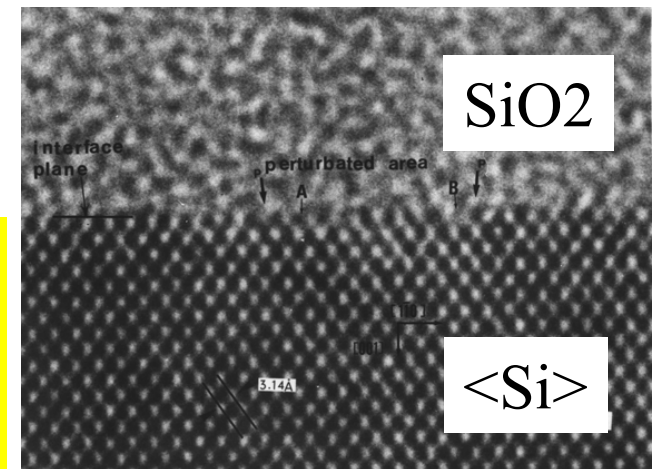
# Thermal Oxidation of Si

- General Properties of  $\text{SiO}_2$
- Applications of thermal  $\text{SiO}_2$
- Deal-Grove Model of Oxidation

Thermal  $\text{SiO}_2$  is **amorphous**.

Weight Density =  $2.20 \text{ gm/cm}^3$

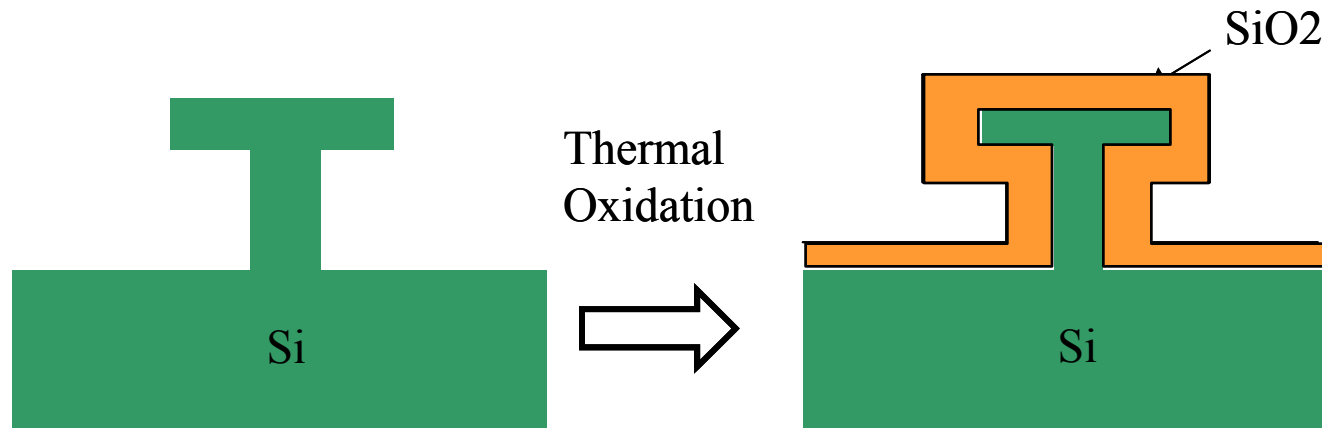
Molecular Density =  $2.3\text{E}22 \text{ molecules/cm}^3$



Crystalline  $\text{SiO}_2$  [Quartz] =  $2.65 \text{ gm/cm}^3$

# Thermal SiO<sub>2</sub> Properties

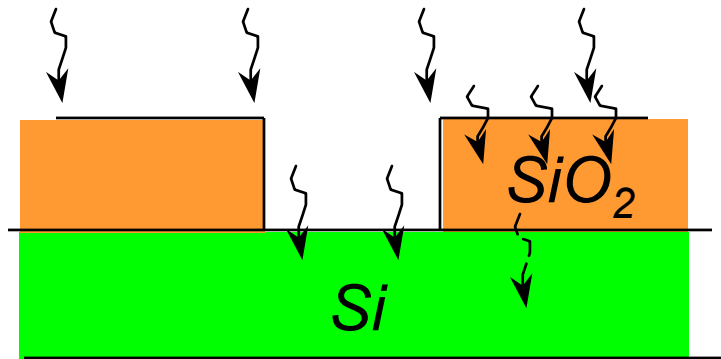
- (1) Excellent Electrical Insulator  
Resistivity > 1E20 ohm-cm  
Energy Gap ~ 9 eV
- (2) High Breakdown Electric Field  
> 10MV/cm
- (3) Stable and Reproducible Si/SiO<sub>2</sub> Interface
- (4) Conformal oxide growth on exposed Si surface



