Lecture 10:

Oxidation

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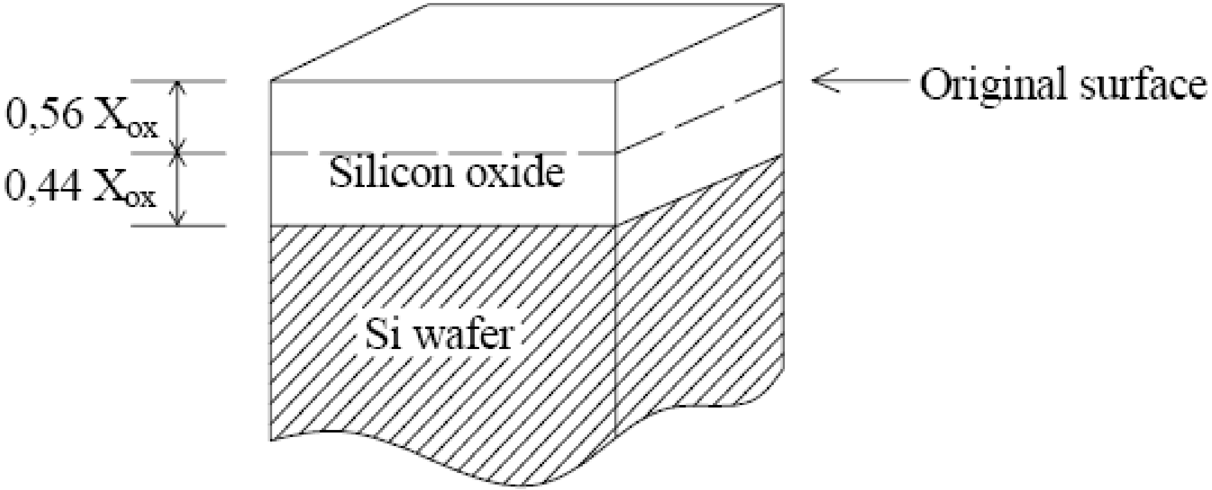
Oxide Formation Depending on Temperature

- T < 200 ℃ :
  - Anodization: ethylene glycol + KNO_3
  - Vacuum deposition : SiO_2 , Si + O_2
  - Sputtering: coverage, stoichiometric
  - Plasma deposition: H containing film
- 250 ℃ < T < 600 ℃ : SiH4
  - ~400 ℃ SiO_2 for passivation
  - doped SiO_2 by B_2H_6, PH_3
- 600 ℃ < T < 900 ℃
  - TEOS (tetra-ethyl-orthosilicate)
  - SiH_4 or $SiCl_4$ + CO_2
- **900 ℃ < T < 1200 ℃: thermal oxidation**
  - **Dry and wet, or Cl incorporated oxidation**

Thermal Oxidation Formation (1)

- Due to the relationships in these reactions and the difference between the densities of silicon and silicon oxide, about 44 % of the silicon surface is *"**consumed**"* during oxidation

$$\frac{Thickness\ of\ Si}{Thickness\ of\ SiO_2} = \frac{Molar\ volume\ (Si)}{Molar\ volume\ (SiO_2)} = \frac{\dfrac{Molecular\ weight\ (Si)}{Density\ (Si)}}{\dfrac{Molecular\ weight\ (SiO_2)}{Density\ (SiO_2)}} = \frac{\dfrac{28.9\ (g/mol)}{2.33\ (g/cm^3)}}{\dfrac{60.08\ (g/mol)}{2.21\ (g/cm^3)}} = 0.44$$



Silicon consumption for oxidation

Thermal Oxidation Formation (2)

- There are two types of the thermal oxidation of SiO_2.
- This type depends on which oxidant type is used (O_2 or H_2O)

  - **Dry oxidation (the oxidant is O_2):**

    Si_2 (solid) + O_2 (vapor) = SiO_2 (solid)

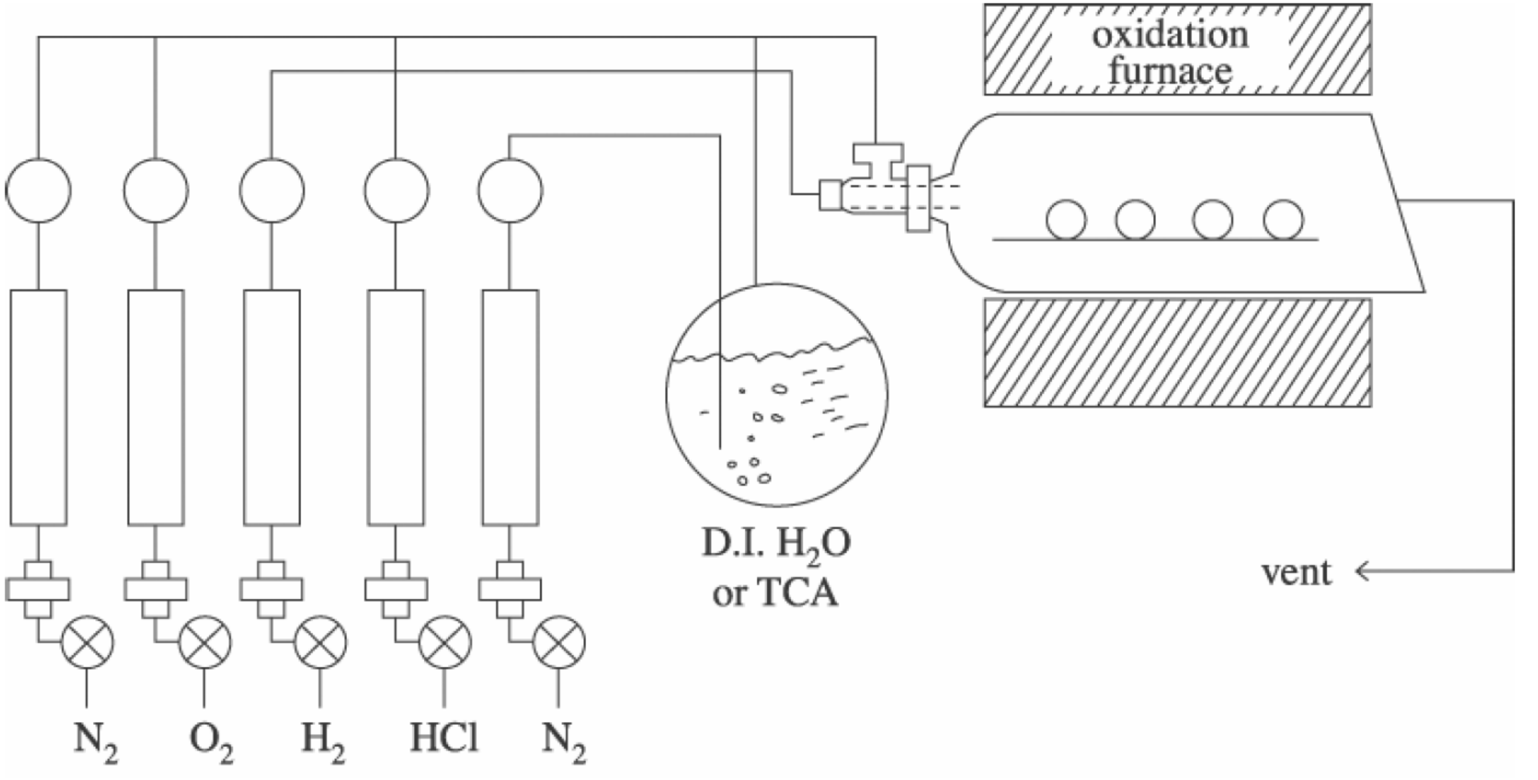
  - **Wet oxidation (the oxidant is H_2O):**

