520/530/580.495
Microfabrication Laboratory
and
520.773
Advanced Topics in
Fabrication and Microengineering

Lecture 4

Thermal Oxidation

Lecture Outline

Reading for this lecture:
(1) May, Chapter 3

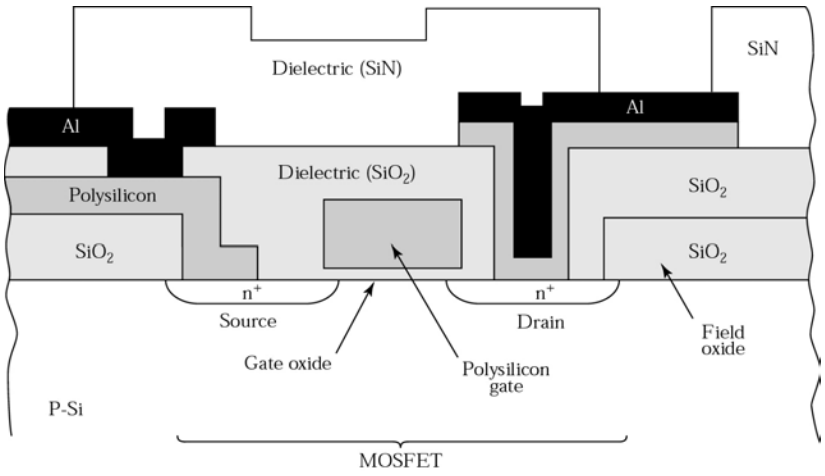
Thermal Oxidation

- A method for growing a film of SiO_2 from a single-crystal silicon (SCS) wafer or a polysilicon thin film
  - high temperature process (700-1200 ^{0}C)
  - used extensively in commercial ICs and MEMS
  - thermal oxidation by far is the most important method for growing a SiO_2 thin film in contrast several other methods : PECVD and electrochemical process.
  - one of the major reasons for the popularity of silicon ICs is the case with which silicon forms an excellent oxide, SiO_2

- Why is it done:
  - Masking materials (Lab #2_WG, Pre-Lab #2_FC)
  - Electrical isolation (Lab #4_FC)
  - Surface modification (eg. refractive index in Lab #5_WG)
  - Biocompability
  - Thermal isolation
  - Sacrificial layer

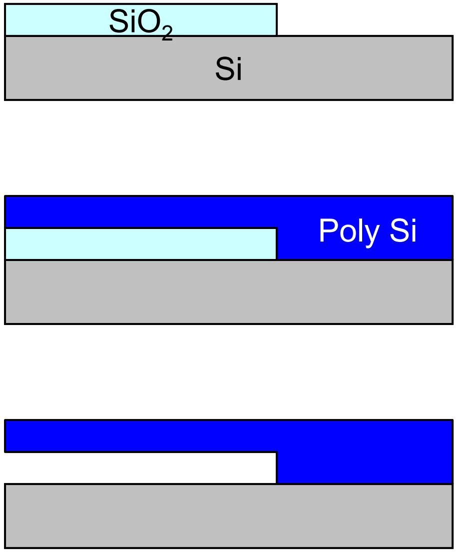
SiO2 fro IC and Surface Micromachining

MOSFET



SiO2 used as gate oxide, field oxide,..