# Thermal SiO<sub>2</sub> Properties – cont.

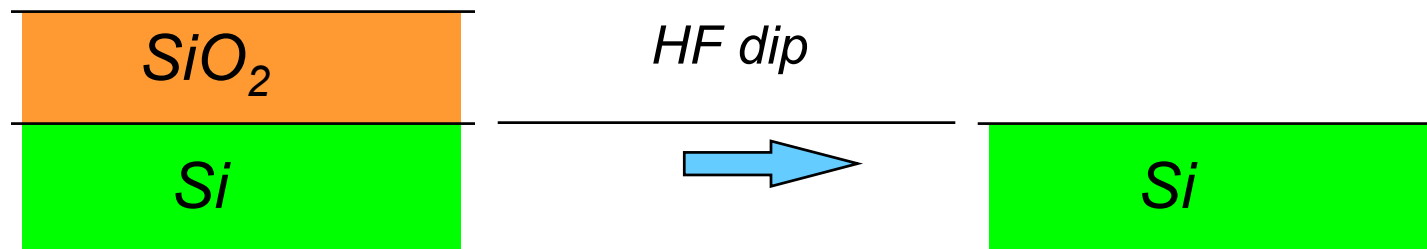
(5) SiO<sub>2</sub> is a good diffusion mask for common dopants

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



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

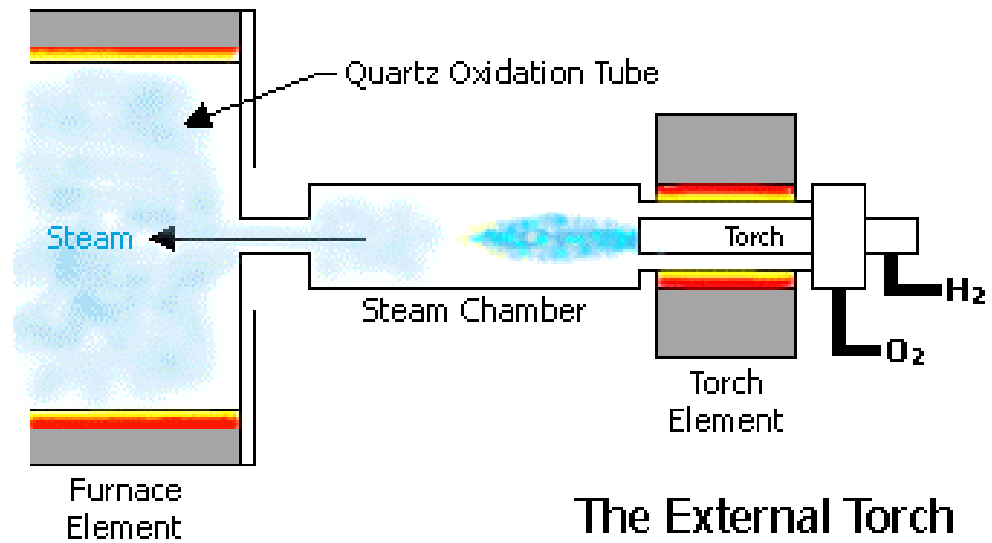
(6) Very good etching selectivity between Si and SiO<sub>2</sub>.



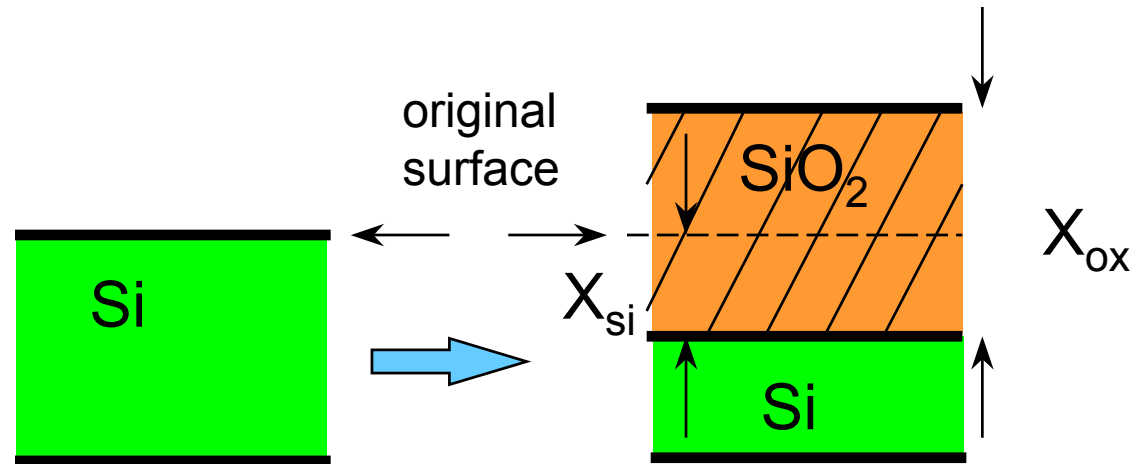


Oxidation Furnace  
(Silicon Valley Group - Thermco Systems)