    Si_2 (solid) + $2H_2O$(vapor) = SiO_2 (solid) + $2H_2$

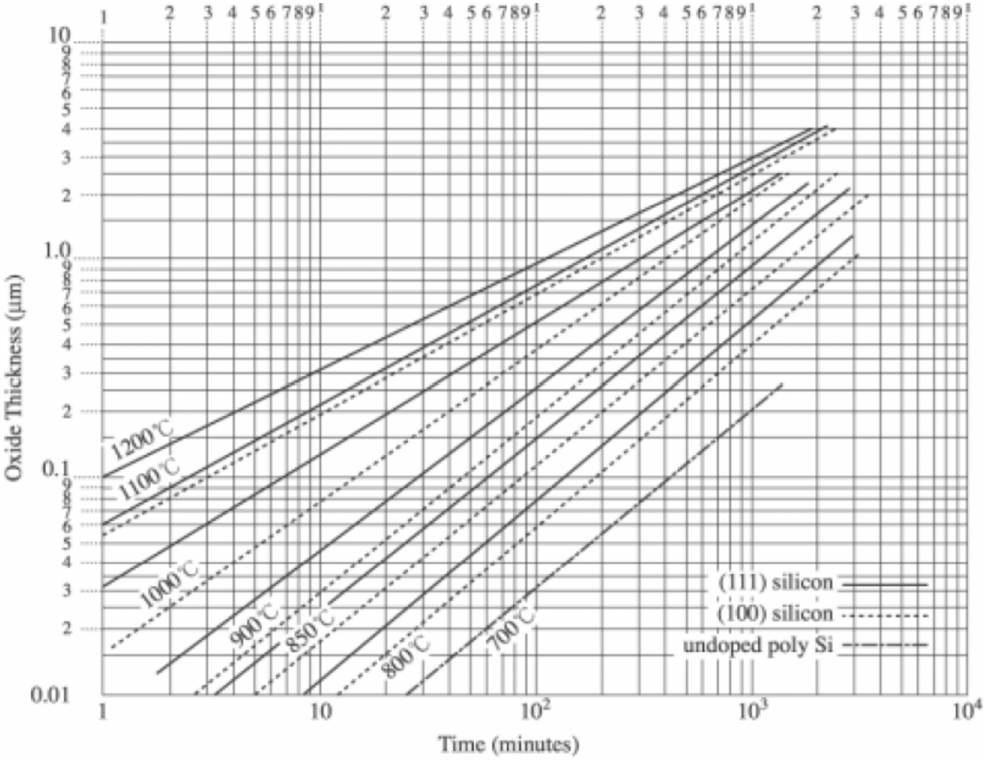
- The growth of oxide is the reaction of surface only
  - The chemical reaction occurs at the Si – SiO_2 surface.
  - After the SiO_2 thickness begins to build up, the arriving oxygen must diffuse through the growing oxide layer to get to the silicon surface

Oxidation Furnace

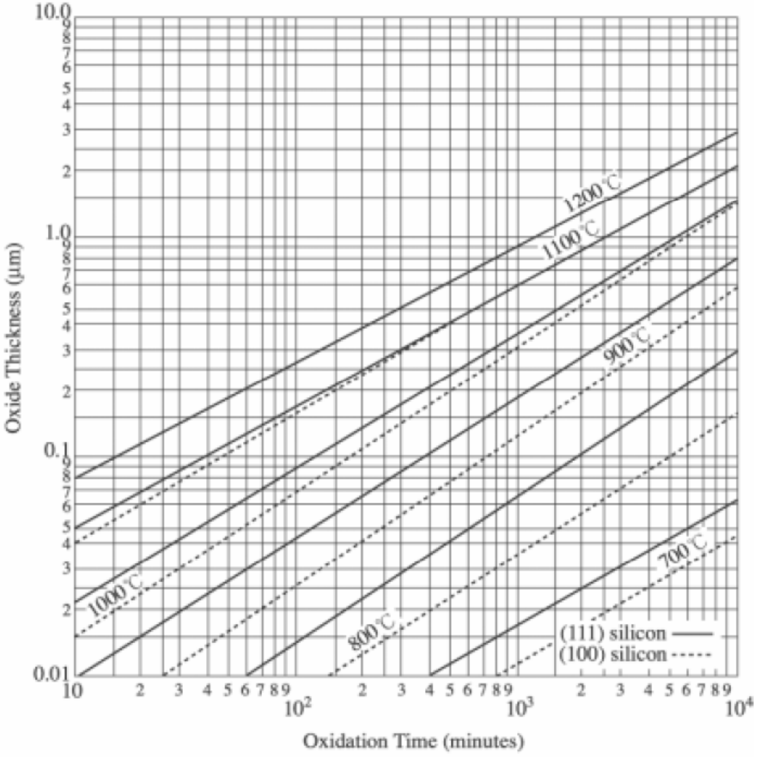
- Electric furnace, tubes and gas lines for oxidation



Oxidation Time vs. Oxide Thickness



Wet oxidation



Dry oxidation

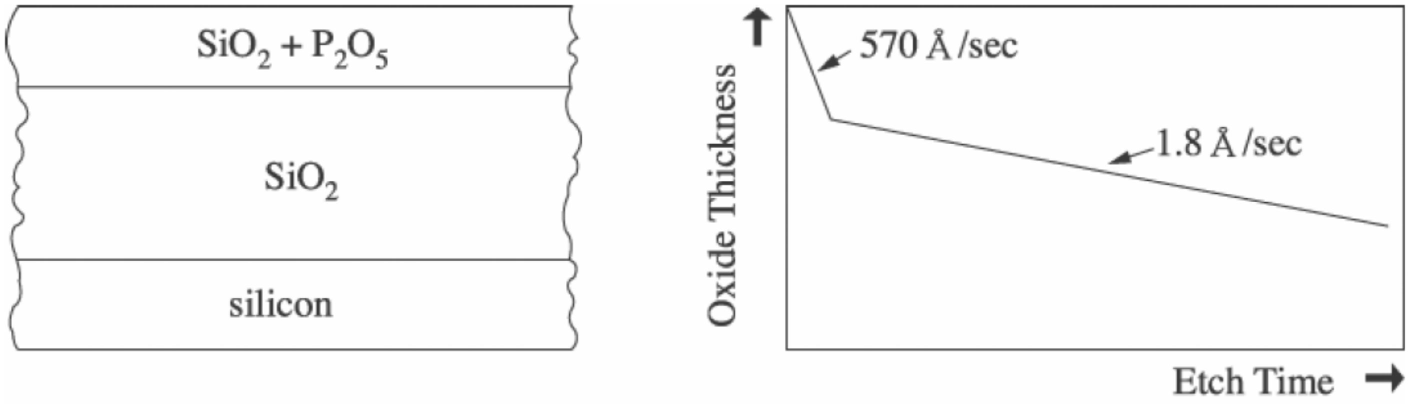
Thermal Oxide Properties

- Thermal oxide properties

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)	2.3 x 10^{22}
Dielectric Strength (V/cm)	5 - 10 x 10^6	Refrctive Index	1.46
Energy Gap (eV)	~ 8	Specific Heat (J/g °C)	1.0
Etch rate in BHF (Å/min)	1000	Stress in film on Si (dyne/cm^2)	2 - 4 x 10^9 (compression)
Infrared Absorption Peak	9.3		
Linear Expansion Coefficient (cm/°C)	5.0 x 10^{-7}	Thermal Conductivity (W/cm°C)	0.014

Characterization of Oxide Film

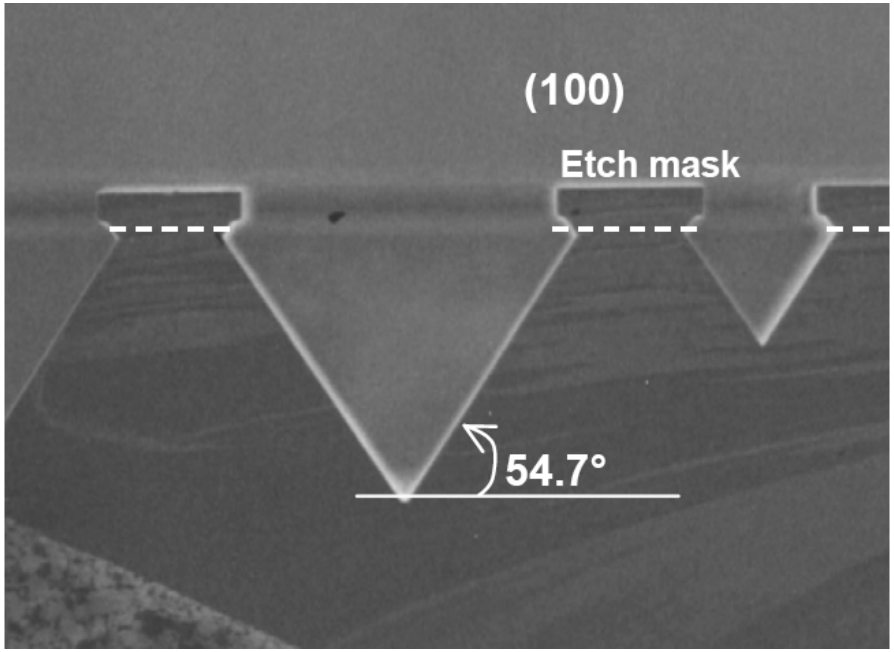
- Oxide thickness
  - UV-visible photospectrometer, ellipsometer, color chart
- Reflection index
  - Ellipsometer
  - Depends on stoichiometric composition
  - SiO_2 (1.46) ~ Si(3.75)
- Etch rate
  - Oxide structure and composition