Thin film beam structure fabricated
By Surface Micromachining



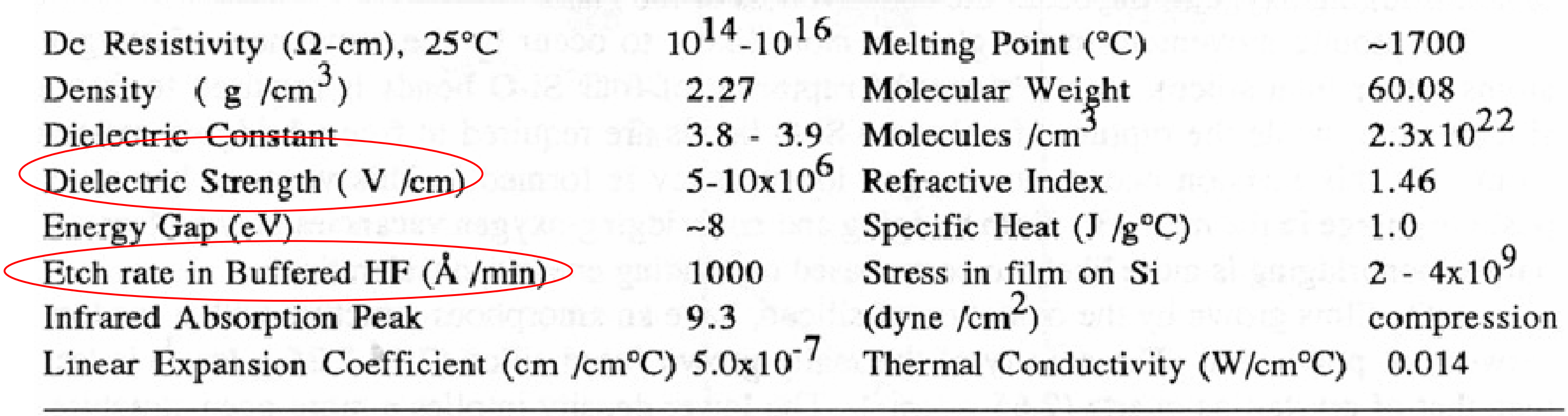
SiO2 used as a sacrificial material

Desired Properties

- Electrical
  - high breakdown strength
  - low amount of undesirable charges
    - interface trapped charge, mobile ion charges

- Mechanical
  - no pin holes
  - uniform (thickness and density)

Selected Physical Constants of Thermal Silicon Oxide

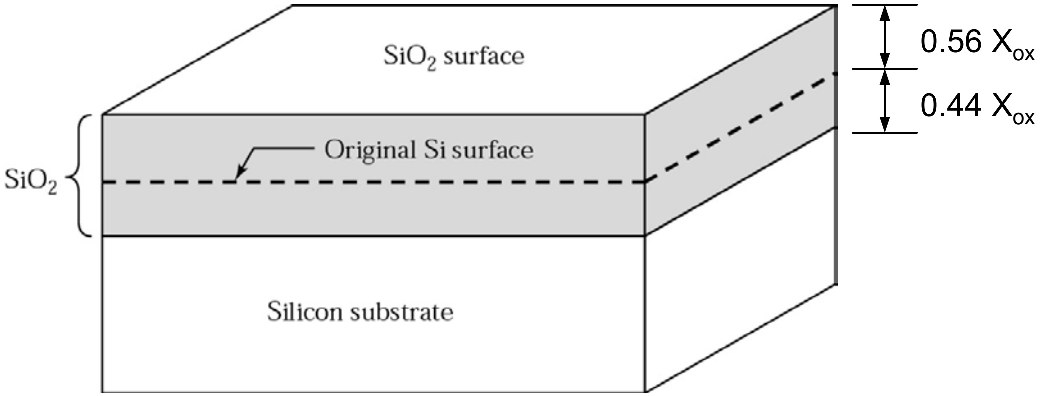


Dc Resistivity (Ω-cm), 25°C	10^{14}-10^{16}	Melting Point (°C)	~1700
Density (g /cm^3)	2.27	Molecular Weight	60.08
Dielectric Constant	3.8 - 3.9	Molecules /cm^3	$2.3x10^{22}$
Dielectric Strength (V /cm)	$5\text{-}10x10^6$	Refractive Index	1.46
Energy Gap (eV)	~8	Specific Heat (J /g°C)	1.0
Etch rate in Buffered HF (Å /min)	1000	Stress in film on Si	$2 - 4x10^9$
Infrared Absorption Peak	9.3	(dyne /cm^2)	compression
Linear Expansion Coefficient (cm /cm°C)	$5.0x10^{-7}$	Thermal Conductivity (W/cm°C)	0.014

How Does Silicon Oxidize ?

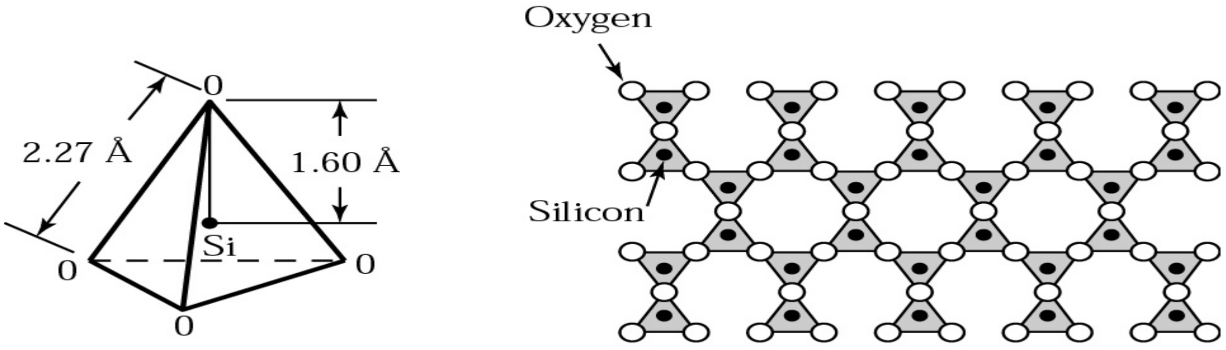
- Dry Oxidization : $\text{Si (solid)} + O_2 \text{ (gas)} \rightarrow SiO_2 \text{ (solid)}$
- Wet Oxidization: $\text{Si (solid)} + 2H_2O \text{ (gas)} \rightarrow SiO_2 \text{ (solid)} + 2H_2 \text{ (gas)}$