Steam generation  
for wet oxidation



# Thickness of Si consumed during oxidation



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

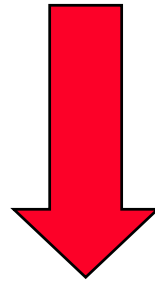
← molecular density of SiO<sub>2</sub>

← atomic density of Si

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

For 1-dimensional planar oxide growth

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



2.17  $\mu\text{m}$  SiO<sub>2</sub>

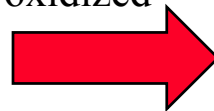
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Suggested calculation exercise:

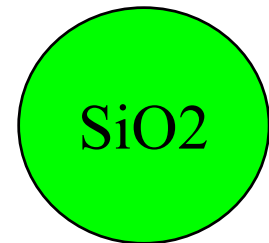
1  $\mu\text{m}$  diameter  
Si *sphere*



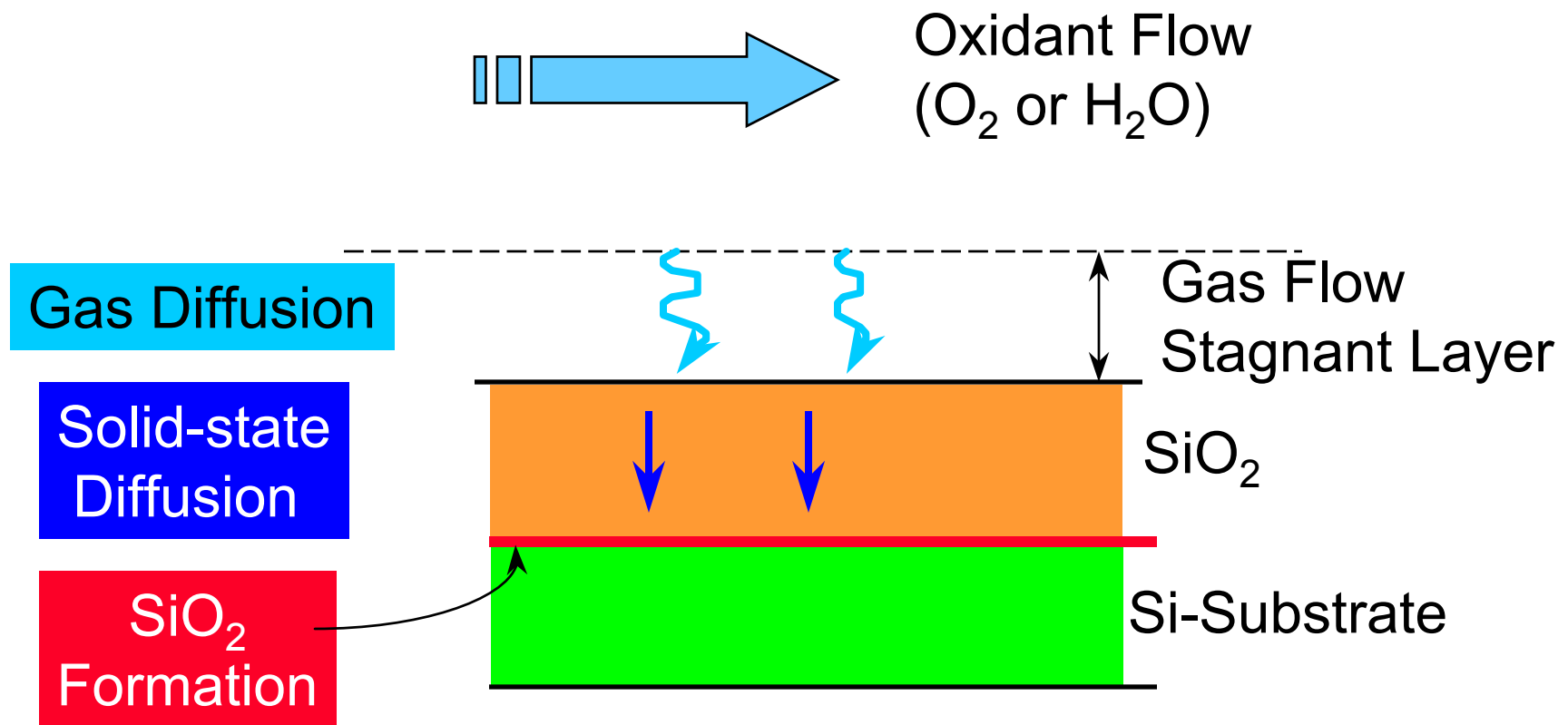
completely  
oxidized



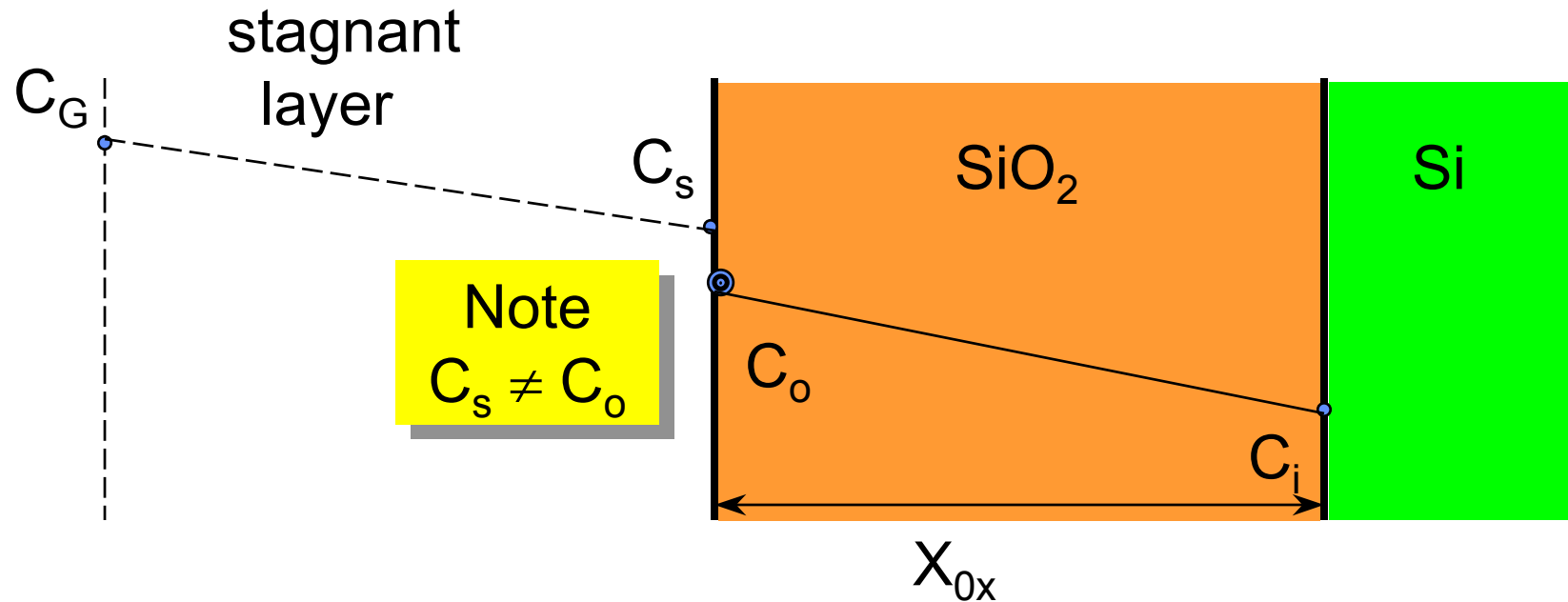
1.3  $\mu\text{m}$  diameter  
SiO<sub>2</sub> *sphere*

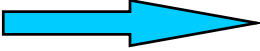



