EE143 – Fall 2016
Microfabrication Technologies

Lecture 5: Thermal Oxidation
Reading: Jaeger Chapter 3

Prof. Ming C. Wu

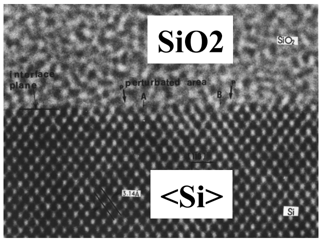
wu@eecs.berkeley.edu

511 Sutardja Dai Hall (SDH)

Properties of SiO_2

Thermal SiO_2 is amorphous.
Weight Density = 2.20 gm/cm^3
Molecular Density = 2.3E22 molecules/cm^3

Crystalline SiO_2 (Quartz) = 2.65 gm/cm^3



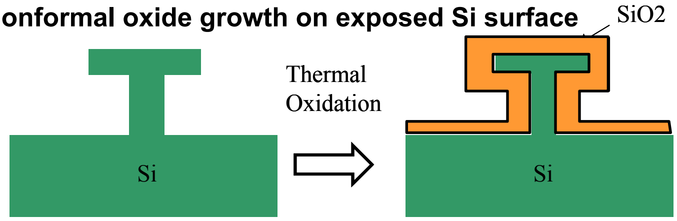
(1) Excellent Electrical Insulator
Resistivity > 1E20 ohm-cm Energy Gap ~ 9 eV

(2) High Breakdown Electric Field > 10MV/cm

(3) Stable and Reproducible Si/SiO_2 Interface

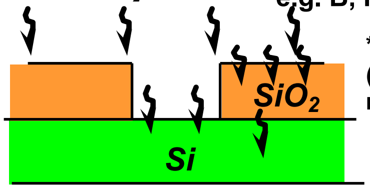
Properties of SiO_2 (cont'd)

(4) Conformal oxide growth on exposed Si surface



(5) SiO_2 is a good diffusion mask for common dopants

$$D_{sio_2} << D_{si}$$

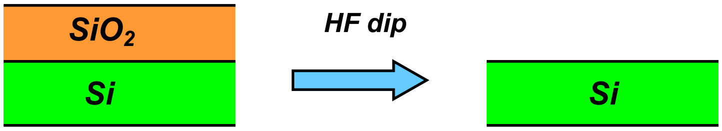


e.g. B, P, As, Sb.

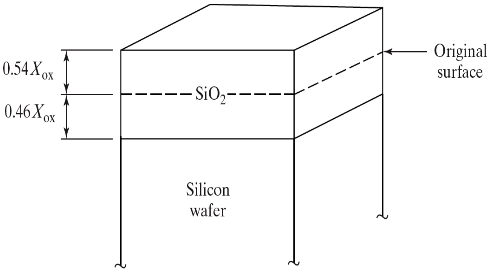
***exceptions are Ga (a p-type dopant) and some metals, e.g. Cu, Au**

Properties of SiO_2 (cont'd)

(6) Very good etching selectivity between Si and SiO_2.



Thermal Oxidation of Silicon



Dry Oxidation

$$Si + O_2 \rightarrow SiO_2$$

Wet Oxidation

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

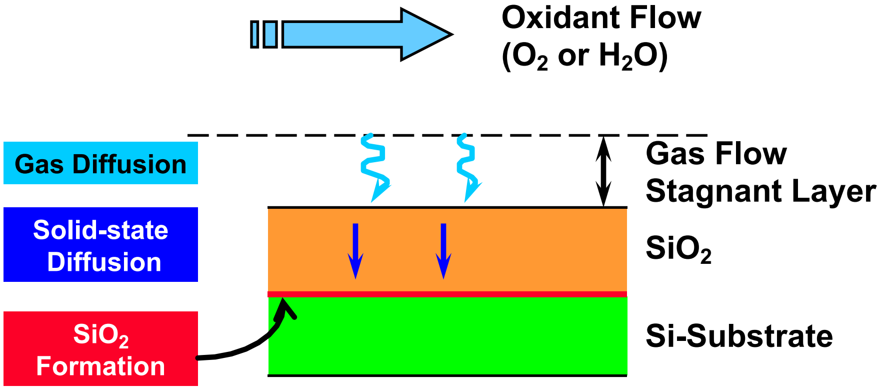
Growth Occurs 54% above and 46% below original surface as silicon is consumed

Thermal Oxidation Equipment

Horizontal Furnace

Vertical Furnace

Kinetics of SiO_2 growth



Oxidant Flow
(O_2 or H_2O)