- Silicon is consumed in the process
- Oxidization occurs at the Si-SiO_2 interface, NOT on top of the oxide
- The interface produced by thermal oxidization is not exposed to atmosphere, minimizing the impurities



$$\frac{\text{Thickness of Si}}{\text{Thickness of SiO}_2} = \frac{\text{Molar volume (Si)}}{\text{Molar volume (SiO}_2\text{)}} = \frac{\dfrac{\text{Molecular weight (Si)}}{\text{Density (Si)}}}{\dfrac{\text{Molecular weight (SiO}_2\text{)}}{\text{Density (SiO}_2\text{)}}} = \frac{\dfrac{28.9\ \text{g/mol}}{2.33\ \text{g/cm}^3}}{\dfrac{60.08\ \text{g/mol}}{2.21\ \text{g/cm}^3}} = 0.44$$

Structures of SiO_2 (Silica)

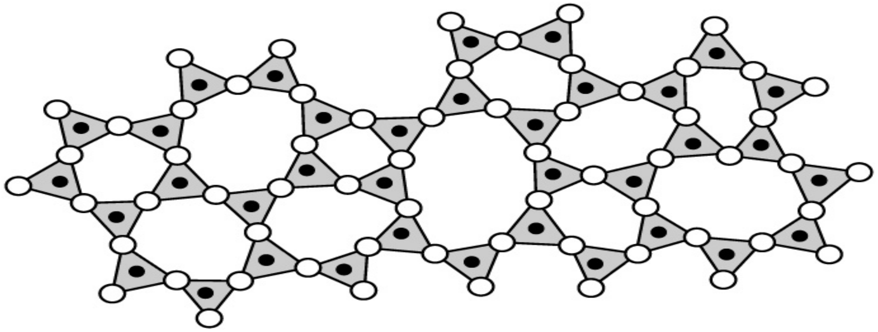


2.65 g/cm^3

(a)

Tetrahedral structure

(b)



2.21 g/cm^3

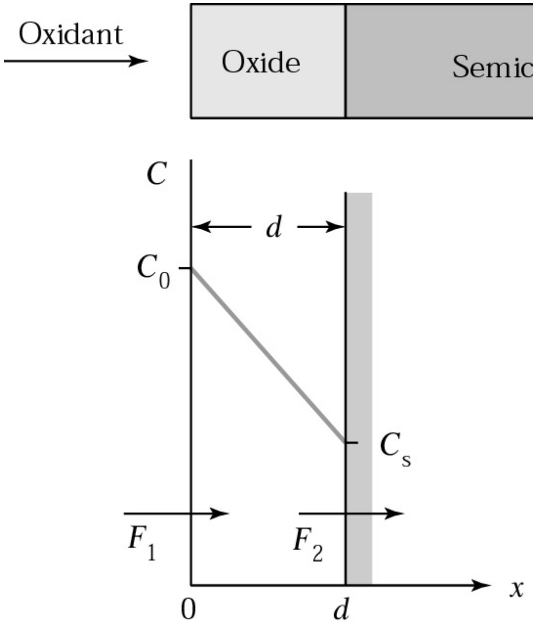
(c)

(a) Basic structural unit of silicon dioxide.
(b) Two-dimensional representation of a crystalline structure of silicon dioxide (quartz crystal lattice).
(c) Two-dimensional representation of the amorphous structure of silicon dioxide.