# Kinetics of SiO<sub>2</sub> Growth




# Deal-Grove Model



$F_1$    
gas  
transport  
flux

$F_2$    
diffusion  
flux  
through  $\text{SiO}_2$

$F_3$    
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 [cm<sup>2</sup>/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 CVD growth rate 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

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

Henry's constant

partial pressure of oxidant at surface [in gaseous form].

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

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

# 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

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

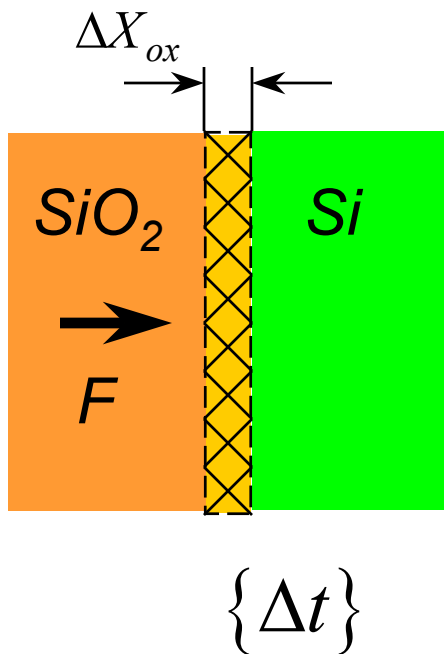
$$C_o = C_i \cdot \left( 1 + \frac{k_s X_{ox}}{D} \right)$$

$$F(= F_1 = F_2 = F_3) = k_s \cdot C_i = \frac{k_s C_A}{1 + \frac{k_s}{h} + \frac{k_s X_{ox}}{D}}$$