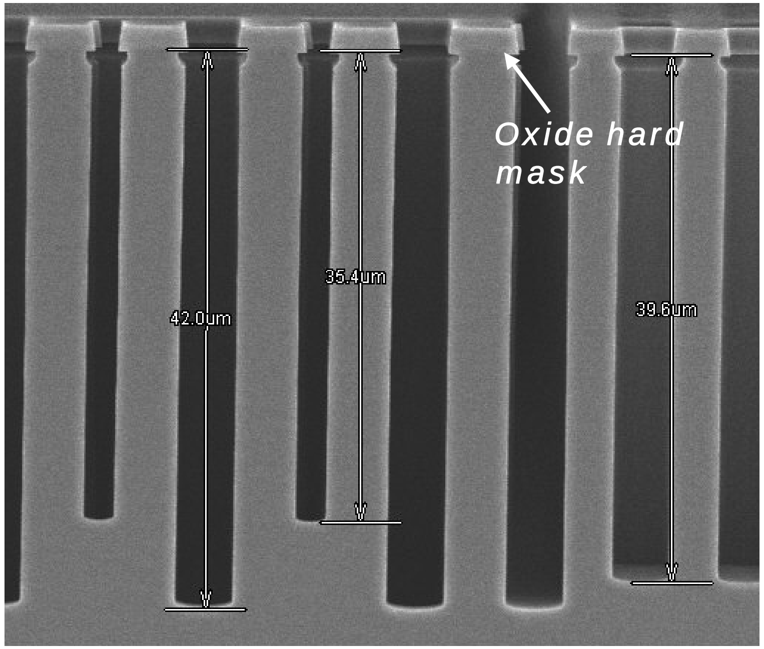
Etch rate depends on oxides (etch solution is $HF:HNO_3:H_2O$ = 15:10:100)

Usages of Oxide in Micromachining (1)

- Oxide hare mask for silicon etching
  - Hard mask for silicon dry etching
    - Typical etch selectivity in deep RIE → **Si:SiO2 = 200:1**
  - Hard mask for silicon wet etching
    - High etch selectivity in KOH and TMAH wet etching → **>1000:1**



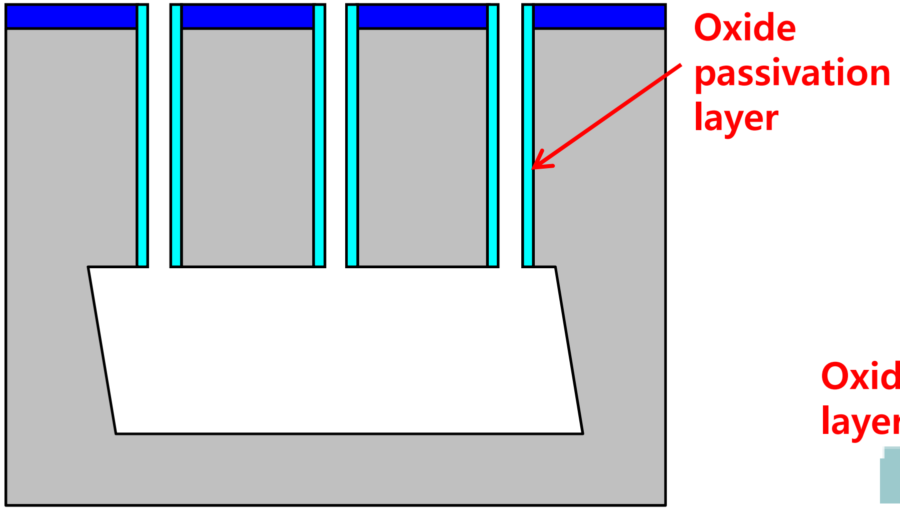
Wet etch mask



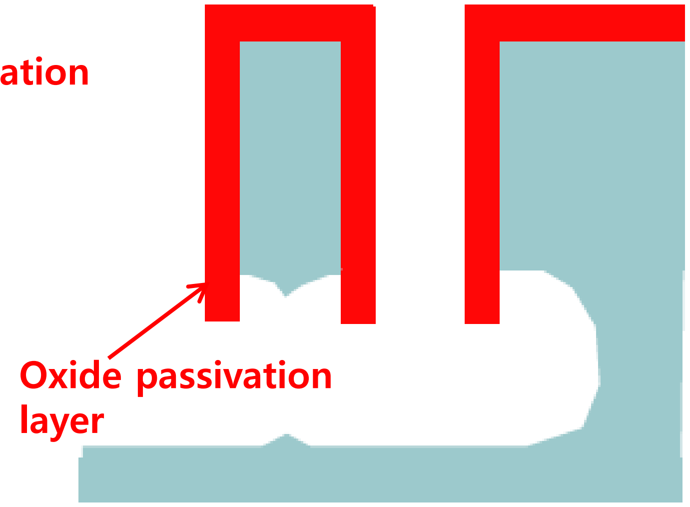
Deep RIE mask

Usages of Oxide in Micromachining (2)

- Sidewall passivation layer
  - Thermal oxide layer protects sidewall of silicon structures in wet etching or dry etching
  - CVD oxide is not suitable for this application, because the CVD oxide can not reach the bottom of deep trenches



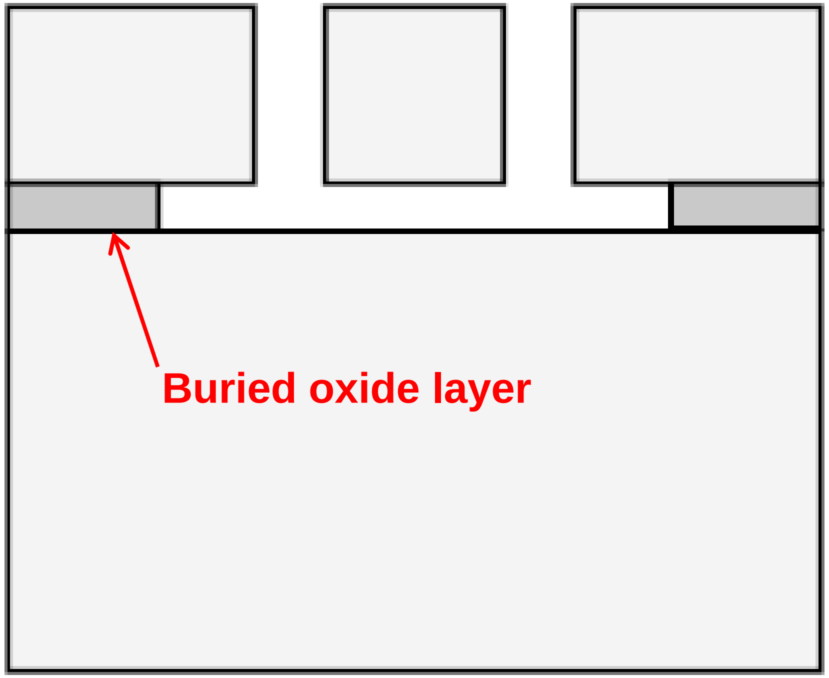
SBM process: sidewall is protected by thermal oxide in anisotropic silicon etch



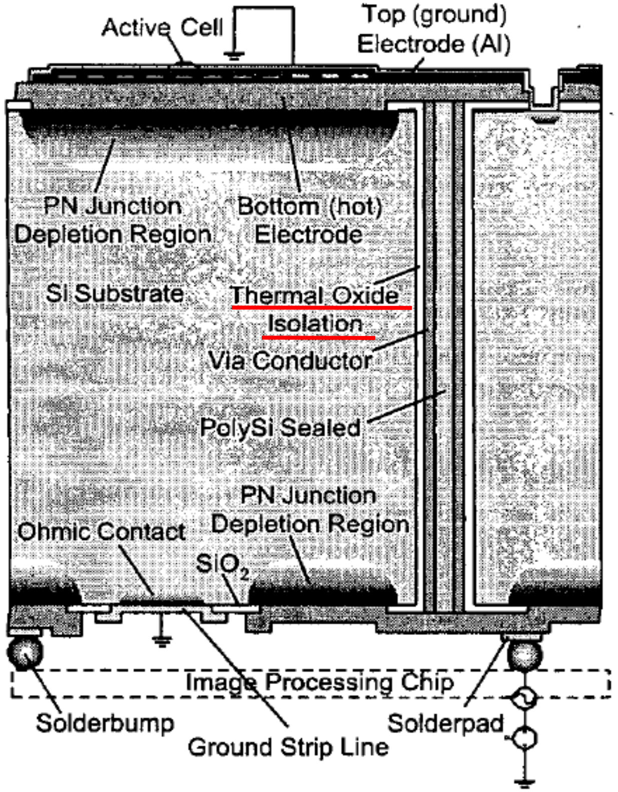
SCREAM process: sidewall is protected by thermal oxide in isotropic silicon etch

Usages of Oxide in Micromachining (3)

- Electrical isolation layer
  - Oxide is excellent electrical insulator for device isolation or interconnection line