Kinetics of Thermal Oxidization

Since oxidization occurs at the Si-SiO_2 interface :

- O_2 or H_2O must diffuse through the previous grown oxide film
- Oxidization (growth) rate will fall with time and oxide thickness



C_0: concentration of the oxidizing species (oxygen or water vapor) at the air-SiO_2 interface, molecules/cm^3

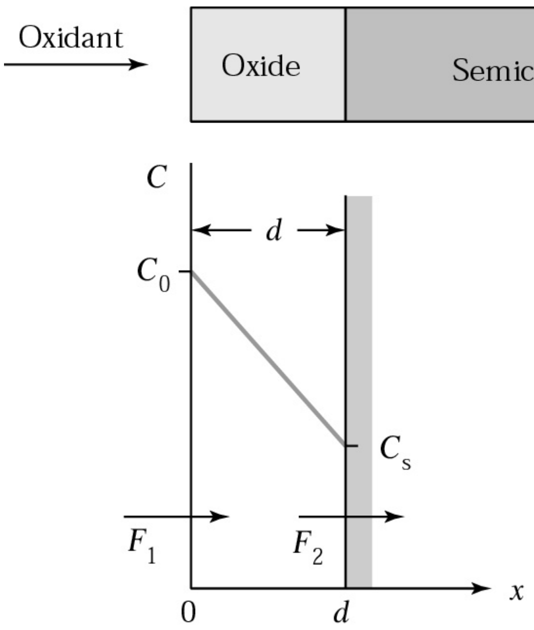
C_s: concentration of the oxidizing species at the SiO_2-Si interface, molecules/cm^3

F_1: oxygen (or water vapor) flux through the oxide layer

F_2: reaction flux

$F=F_1=F_2$

Kinetics of Thermal Oxidization (Cont.)



- Fick's first law of diffusion

$$F_1 = D\frac{dC}{dx} \cong \frac{D(C_0 - C_s)}{x}$$

D: diffusion coefficient of the oxidizing species
X: the thickness of the oxide layer already present

- Reaction of the oxidizing species with Si

$$F_2 = \kappa C_s$$

κ: the surface reaction rate constant for oxidization

- Steady state

$$F = F_1 = F_2 \quad \Longrightarrow \quad F = \frac{DC_0}{x + (D/\kappa)}$$

- Growth rate of the oxide layer thickness

$$\frac{dx}{dt} = \frac{F}{C_1} = \frac{DC_0 / C_1}{x + (D/\kappa)}$$

C_1 : the number of molecules of the oxidizing
species in a unit volume of silicon oxide.
for O_2: C_1=2.2x10^{22} /cm^3
H_2O: C_1=4.4x10^{22} /cm^3

- Initial condition: x(t=0) = d_0

$$x^2 + \frac{2D}{\kappa}x = \frac{2DC_0}{C_1}(t + \tau)$$

d_0 : initial oxide thickness

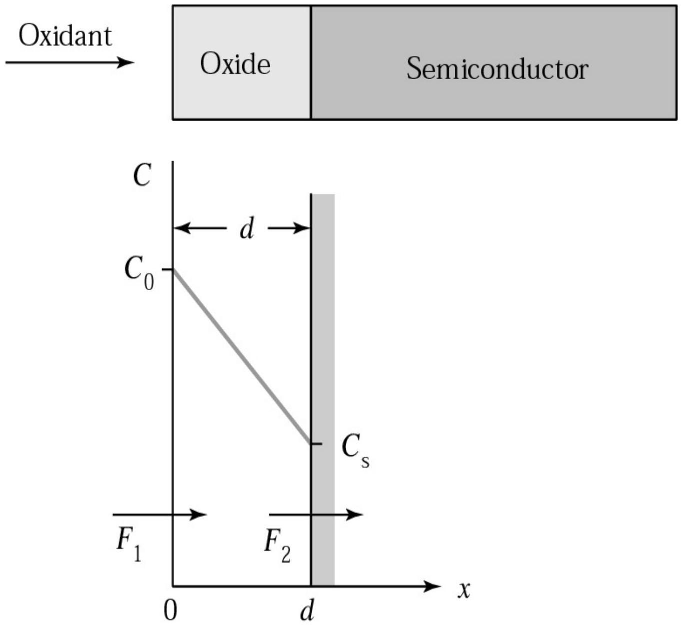
$$\tau \equiv (d_0^2 + 2Dd_0/\kappa)C_1/2DC_0$$

τ: time coordinate shift to account for the initial oxide layer d_0

Model of Thermal Oxidization (Cont.)

- General relationship for the oxidization of Si

$$x^2 + \frac{2D}{\kappa}x = \frac{2DC_0}{C_1}(t+\tau)$$



- The oxide thickness after an oxidizing time t

$$\boxed{x = \frac{D}{\kappa}\left[\sqrt{1+\frac{2C_0\kappa^2(t+\tau)}{DC_1}}-1\right]}$$