Now, convert  $F$  into Oxide Thickness Growth Rate

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

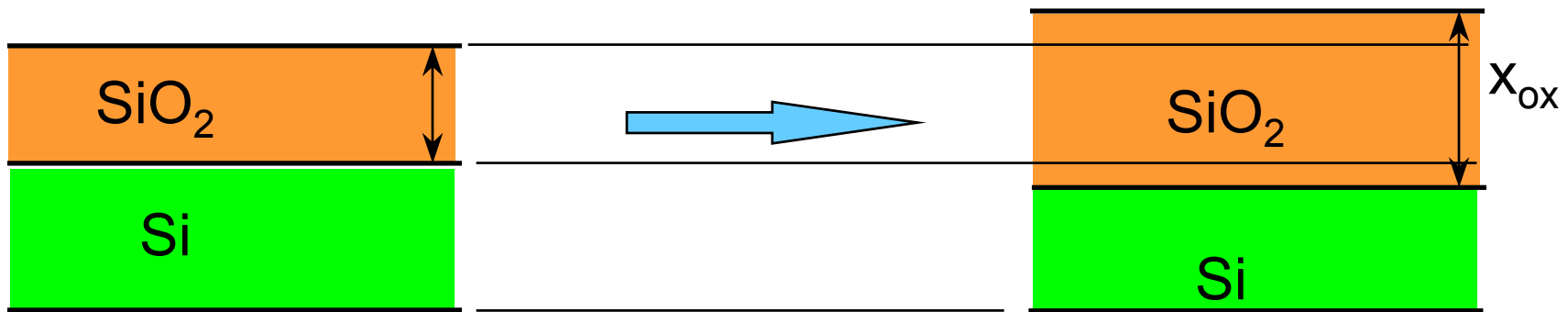
Oxidant molecules/unit volume required to form a unit volume of  $\text{SiO}_2$ .



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

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

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

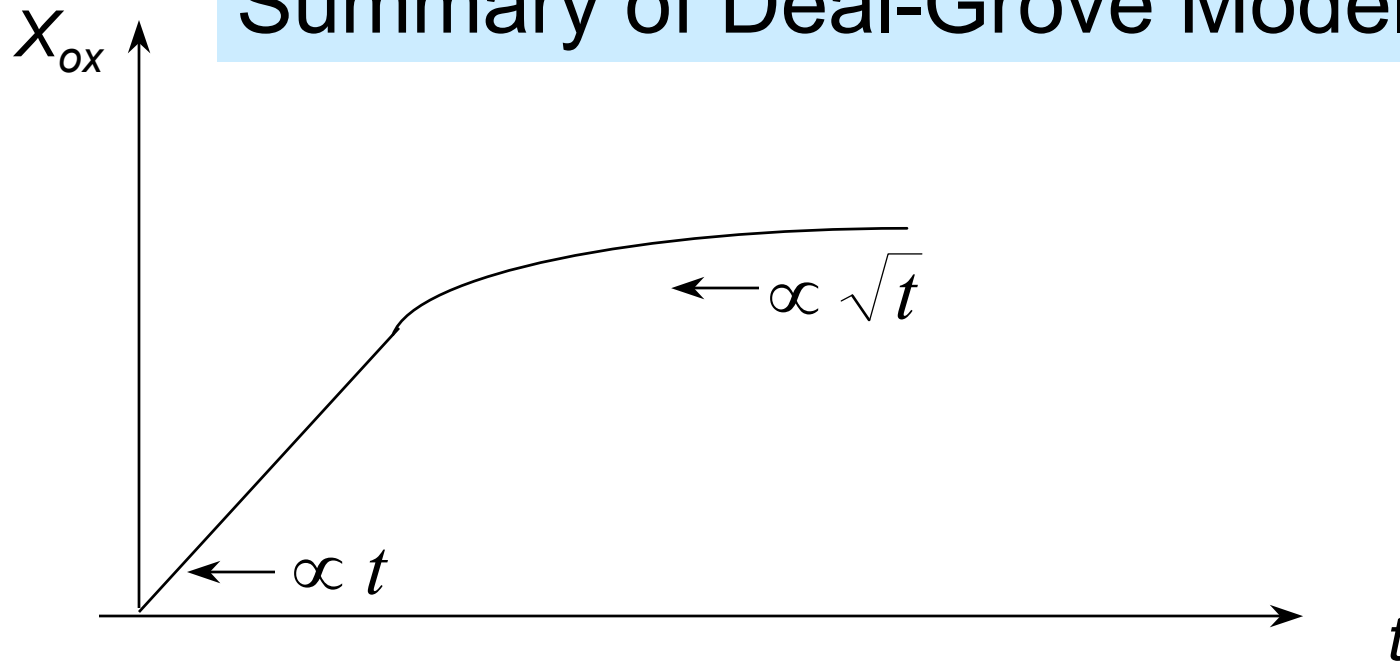
Note : “dry” and “wet” oxidation have different  $N_1$  factors