Gas Diffusion

Solid-state Diffusion

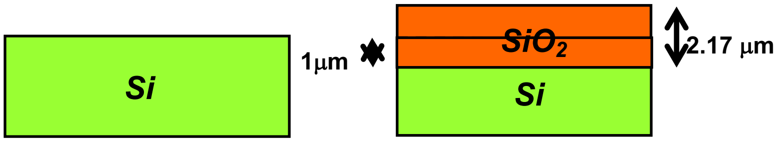
SiO_2 Formation

Gas Flow Stagnant Layer

SiO_2

Si-Substrate

Silicon consumption during oxidation



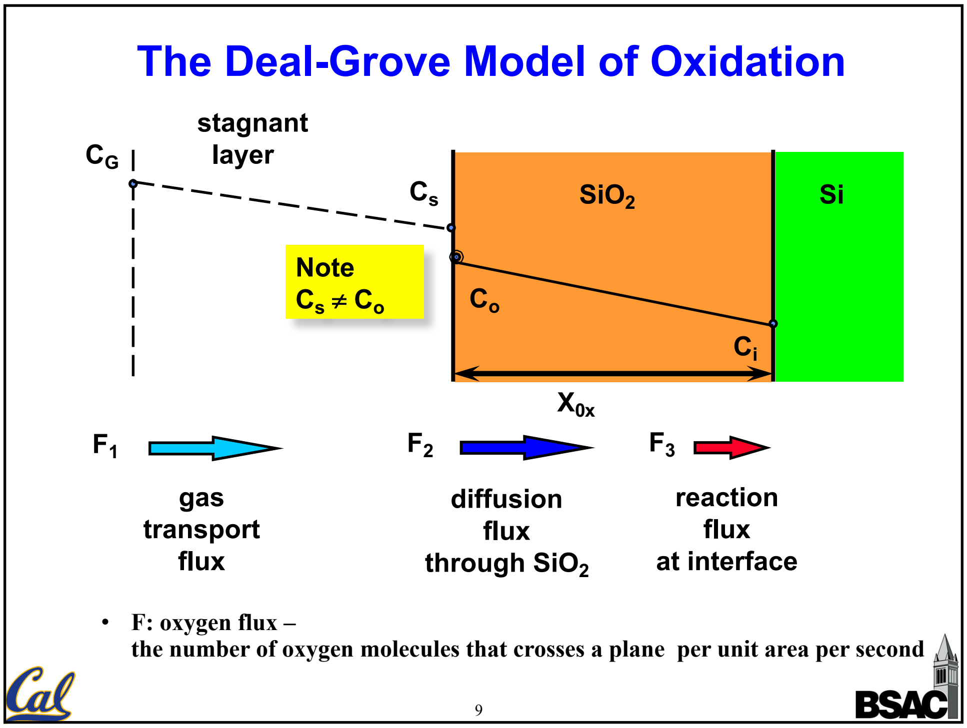
1µm Si oxidized → 2.17 µm SiO_2

$$\boxed{X_{si}} = X_{ox} \bullet \frac{N_{ox}}{N_{si}}$$

molecular density of SiO2

atomic density of Si

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



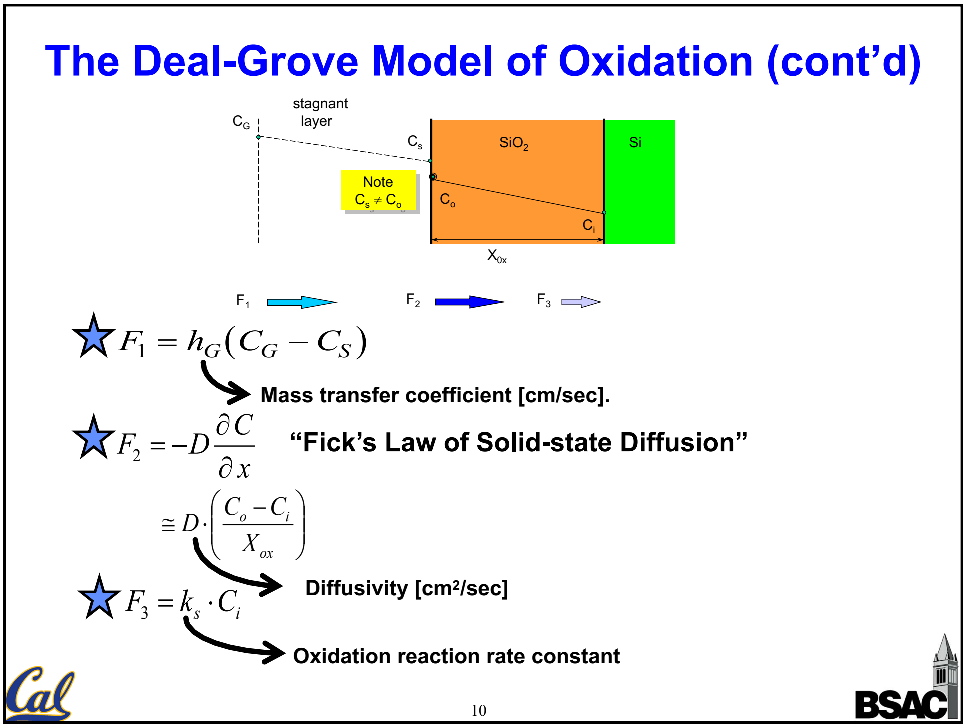
The Deal-Grove Model of Oxidation

gas transport flux

diffusion flux through SiO_2

reaction flux at interface

- F: oxygen flux –
  the number of oxygen molecules that crosses a plane per unit area per second



The Deal-Grove Model of Oxidation (cont'd)

★ $F_1 = h_G(C_G - C_S)$

h_G → Mass transfer coefficient [cm/sec].