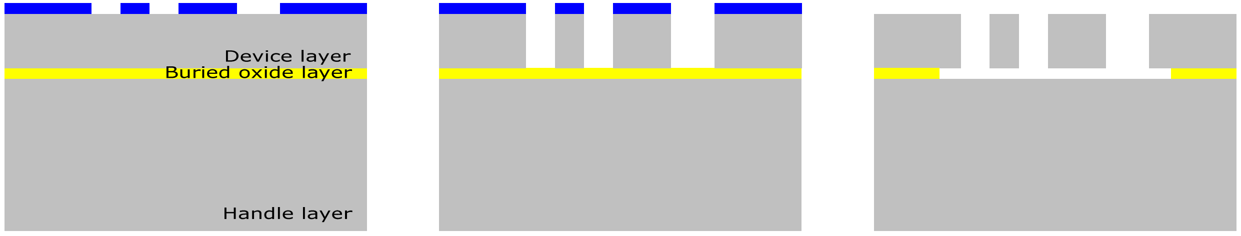
Electrical isolation layer in SOI process



Electrical isolation layer in through-hole inter connection

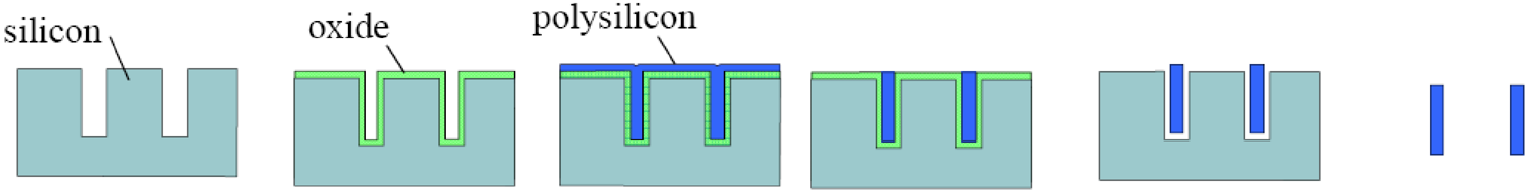
Usages of Oxide in Micromachining (4)

- Sacrificial layer in structure releasing
  - SOI (Silicon On Insulator) process
    - Structures are released by etching the sacrificial buried oxide layer
  - HEXSIL (High aspect ratio molded polysilicon) process
    - Poly-Si structure is demolded by etching away the sacrificial oxide



(a) (b) (c)

Typical SOI Process: (a) Oxide hard mask patterning. (b) Deep RIE. (c) HF release

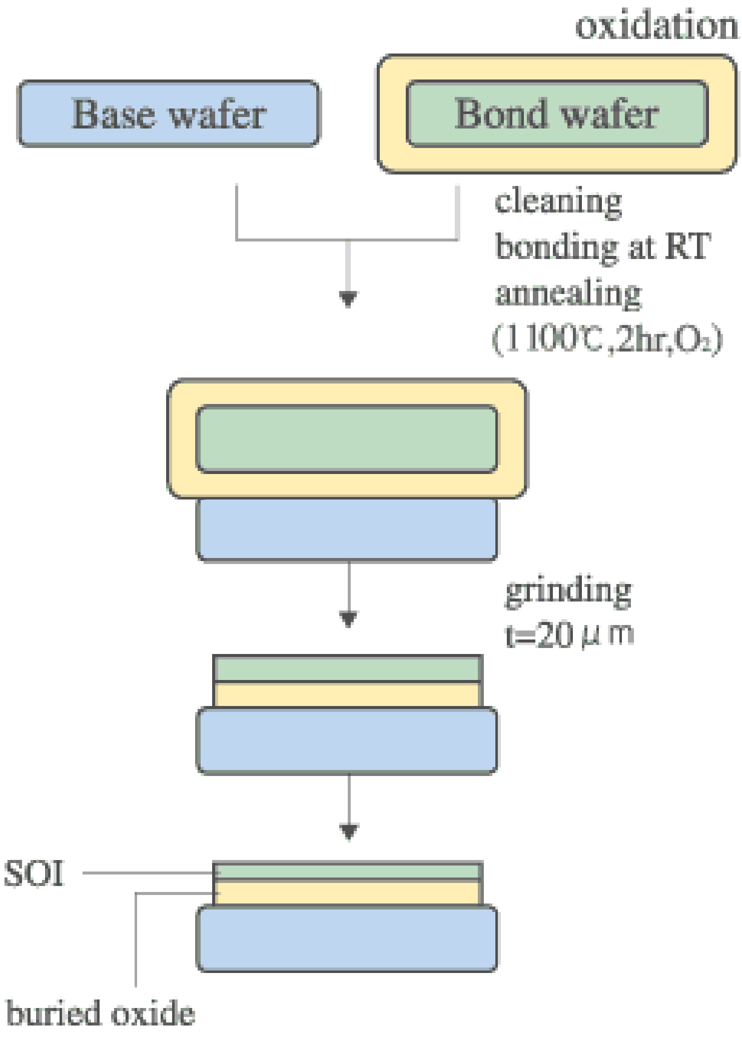


(a) (b) (c) (d) (e) (f)

Basic HexSil process: (a) Silicon DRIE. (b) Oxidation. (c) LPCVD polysilicon. (d) CMP.
(e) HF etch. (f) Release of substrate mold.

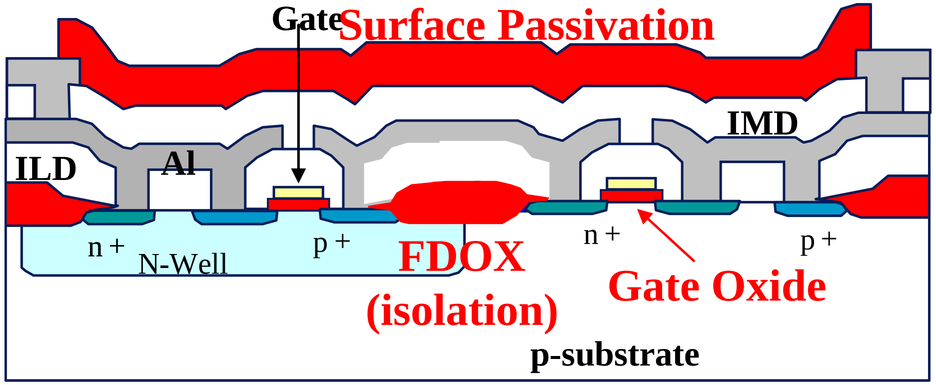
Usages of Oxide in Micromachining (5)

- Bonded SOI wafer
  - By using bonding chemistry between Si and SiO_2 or between SiO_2 and SiO_2 effectively, two Si wafers are tightly bonded with a SiO_2 layer
  - After one side of the Si bulk is thinned down properly with a desired active layer thickness, bonded SOI wafers are obtained
  - The fabrication process
    - The first step is to mate **a thermally oxidized wafer** on a non-oxidized wafer at room temperature.
    - The second step is to anneal the bonded pair to increase bonding strength.
    - The third step is to thin down one side of the bonded pair to an appropriate thickness by grinding, etching and polishing.



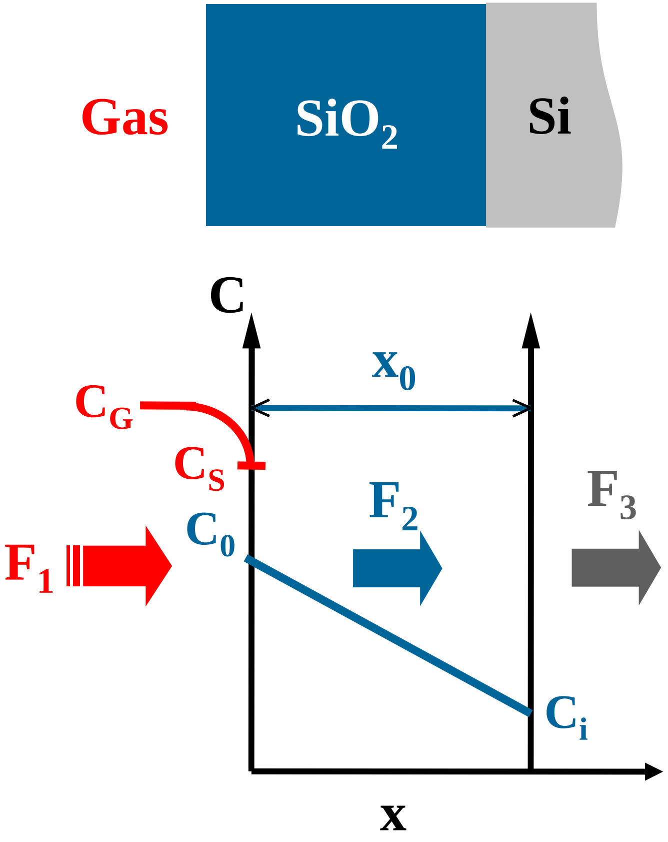
Usages of Oxide in CMOS

- Diffusion masking material
- Passivation layer
- Resistive layer(ρ ≈ 1018 Ω·cm)
- Doping source
- Gate oxide(gate capacitor)
  - gate length/oxide thickness: 1 μm/250 Å, 0.5 μm/150 Å, 0.2 μm/70 Å, 0.1 μm/30 Å
- Field oxide