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

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



# 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

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

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

$Q = \text{activation energy for diffusion}$

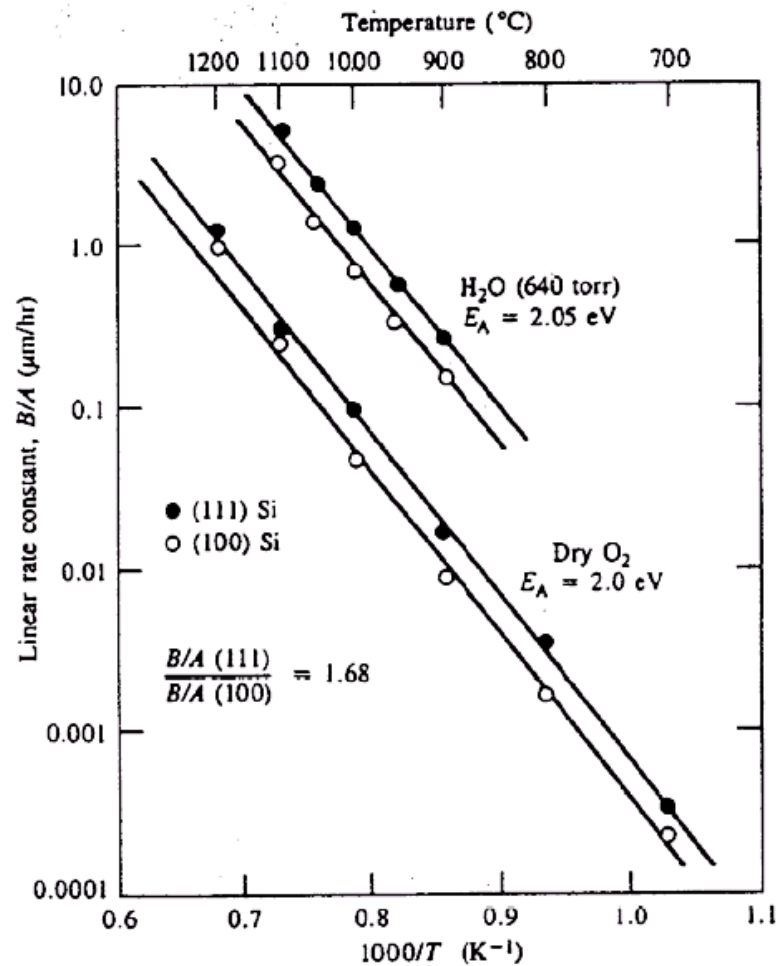
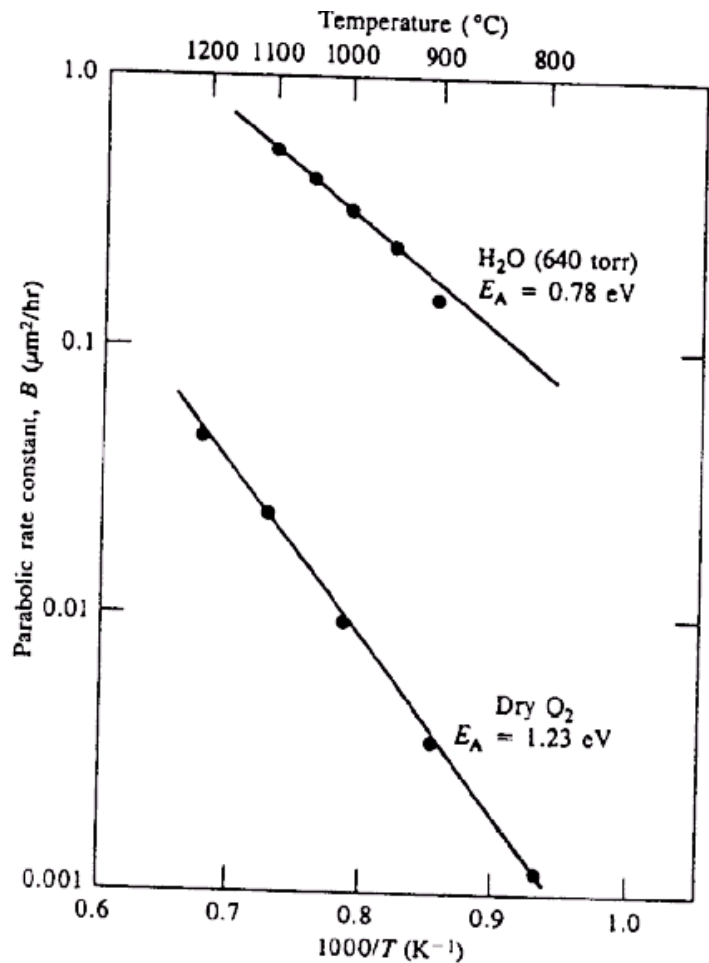
$$(2) \quad \frac{B}{A} = \frac{1}{\left(\frac{1}{h} + \frac{1}{k_s}\right)} \frac{C_A}{N_1}$$