★ $F_2 = -D\dfrac{\partial C}{\partial x}$ "Fick's Law of Solid-state Diffusion"

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

D → Diffusivity [cm²/sec]

★ $F_3 = k_s \cdot C_i$

k_s → Oxidation reaction rate constant

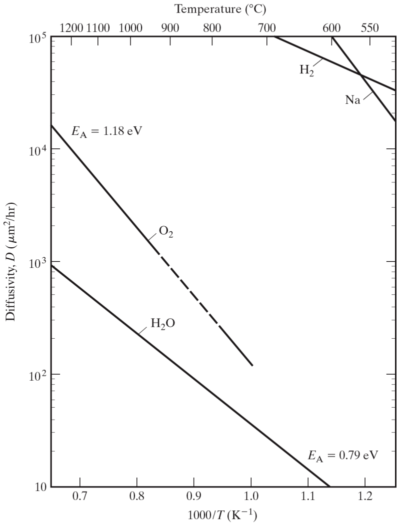
Diffusivity: the diffusion coefficient

$$D = D_O \exp\left(-\frac{E_A}{kT}\right)$$ **Arrhenius equation**

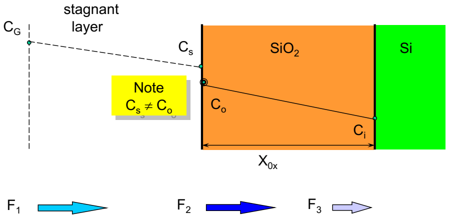
E_A = activation energy

k = Boltzmann's constant = 1.38×10^{-23} J/K

T = absolute temperature



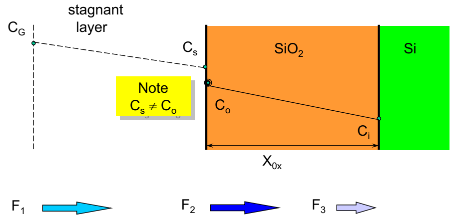
The Deal-Grove Model of Oxidation (cont'd)



- 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 Co and Ci are the 2 unknown variables which can be solved from the steady-state condition: F1 = F2 = F3 (2 equations)

The Deal-Grove Model of Oxidation (cont'd)



$$C_o = H \cdot P_s$$ **Henry's Law**

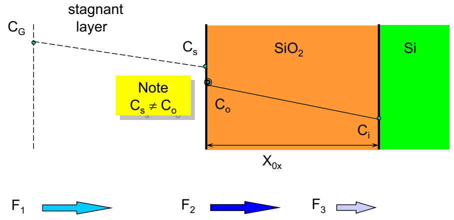
Henry's constant

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

$$= H \cdot (kT \cdot C_s)$$ **from ideal gas law PV= NkT**

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

The Deal-Grove Model of Oxidation (cont'd)



Define

$$C_A \equiv (HkT \cdot C_G)$$

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

Similarly, we can set up equations for F_2 and F_3
Using the steady-state condition:

$$\underbrace{F_1 = F_2}_{①}\underbrace{= F_3}_{②}$$ **We therefore can solve for C_o and C_i**

The Deal-Grove Model of Oxidation (cont'd)

We have: $F_2 \cong D \cdot \left(\frac{C_o - C_i}{X_{ox}} \right)$ $\quad F_3 = k_s \cdot C_i$

At equilibrium: $F_1 = F_2 = F_3$

Solving, we get:

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

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

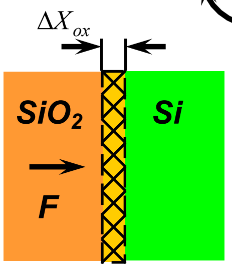
where $h = h_g / HkT$

The Deal-Grove Model of Oxidation (cont'd)

We can convert flux into growth thickness from:

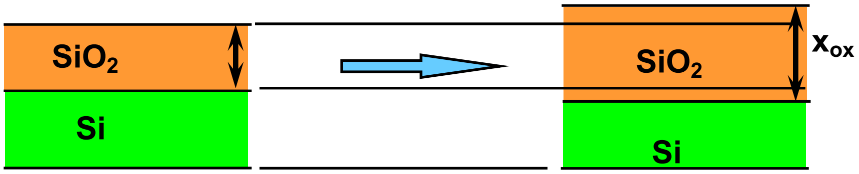
$$\frac{F}{N_1} = \left(\frac{dX_{ox}}{dt} \right)$$