Oxidation Kinetics

- Oxidation Kinetics Model by Deal and Grove:
  - Oxidation proceeds by *the diffusion of an oxidant* (molecular H_2O or O_2)
  - Reaction occurs at the Si/SiO_2 interface.
  - Si is consumed and the interface moves into Si



- Concentration of oxidants :
  - C_G : concentration of oxidant in the bulk of the gas
  - C_S : concentration of oxidant at the oxide surface
  - C_0 : equilibrium C of the oxidant at the oxide surface
  - C_i : concentration of the oxidant at growth interface
- Flux of oxidant :
  - F_1 : the bulk of the gas → the gas/oxide interface
  - F_2 : the diffusion through the existing oxide
  - F_3 : the reaction. at the SiO2/Si

Oxidation Kinetics (Flux in Gas Phase)

F_1 : Due to the concentration difference between C_G and C_S

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

h_G : mass transfer coefficient

From the ideal gas law PV = NRT

$$C = \frac{N}{V} = \frac{P}{kT} \qquad C_G = \frac{P_G}{kT} \qquad C_S = \frac{P_S}{kT}$$

From Henry's law: *" The concentration of a species dissolved in a solid at Equilibrium is proportional to the partial pressure of the species at the solid surface"*

$C_0 = K_H P_S$, $C^* = K_H P_G$

K_H : Henrian Constant
C^* : equilibrium concentration in the oxide

$$F_1 = h_G(C_G - C_S) = \frac{h_G}{kT}(P_G - P_S) = \frac{h_G}{K_H kT}(C^* - C_0)$$

$$\therefore \quad F_1 = h(C^* - C_0)$$

$h = h_G/K_H kT$

Oxidation Kinetics (Flux in Oxide and Silicon)

F_2 : Due to the concentration difference between C_o and C_i

From the Fick's first law

$$F_2 = -D\left(\frac{dC}{dx}\right) = -D\frac{(C_i - C_0)}{x_0 - 0} = D\frac{(C_0 - C_i)}{x_0}$$

D : diffusion coefficient of the oxidant in oxide

F_3 : Due to the consumption by the interface reaction at SiO_2/Si

Proportional to the concentration of the oxidant at the interface

$$F_3 = k_S C_i$$

k_S : chemical rxn. rate const.

Oxidation Kinetics (Steady-State Flux)

Under steady-state condition
(no build-up or depletion of oxidizing species)

$$F_1 = F_2 = F_3 = F \quad \Rightarrow \quad C_i = \frac{C^*}{1 + \frac{k_S}{h} + \frac{k_S x_0}{D}} \qquad C_0 = \frac{(1 + k_S \frac{x_0}{D})C^*}{1 + \frac{k_S}{h} + \frac{k_S x_0}{D}}$$

Since $h \gg k_S$ $\Rightarrow$ $C_i = \dfrac{C^*}{1 + \frac{k_S x_0}{D}}$ and $C_0 \cong C^*$

$$\therefore \quad C_i \cong \frac{C_0}{1 + \frac{k_S x_0}{D}}$$

$$\therefore \quad F = k_S \frac{C_0}{1 + \frac{k_S x_0}{D}} = \frac{D C_0 k_S}{D + k_S x_0}$$

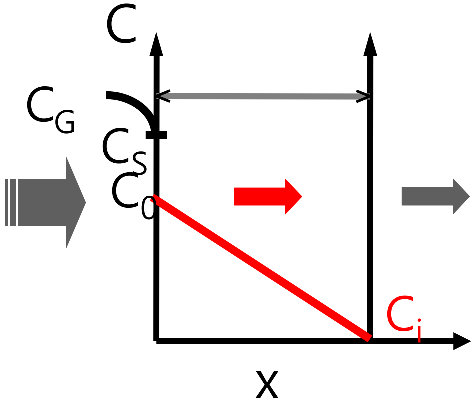
Oxidation Kinetics (Rate Limiting Step)

I. When the diffusion constant D is very small,

$$D \ll k_S x_0 \Rightarrow C_i \cong \frac{C_0}{1+\cancelto{\infty}{\frac{k_S x_0}{D}}} \Rightarrow \therefore\ C_i \rightarrow 0$$

$$\therefore\ C_0 \rightarrow C^*$$

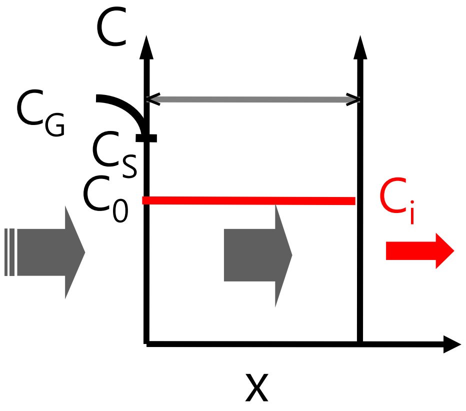
Diffusion Controlled



II. When the diffusion constant D is very large,

$$D \gg k_S x_0 \Rightarrow C_i \cong \frac{C_0}{1+\cancelto{0}{\frac{k_S x_0}{D}}} \Rightarrow \therefore\ C_i \rightarrow C_0$$

Reaction Controlled



Oxidation Kinetics (Oxidation Rate)

Oxidation Rate

$$\frac{dx_0}{dt} = \frac{F}{N} = \frac{1}{N}\frac{DC_0k_S}{D+k_Sx_0}$$

Boundary Condition
$x = x_i$,when $t = 0$

N : # of oxidant molecules per unit volume
N(dry) = 2.3 x 10^{22} cm^{-3}
N(wet) = 2.3 x 10^{22} cm^{-3}

$$\int_{x_i}^{x_0}(D+k_Sx_0)\,dx_0 = \frac{DC_0k_S}{N}\int_0^t dt$$

$$\frac{1}{2}k_Sx_0^2 + Dx_0 = \frac{DC_0k_S}{N}t + \frac{1}{2}k_Sx_i^2 + Dx_i$$

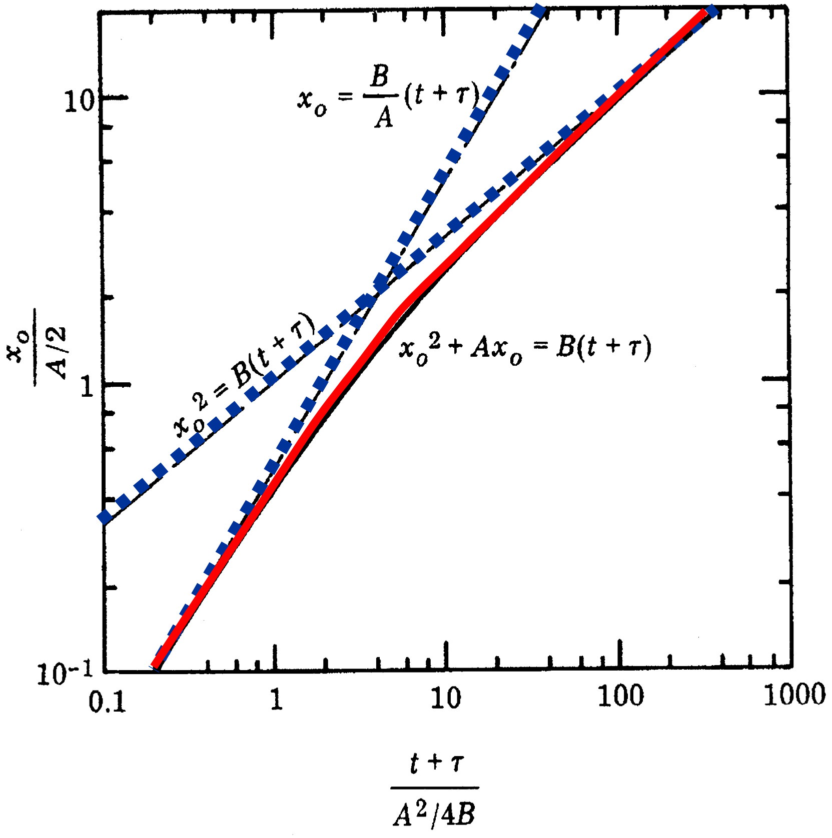
$$x_0^2 + \frac{2D}{k_S}x_0 = \frac{2DC_0}{N}t + x_i^2 + \frac{2D}{k_S}x_i$$

$$\therefore \quad x_0^2 + Ax_0 = B(t+\tau)$$

$A = 2D/k_S,$
$B = 2DC_0/N,$
$\tau = (x_i^2+Ax_i)/B$

Oxidation Kinetics (Oxidation Rate)

$$x_0 = \frac{A}{2}\left(\sqrt{1+\frac{t+\tau}{A^2/4B}}-1\right)$$



I. For short time ($t + \tau \ll A^2/4B$)

$x_0 = B/A\ (t + \tau)$: Linear Growth Law

linear rate constant B/A

B/A = C^*/N : independent of D

II. For long time ($t + \tau \gg A^2/4B$)

$x_0^2 = B(t + \tau)$: Parabolic Growth Law

parabolic rate constant B

B = $2DC^*/N$

→ *proportional to D*

(diffusion controlled)