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

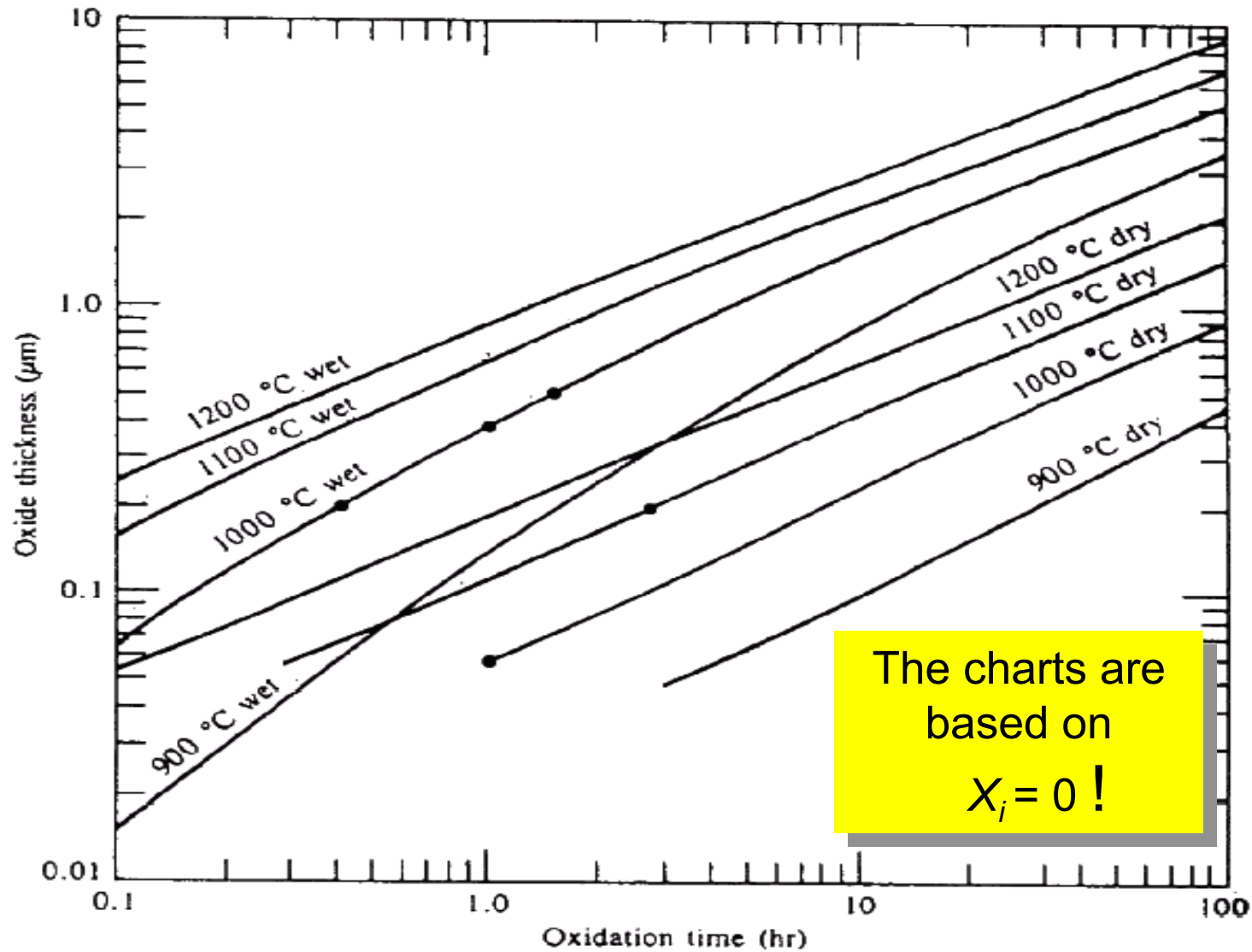
$Q' = \text{activation energy for interface reaction}$

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**



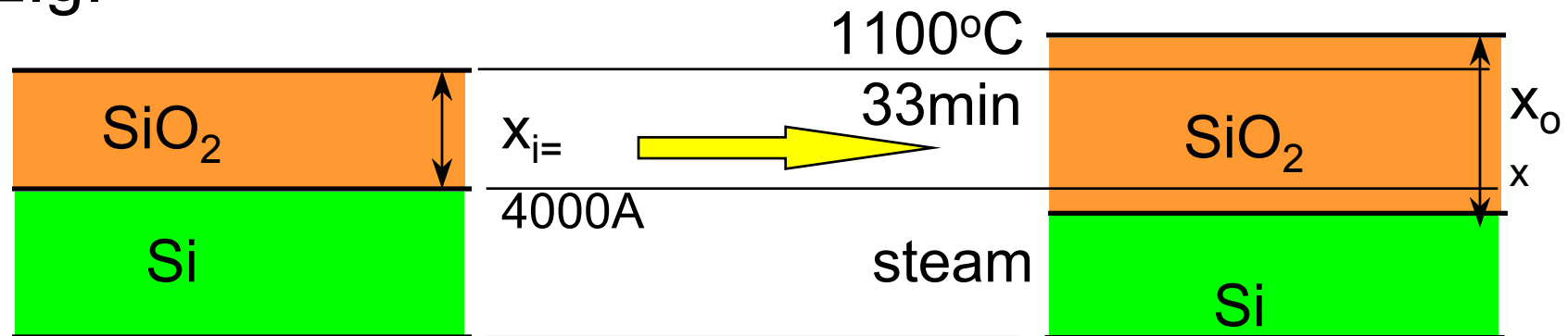
# Oxidation Charts



Wet and dry silicon dioxide growth for <100> silicon

## Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

E.g.