- for small value of t

$$x \cong \frac{C_0\kappa}{C_1}(t+\tau)$$

- for large value of t

$$x \cong \sqrt{\frac{2DC_0}{C_1}(t+\tau)}$$

- Compact form of the oxidization of SI

$$x^2 + Ax = B(t+\tau)$$

where A=2D/κ, B=2DC$_0$/C$_1$

$$\boxed{x(t) = \frac{1}{2}A\left[\left(\sqrt{1+\frac{4\cdot B}{A^2}(t+\tau)}\right)-1\right]}$$

$$A = \frac{2\cdot D}{\kappa} \qquad B = \frac{2\cdot D\cdot C_0}{C_1}$$

$$\tau \equiv (d_0^2 + 2Dd_0/\kappa)C_1/2DC_0$$

Growth Rate Regimes

$$\boxed{x(t)=\frac{1}{2}A\left[\left(\sqrt{1+\frac{4\cdot B}{A^2}(t+\tau)}\right)-1\right]}$$

Short Times with $(t+\tau) \ll A^2/4B$:

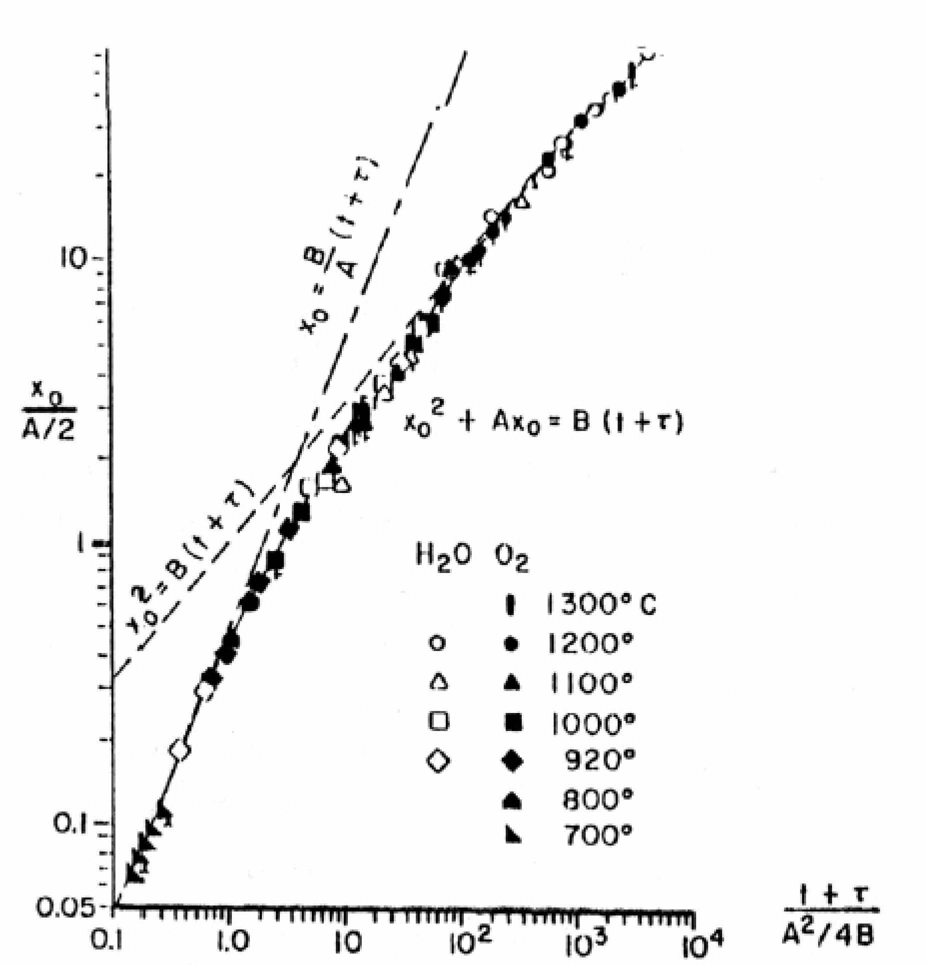
$$x=\frac{B}{A}(t+\tau)$$

Linear rate constant

Long Times with $(t+\tau) \gg A^2/4B$, $t \gg \tau$:

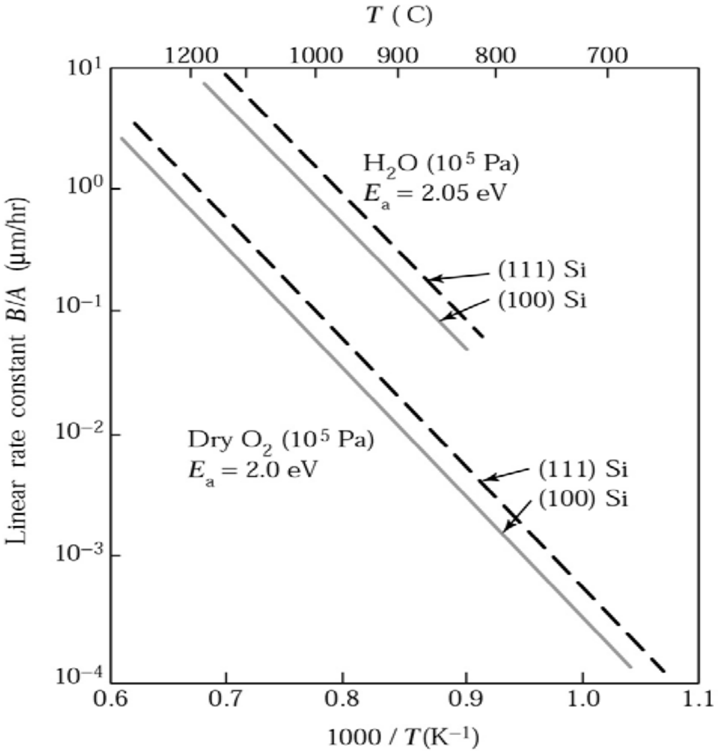
$$x^2=B(t+\tau)$$

Parabolic rate constant

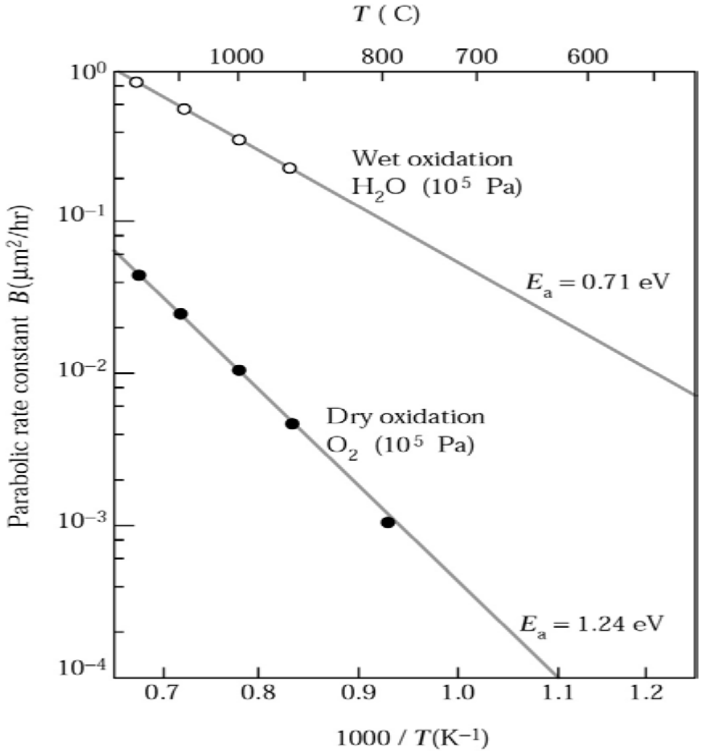


Linear and Parabolic Rate Constant v.s. Temperature

(linear: reaction limit)



(parabolic : diffusion limit)



Arrhenius Relationship

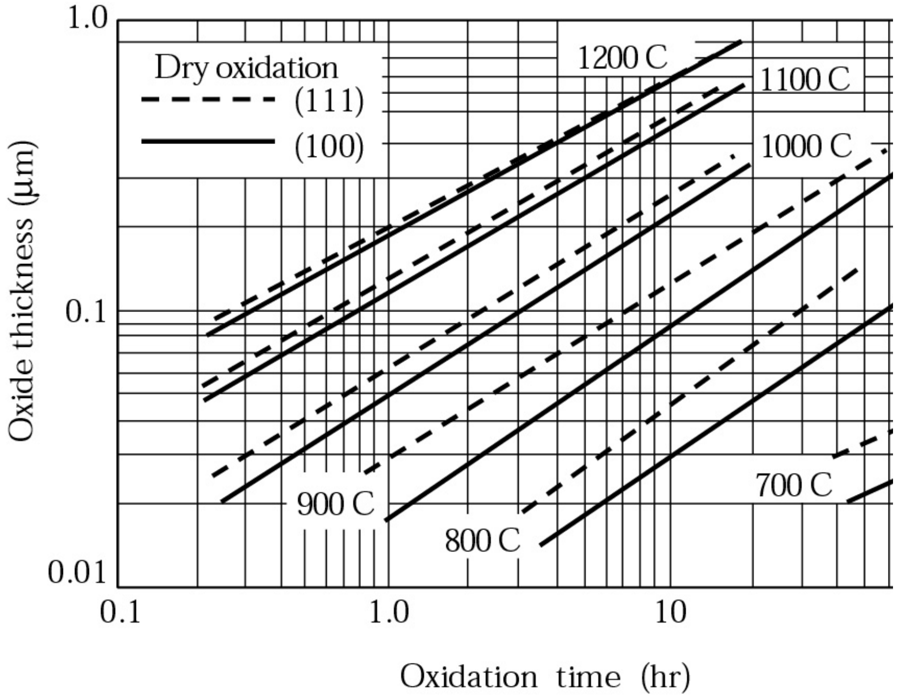
$$B = B_0 \cdot e^{-\left(\frac{E_a}{kT}\right)}$$