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



The Deal-Grove Model of Oxidation (cont'd)

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



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

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

Note: $h_g >> k_s$ for typical oxidation condition

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

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

Dry / Wet Oxidation

Note : "dry" and "wet" oxidation have different N1 factors

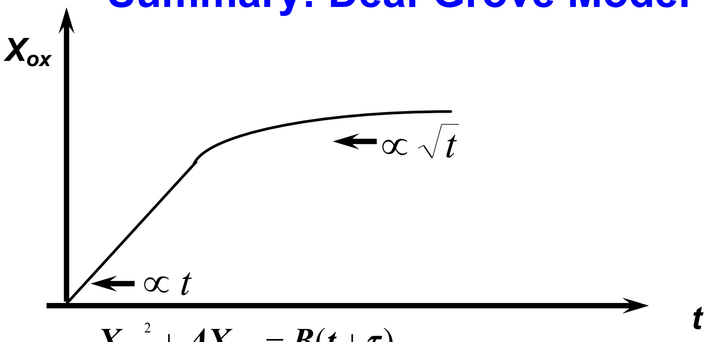
$N_1 = \boxed{2.3 \times 10^{22} \; / \, cm^3}$ ***for O_2 as oxidant***

$$Si + O_2 \rightarrow SiO_2$$

$N_1 = \boxed{4.6 \times 10^{22} \; / \, cm^3}$ ***for H_2O as oxidant***

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2 \uparrow$$

Summary: Deal-Grove Model



$$X_{ox}{}^{2} + AX_{0x} = B(t+\tau)$$

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

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

Oxide Growth Rate slows down with increase of oxide thickness

---

Solution: Oxide Thickness Regimes

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

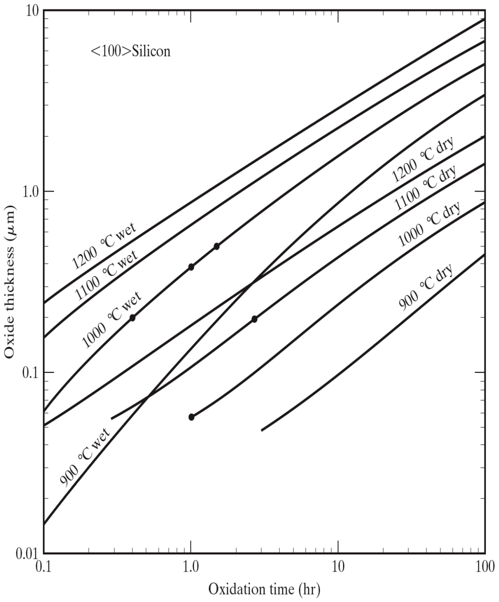
(Case 1) Large *t* [large *X*$_{ox}$]

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

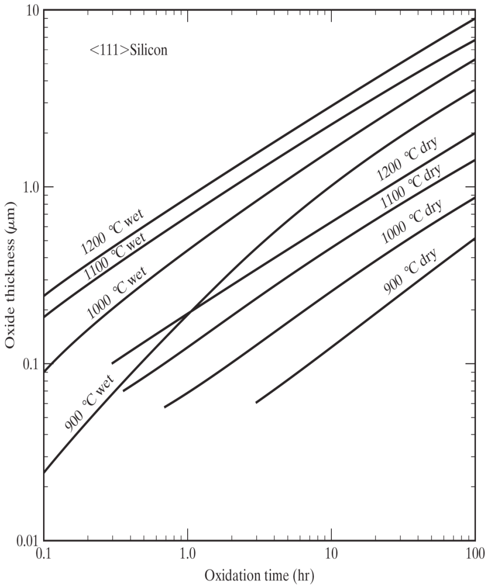
(Case 2) Small *t* [Small *X*$_{ox}$]

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

Thermal Oxidation on <100> Silicon



Thermal Oxidation on <111> Silicon



Thermal Oxidation Example

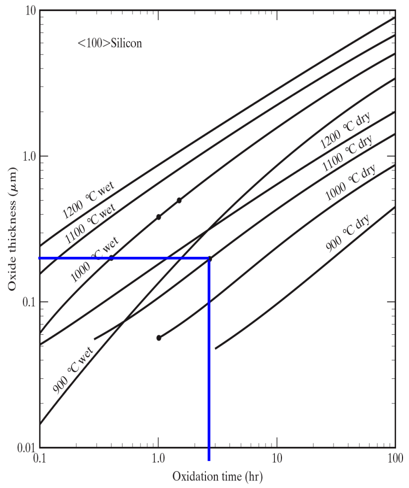
A <100> silicon wafer has a 2000-Å oxide on its surface

(a) How long did it take to grow this oxide at 1100° C in dry oxygen?