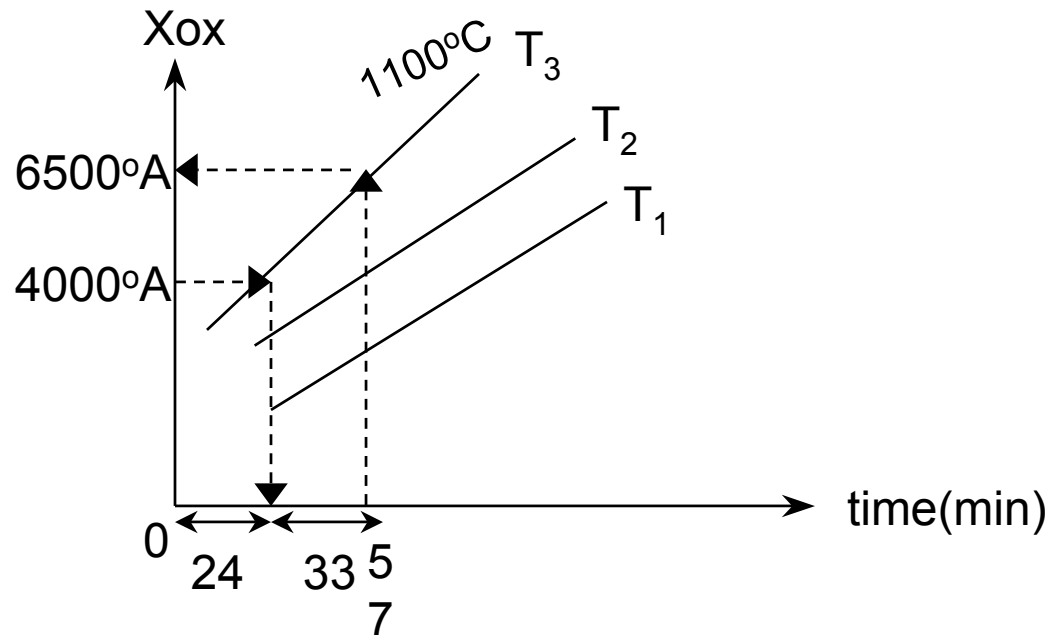


Method 1: Find B & B/A from Charts

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

# Two Ways to Calculate Oxide Thickness Grown by Thermal Oxidation

## Method 2: Use Oxidation Charts



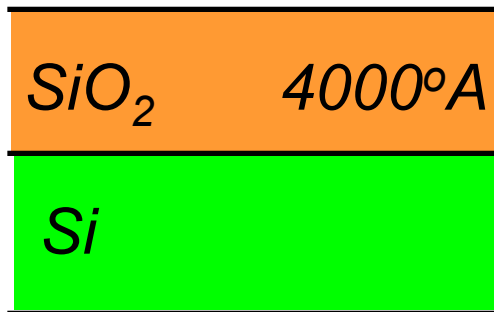
The charts are based on  $X_i = 0$  !

$X_i = 4000 \text{ A} \Rightarrow \tau = 24 \text{ min}$  at  $1100^\circ\text{C}$  from chart

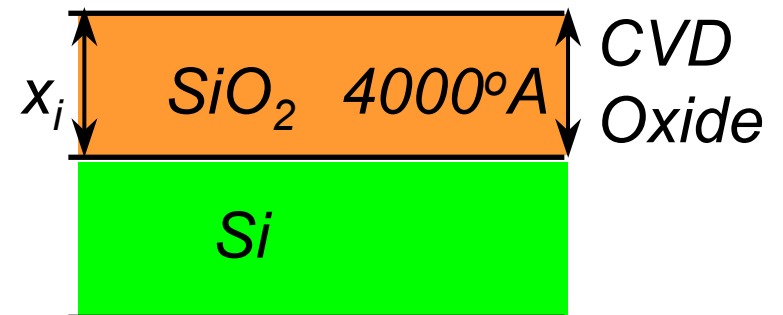
$\therefore$  Total effective oxidation time

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

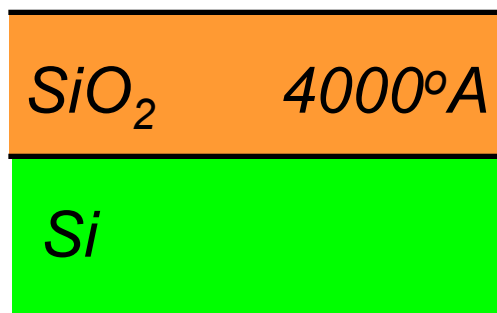
(1) Grown at  $1000^{\circ}\text{C}$ ,  $5\text{hrs}$



(3) CVD Oxide



(2) Grown at  $1100^{\circ}\text{C}$ ,  $24\text{min}$



For same  $X_i$ ,  
 $\tau$  is the same for all three  
 cases shown here