Factors Affecting Oxidation Rate

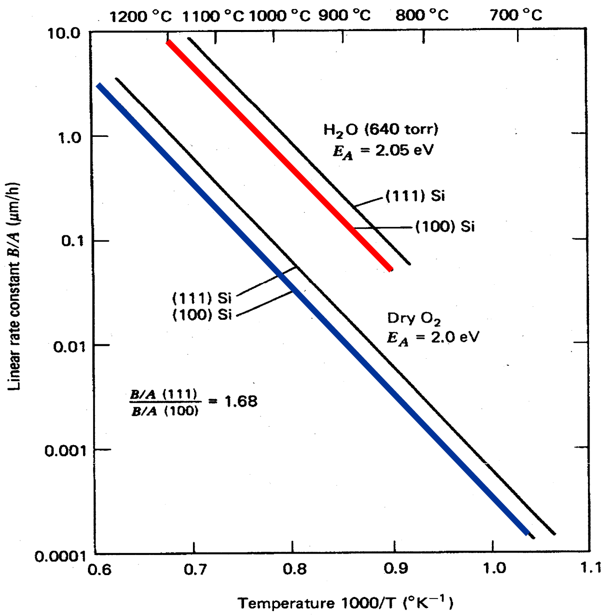
- Oxidant Species (Dry and Wet), temperature
- Oxidant Gas Pressure
- Crystallographic Orientation of Si Substrate
- Substrate Doping
- Gas Ambient

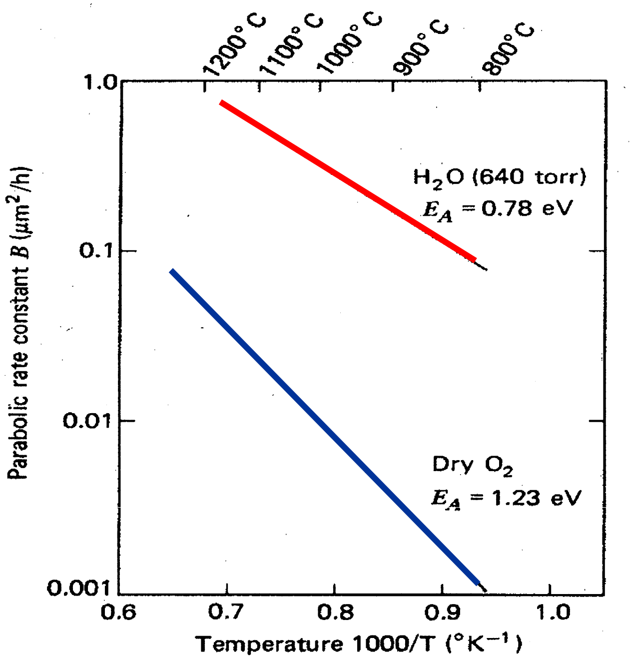
Oxidation Rate (Temperature & Oxidant)

Parabolic $B = C_1\ exp(-E_1/kT)$

Linear $B/A = C_2\ exp(-E_2/kT)$

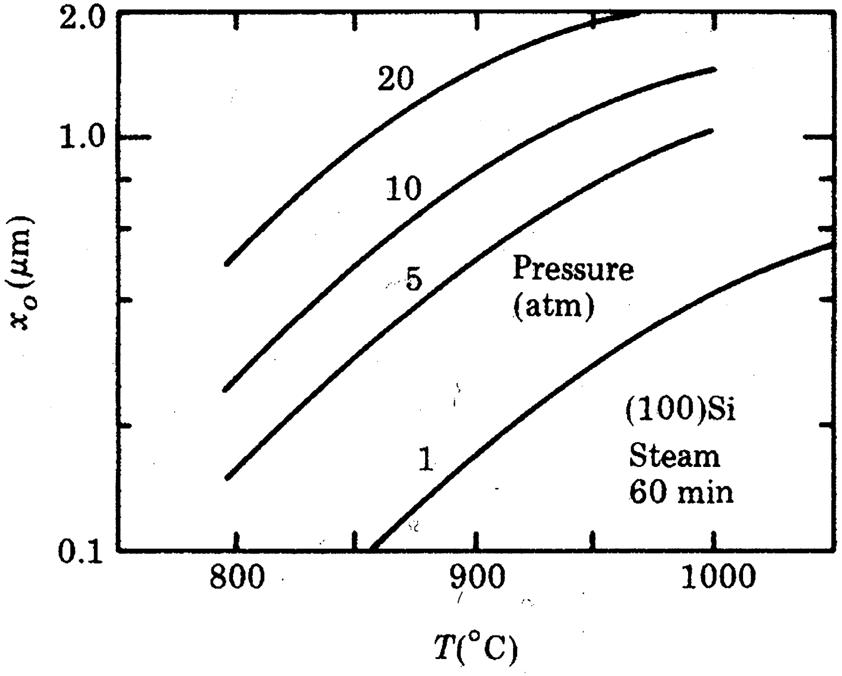
Dry O_2	$C_1 = 7.72 \times 10^2$ µm²/h $C_2 = 3.71 \times 10^6$ µm²/h	$E_1 = 1.23$ eV $E_2 = 2.00$ eV
Wet H_2O (640 Torr)	$C_1 = 3.86 \times 10^2$ µm²/h $C_2 = 0.97 \times 10^8$ µm⁸/h	$E_1 = 0.78$ eV $E_2 = 1.96$ eV





Oxidation Rate (Pressure)

- High pressure increases the oxide growth rate, by increasing the linear and parabolic rate constants. (The increase in the rate constants arises from the increased *C**.)



$$\frac{B}{A}=\frac{k_S C_0}{N}\cong\frac{k_S}{N}C^*=\frac{k_S}{N}K_H P_G$$

$$B=\frac{2DC_0}{N}\cong\frac{2D}{N}C^*=\frac{2D}{N}K_H P_G$$

Trade off: ΔP = 1 atm ⇔ ΔT = 30 °C

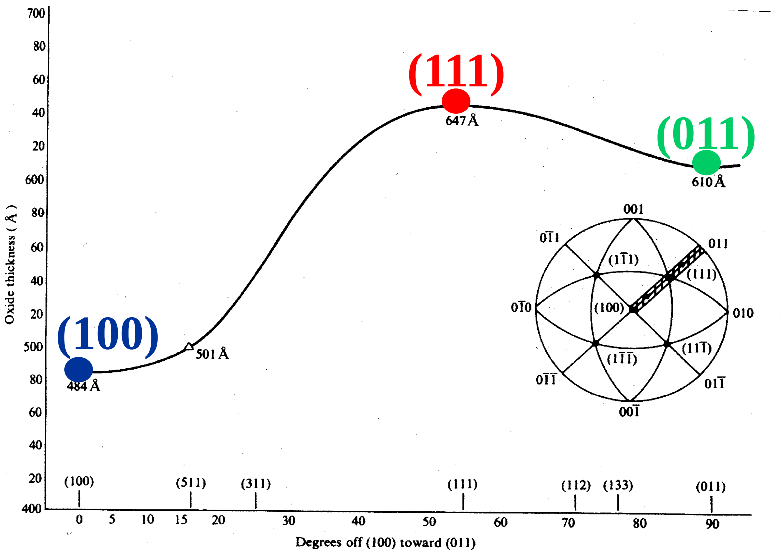
➢ Low temperature oxidation can be achieved by high pressure oxidation for the same oxidation rate.