(b)The wafer is put back in the furnace in wet oxygen at 1000° C. How long will it take to grow an additional 3000 Å of oxide?

Thermal Oxidation Example

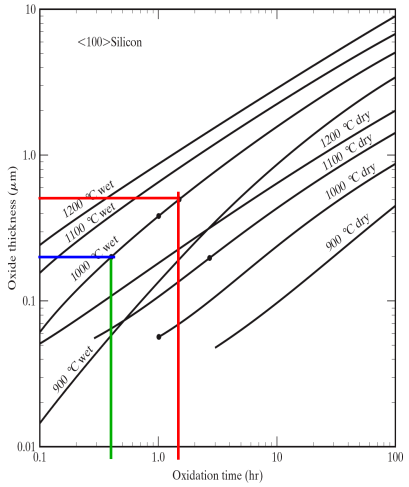
Graphical Solution



(a) According to Fig. 3.6, it would take 2.8 hr to grow 0.2 μm oxide in dry oxygen at 1100° C.

Thermal Oxidation Example

Graphical Solution



(b) The total oxide thickness at the end of the oxidation would be 0.5 μm which would require 1.5 hr to grow if there was no oxide on the surface to begin with. However, the wafer "thinks" it has already been in the furnace 0.4 hr. Thus the additional time needed to grow the 0.3 μm oxide is 1.5-0.4 = 1.1 hr.

Thermal Oxidation Example

Mathematical Solution

(a) From Table 3.1,

$$B = 7.72x10^2 \exp\left(\frac{-1.23}{kT}\right)\frac{\mu m^2}{hr} \qquad \frac{B}{A} = 3.71x10^6 \exp\left(\frac{-2.00}{kT}\right)\frac{\mu m}{hr} \qquad X_i = 25nm$$

$$\text{For T} = 1373\text{ K, B} = 0.0236\frac{\mu m^2}{hr} \text{ and } \frac{B}{A} = 0.169\frac{\mu m}{hr}$$

$$\tau = \frac{(0.025\mu m)^2}{0.0236\frac{\mu m^2}{hr}} + \frac{0.025\mu m}{0.169\frac{\mu m}{hr}} = 0.174\, hr$$

$$t = \frac{(0.2\mu m)^2}{0.0236\frac{\mu m^2}{hr}} + \frac{0.2\mu m}{0.169\frac{\mu m}{hr}} - 0.174 hr = 2.70\, hr$$

Thermal Oxidation Example

Mathematical Solution

(b) From Table 3.1,

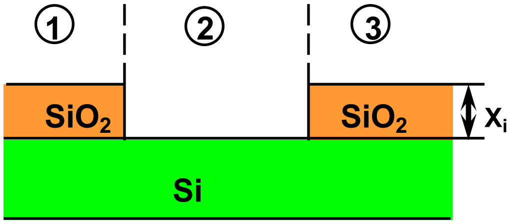
$$B = 3.86x10^{2} \exp\left(\frac{-0.78}{kT}\right)\frac{\mu m^{2}}{hr} \qquad \frac{B}{A} = 9.70x10^{7} \exp\left(\frac{-2.05}{kT}\right)\frac{\mu m}{hr} \qquad X_{i} = 0$$

$$\text{For T} = 1273\text{ K, B} = 0.314\frac{\mu m^{2}}{hr} \text{ and } \frac{B}{A} = 0.742\frac{\mu m}{hr}$$

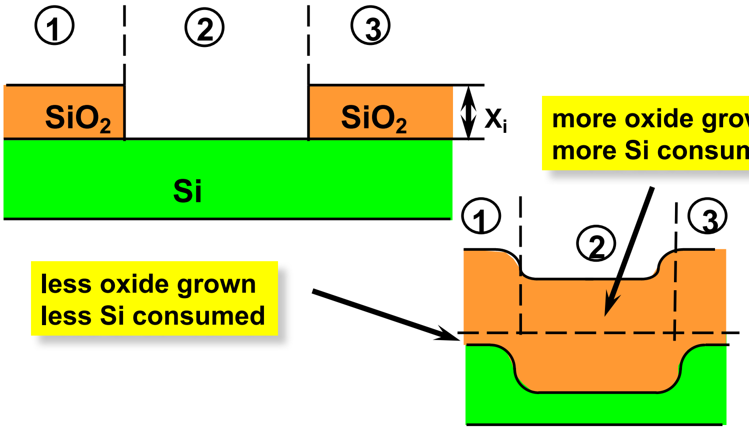
$$\tau = \frac{(0.2\mu m)^{2}}{0.314\frac{\mu m^{2}}{hr}} + \frac{0.2\mu m}{0.742\frac{\mu m}{hr}} = 0.398\,hr$$

$$t = \frac{(0.5\mu m)^{2}}{0.314\frac{\mu m^{2}}{hr}} + \frac{0.5\mu m}{0.742\frac{\mu m}{hr}} - 0.398hr = 1.07\,hr$$