$$\frac{B}{A} = \left(\frac{B}{A}\right)_0 \cdot e^{-\left(\frac{E_a}{kT}\right)}$$

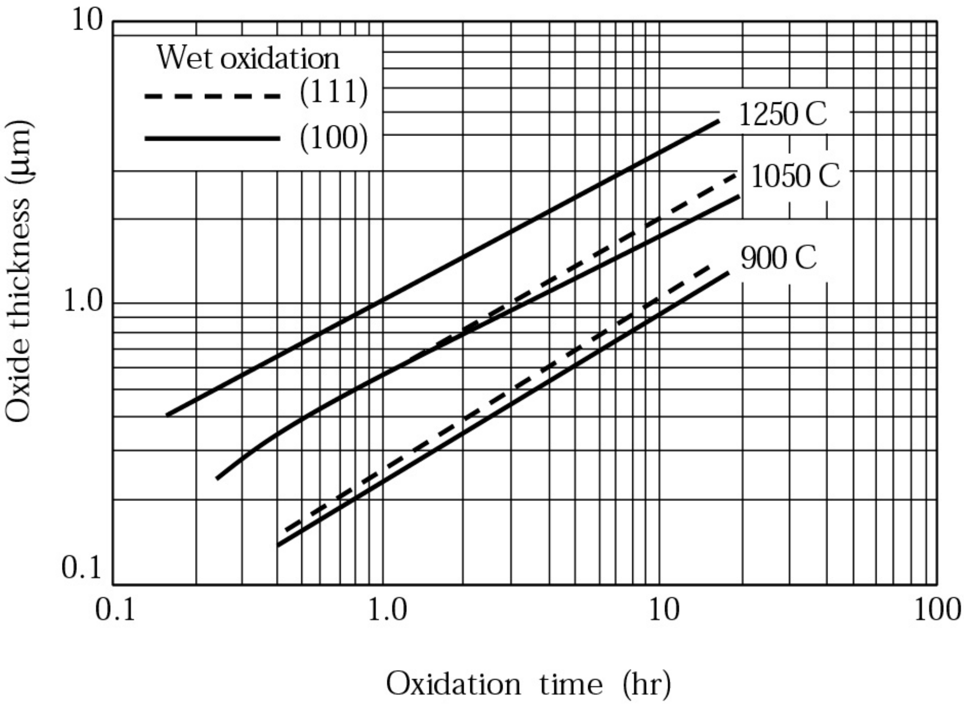
- Rate constant (B/A) varies as exp(-E_a/kT)
  Ea (~2 eV) agrees with the energy to break Si-Si bond (1.83 eV)
- Rate constant depends on orientation

- Rate constant (B) varies as exp(-E_a/kT)
  Ea (1.24 eV for dry and 0.71 for wet oxidization) agrees with the activation energy of diffusion (1.18 ev for O_2 and 0.79 for H_2O).

Oxidization Graph



(a)