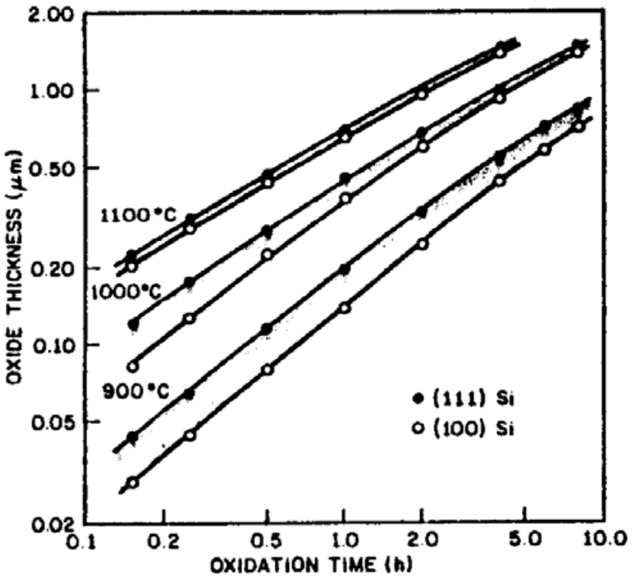
Method

1. Pressurizing water-pumping
2. Producing water by pyrogenic system

Oxidation Rate (Crystallographic Orientation)

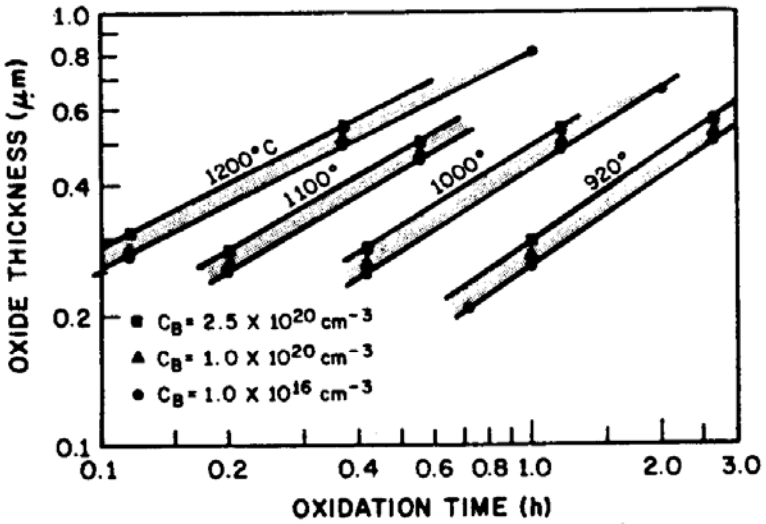
- SiO2/Si interface is strongly related to the cystallographic orientation of Si.
  - i.e., # of available Si-Si bonds per unit area
- The growth rate ratio (*v*111/*v*100) decreases at high temperatures, since the parabolic rate constant is predominant.



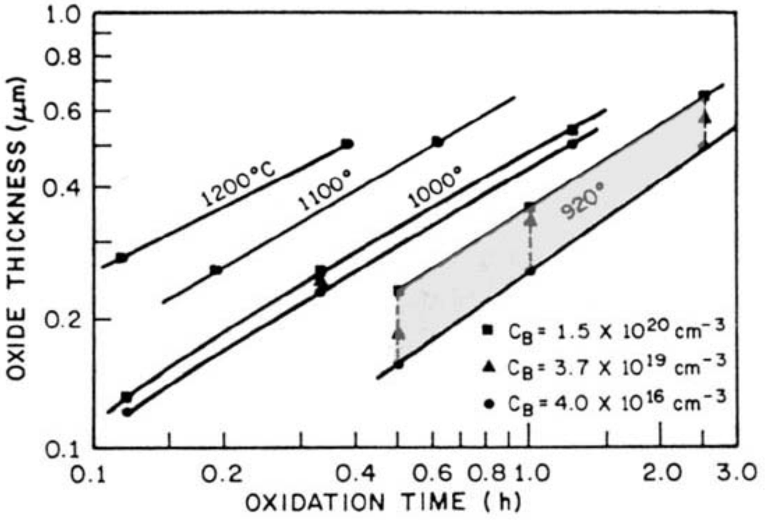


Oxidation Rate (Doping)

- Group III and V dopants enhance the oxidation rate when heavily doped.
- The oxidation rate depends on
  - the C_B in SiO_2 for diffusion controlled oxidation (B dominates).
  - the C_B at Si surface for reaction controlled oxidation (B/A dominates).



Boron segregated in SiO_2 weakens the SiO_2 bond structures.
- Rapid diffusion of O_2 and H_2O



Phosphorous piles up at Si surface.
- Enhanced oxidation rate in the reaction controlled regime

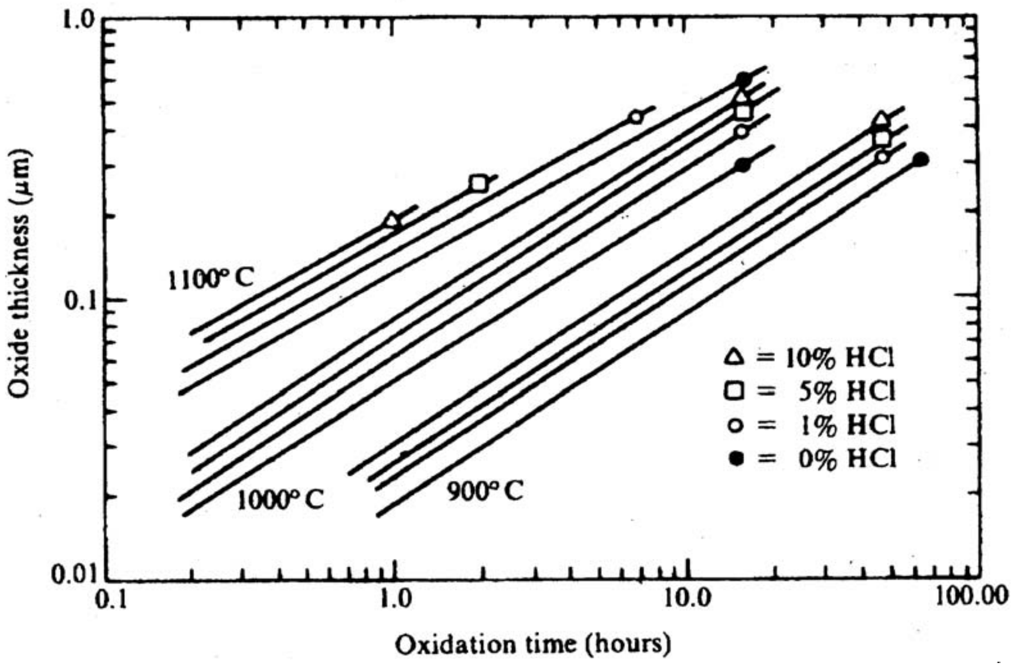
Oxidation Rate (Additional Gases)

- Halogenic Oxidation:

  The presence of chlorine mixed with O_2 gas during dry oxidation

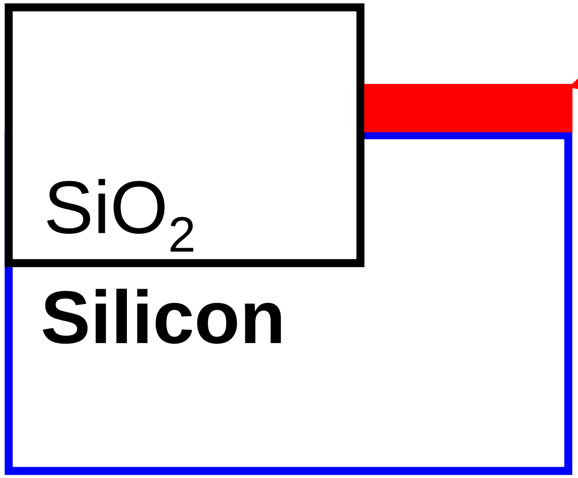
  - Enhance the oxidation rate.
  - Improves device characteristics.

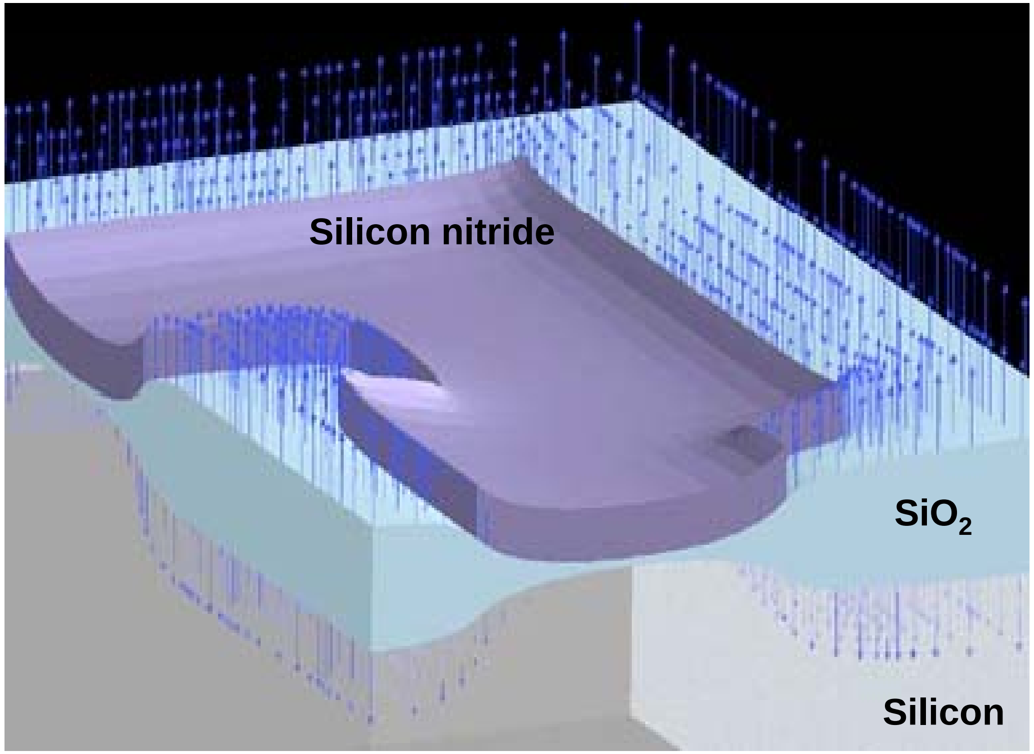
  * Chlorine-containing gases: Cl_2, HCl, TCE, TCA