Effect of Xi on Wafer Topography



Effect of X_i on Wafer Topography



more oxide grown
more Si consumed

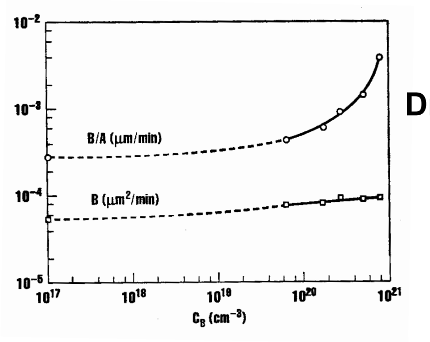
less oxide grown
less Si consumed

Factors Influencing Thermal Oxidation

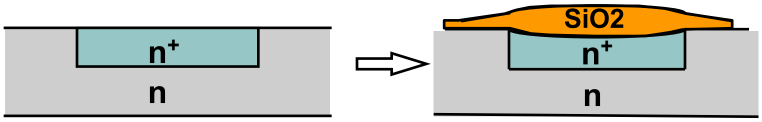
- Temperature
- Ambient Type (Dry O_2, Steam, HCl)
- Ambient Pressure
- Substrate Crystallographic Orientation
- Substrate Doping

High Doping Concentration Effect

Coefficients for dry oxidation at 900°C
as function of surface Phosphorus concentration



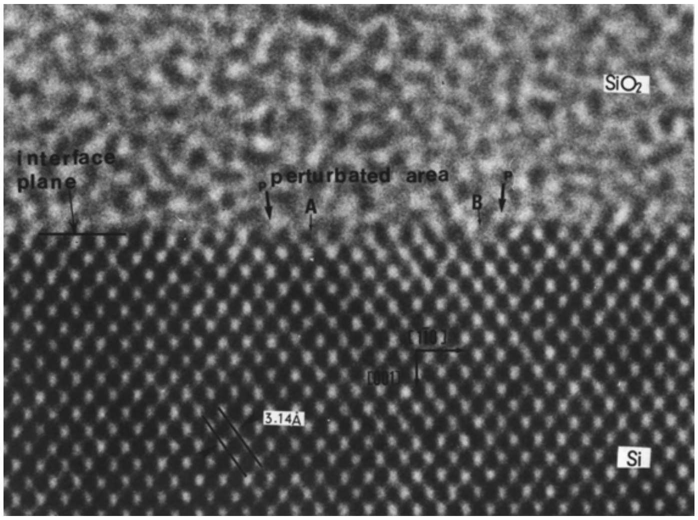
Dry oxidation, 900°C



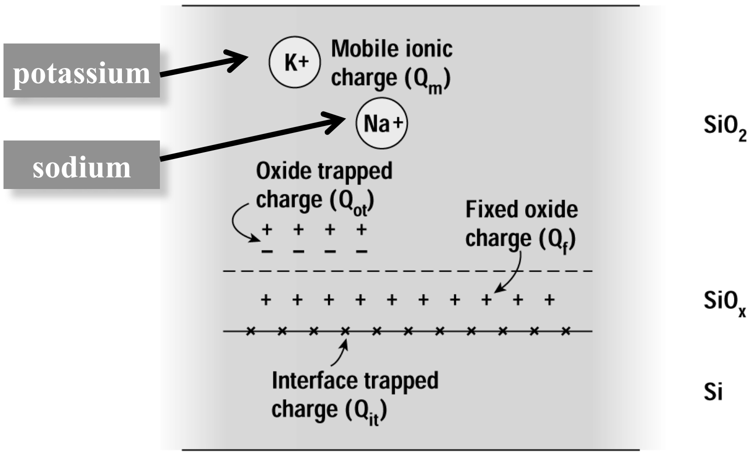
Transmission Electron Micrograph of Si/SiO_2 Interface

Amorphous SiO_2

Crystalline Si



Thermal Oxide Charges



Oxide Quality Improvement

- To minimize Interface Charges Q_f and Q_{it}
- Use inert gas ambient (Ar or N_2) when cooling down at end of oxidation step
- A final annealing step at 400-450°C is performed with 10%H_2+90%N_2 ambient ("*forming gas*") after the IC metallization step.