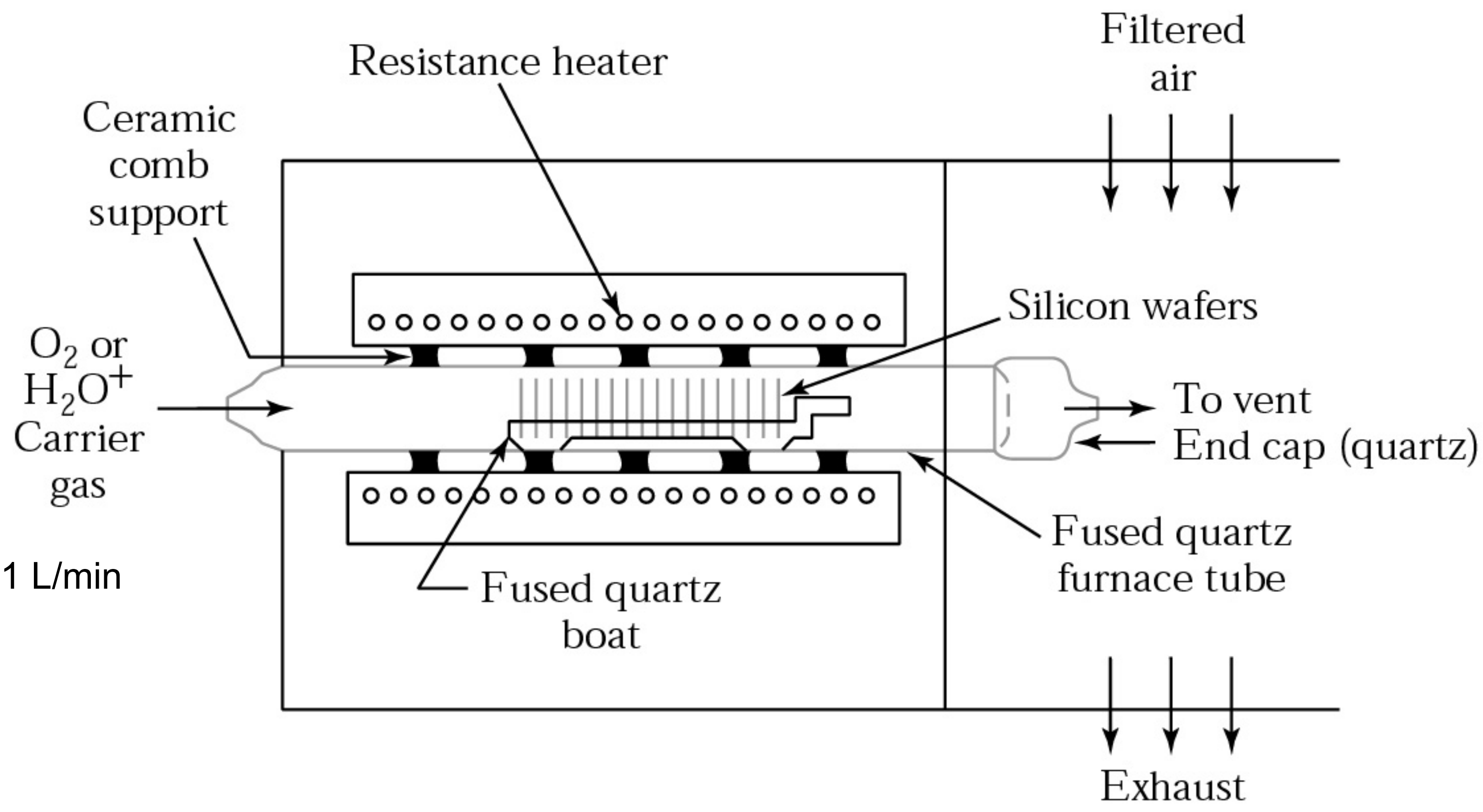


(b)

- Used for quick look-up or confirming the calculations

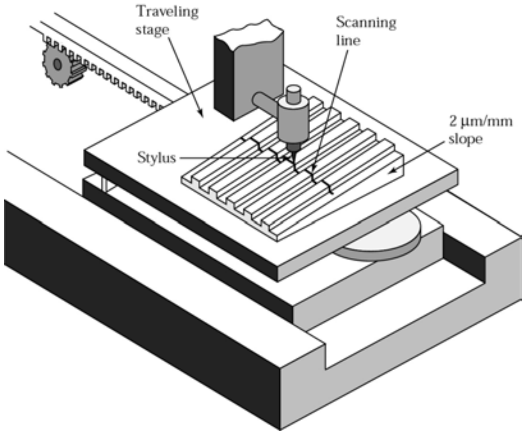
- How long does it take to grow 0.2 um oxide using Dry Oxidation at 1200 C ?
- How long does it take to grow 1 um oxide with 0.2 um initial oxide using Wet oxidation at 1050 C

Oxidization Furnace



Oxidize Thickness Characterization

- **Profilometry:**
Oxide etched away over part of the wafer and a mechanical stylus is dragged over the resulting step.



- **Ellipsometry:**
Polarized laser light is incident on the oxide covered wafer. The polarization of the reflected light, which depends on the thickness and index of refraction (known) of the oxide layer, is determined and used to calculate the oxide thickness.

- **Color (P.55 a reference color chart for thermally grown oxide)**
Light reflected from the surface of an oxidized silicon wafer will experience constructive interference when the path length in the oxide is equal to an integer multiple of the wavelength of the light.

$$2x_0 = k\lambda / n$$

x_0: oxide thickness
k: 1,2,3,…
λ : wavelength of the incident light
n: refractive index of SiO_2, 1.46