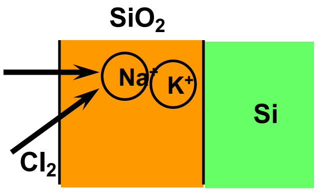
Oxidation with Chlorine-containing Gas

- **Introduction of halogen species during oxidation**

_e.g._ add ~_1- 5%_ HCl or TCE (trichloroethylene) to O_2

→ reduction in metallic contamination

→ improved SiO_2/Si interface properties

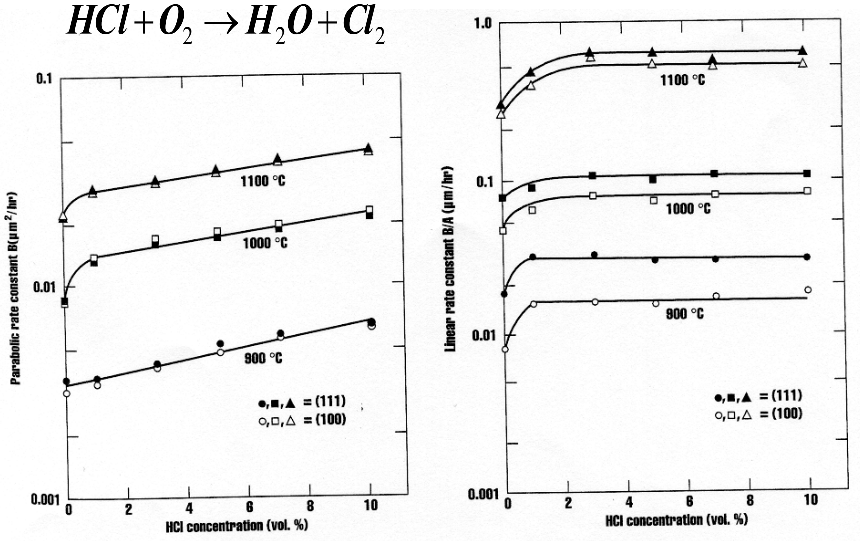


$$M + Cl \rightarrow MCl$$

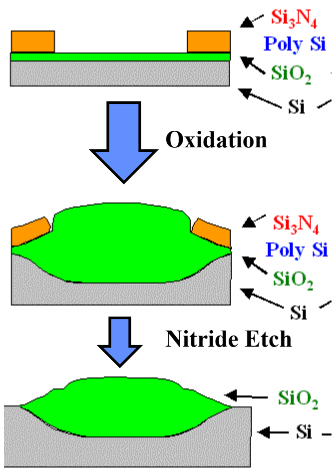
Na^+ or K^+ in SiO_2 are mobile!

Effect of HCl on Oxidation Rate

$$HCl + O_2 \rightarrow H_2O + Cl_2$$



Local Oxidation of Si (LOCOS)

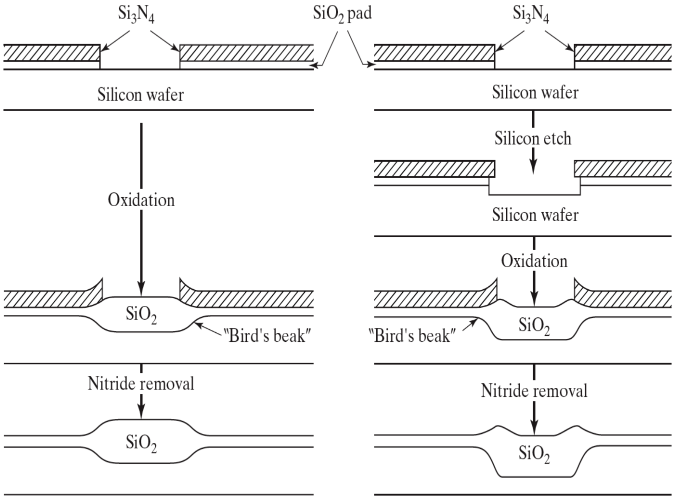


~100 A SiO_2 (thermal) - pad oxide
to release mechanical stress between nitride and Si.

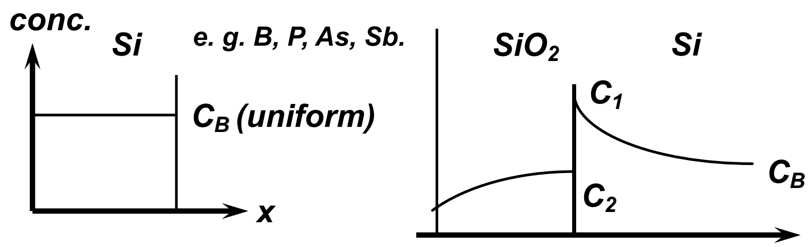
Local Oxidation of Silicon (LOCOS)

Standard process suffers for significant bird's beak

Fully recessed process attempts to minimize bird's beak



Dopant Redistribution during Thermal Oxidation



Segregation Coefficient

Fixed ratio

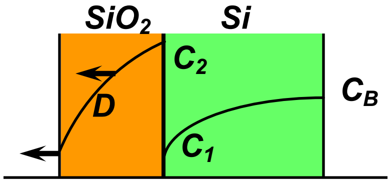
$$m \equiv \frac{\text{equilibrium dopant conc. in Si}}{\text{equilibrium dopant conc. in SiO}_2}$$

$$= \frac{C_1}{C_2}$$

(can be > 1 or < 1)

Four Cases of Interest

(A) m < 1 and dopant <u>diffuses slowly</u> in SiO_2



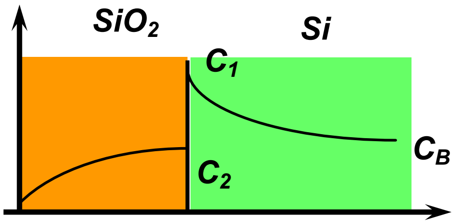
e. g. B (m = 0.3)

flux loss through SiO_2 surface not considered here.

$\Rightarrow$ B will be depleted near Si interface.

Four Cases of Interest

(B) m > 1, <u>slow diffusion in SiO_2</u>.

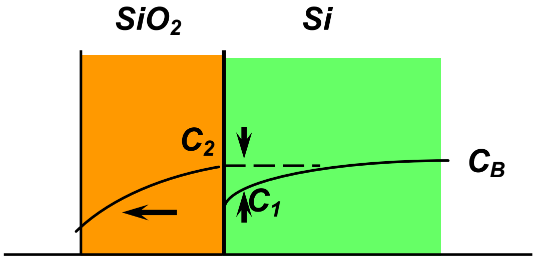


e.g. P, As, Sb

⇒ dopant piling up near Si interface for P, As & Sb

Four Cases of Interest

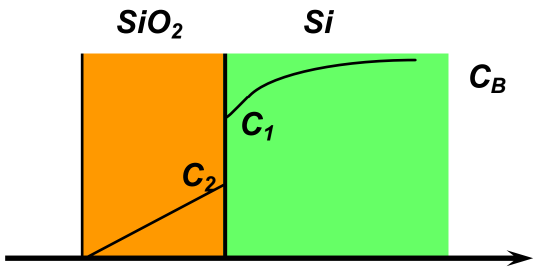
(C) m < 1, fast diffusion in SiO_2



e. g.
B,
oxidize with
presence of H_2

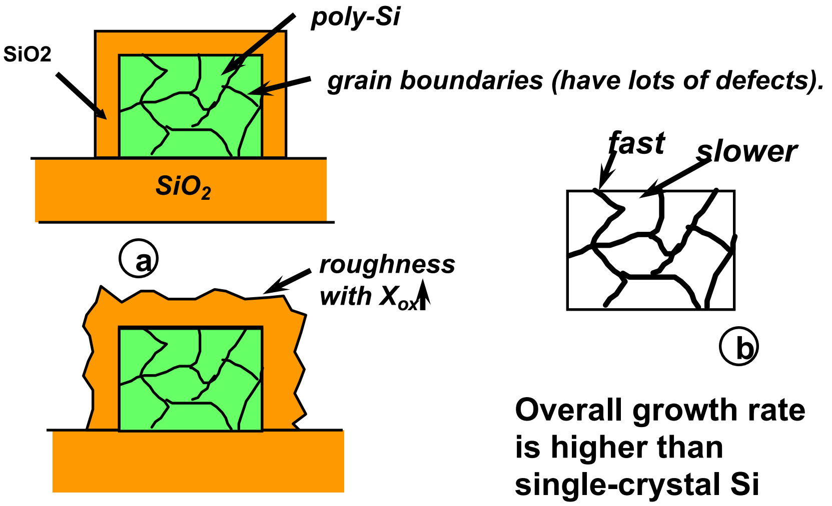
Four Cases of Interest

(D) m > 1, fast diffusion in SiO_2



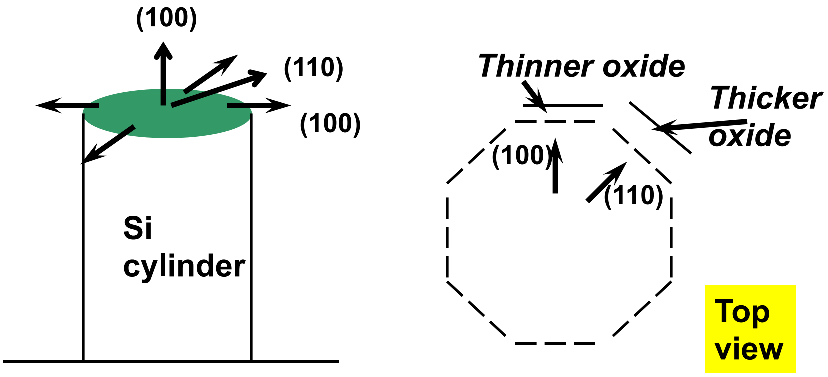
e. g. Ga (m=20)

Polycrystalline Si Oxidation



Overall growth rate is higher than single-crystal Si

2-Dimensional oxidation effects



Mechanical stress created by SiO_2 volume expansion **also affects oxide growth rate**