Mask for Thermal Oxidation

- Oxidation can be masked with silicon nitride, which prevents O_2 diffusion





Color Chart (1)

Film Thickness (microns)	Order (5450Å)	color and comments
0.050		Tan
0.075		Brown
0.100		Dark violet to red violet
0.125		Royal blue
0.150		Light blue to metallic blue
0.175	I	Metallic to very light yellow-green
0.200		Light gold or yellow slightly metallic
0.225		Gold with slight yellow orange
0.250		Orange to melon
0.275		Red-violet
0.300		Blue to violet-blue
0.310		Blue
0.325		Blue to blue-green
0.345		Light green
0.350		Green to yellow-green
0.365	II	Yellow-green
0.375		Green-yellow
0.390		Yellow

Color Chart (2)

Film Thickness (microns)	Order (5450Å)	color and comments
0.412		Light orange
0.426		Carnation pink
0.443		Violet-red
0.465		Red-violet
0.476		Violet
0.480		Blue-violet
0.493		Yellow
0.502		Blue-green
0.520		Green(broad)
0.540		Yellow-green
0.560	III	Green-yellow
0.574		Yellow to "yellowish"
0.585		Light orange or yellow to pink borderline
0.60		Carnation pink
0.63		Violet-red
0.68		"Bluish"

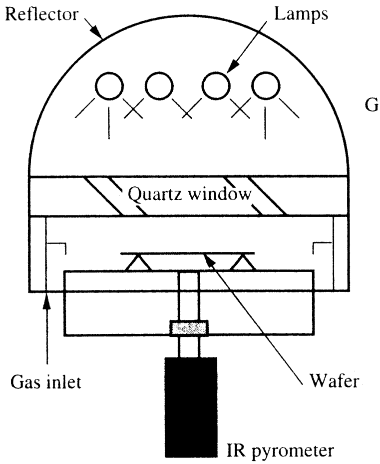
Color Chart (3)

Film Thickness (microns)	Order (5450Å)	color and comments
0.72	Ⅳ	Blue-green to green (quite broad)
0.77		"Yellowish"
0.80		Orange(rather broad for orange)
0.82		Salmon
0.85		Dull,light red-violet
0.86		Violet
0.87		Blue-violet
0.89		Blue
0.92	Ⅴ	Blue-green
0.95		Dull yellow-green
0.97		Yellow to "yellowish"
0.99		Orange
1.00		Carnation pink
1.02		Violet-red
1.05		Red-violet
1.06		Violet
1.07		Blue-violet

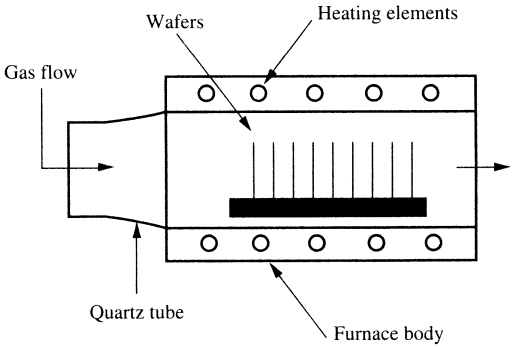
Color Chart (4)

Film Thickness (microns)	Order (5450Å)	color and comments
1.10		Green
1.11		Yellow-green
1.12	VI	Green
1.18		Violet
1.19		Red-violet
1.21		Violet-red
1.24		Carnation pink to salmon
1.25		Orange
1.28		“yellowish”
1.32	VII	Sky blue to green-blue
1.40		Orange
1.45		Violet
1.46		Blue-violet
1.50	VIII	Blue
1.54		Dull yellow-green

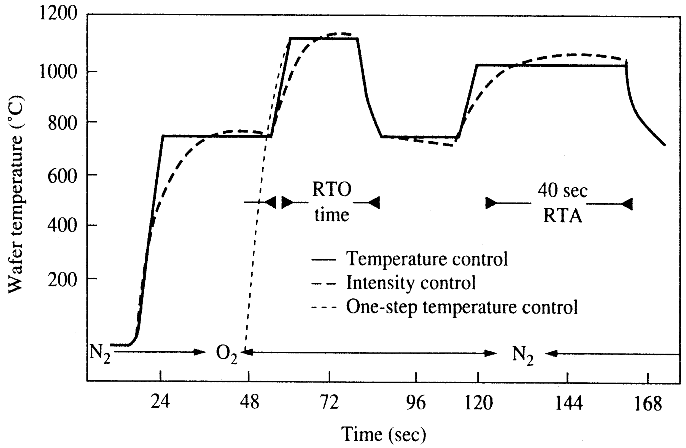
Rapid Thermal Oxide (RTO)



(a) RTP system



(b) Batch-furnace system



Furnace	RTP
Batch	Single-wafer
Hot wall	Cold wall
Long time	Short time
Small dT/dt	Large dT/dt (100 - 300 ^oC/sec)
High cycle time	Low cycle time
Environment temp. measure	Wafer temp.
Issues	
Thermal budget	Uniformity
Particles	Repeatability
Atmosphere	Throughput
	Wafer stress
	Absolute temp.

Wet Oxidation Recipe

- Standard wet oxidation recipe in ISRC

STANDBY 900℃	PUSH	PRE-HEAT	RAMP UP	STABILIZ.	PRE OXID.	WET OXID.	RAMP DOWN	PULL
N_2	5.00 SLPM	5.00 SLPM	5.00 SLPM	5.00 SLPM			5.00 SLPM	5.00 SLPM
LOW O_2	0.2 SLPM	0.2 SLPM	0.2 SLPM	0.2 SLPM				
HIGH O_2					4.50 SLPM	4.50 SLPM		
H_2						6.75 SLPM		
TIME	10 MIN	10 MIN	20 MIN	5 MIN	3 MIN	144 MIN	30 MIN	10 MIN

Furnace at ISRC (CMOS)

- Model No : SELTRON CO. SHF - Series
  - Annealing, Wet Oxidation, Dry Oxidation, Reflow, $POCl_3$, Drive-in, Alloy
  - Wet oxidation
    - Gas : H_2 , O_2 , N_2
    - Process temp. : 800~1000 ℃
    - Wafer size/quantities : 6″ or 4″ wafer/ 1~25
    - Temperature uniformity : ±1 ℃
    - Oxide thickness uniformity : ±1%

Furnace at ISRC (MEMS)

- Model No : Sungjin Semitech JSF-2000-T43
  - Annealing , Wet oxidation , Reflow , $POCl_3$
  - Wet oxidation
    - Gas : H_2 , O_2 , N_2
    - Process temp. : 900~1000 ℃
    - Wafer size/quantities : 4"wafer/ 1~25
    - Temperature uniformity : ±1 ℃
    - Oxide thickness uniformity: ±1%

Furnace at ISRC (mini)

- Model No : Seoul Electron SMF-800
  - Dry oxidation, Annealing, Alloy
    - Dry Oxidation : <2000Å, 1000℃ (gas : N_2, O_2)
    - Annealing : N+, P+ annealing, <1000℃

RTP/RTA at ISRC (CMOS)

- RTP (Rapid Thermal Process)
  - Model No : NYMTECH.CO., RTA200H-SVP1
    - RTA (Rapid Thermal Annealing),
      RTO (Rapid Thermal Oxidation),
      RTN (Rapid Thermal Nitridation)
    - Rapid annealing : < 1250℃
    - Temperature uniformity : ± 2.0℃
    - MFC (N_2, O_2, Ar, NH_3)

RTP (Rapid Thermal Process)

- RTA (Rapid Thermal Annealing)
  - Model No : Korea Vacuum Tech., KVRTP-020
    - Annealing, Alloy
    - Wafer Size : 4"~6"wafer, chip
    - Temperature uniformity : ±5℃
    - Process time : < 60sec

RTA (Rapid Thermal Annealing)

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- K. A. Shaw, Z. L. Zhang, and N. C. MacDonald, “SCREAM I: A single mask, single-crystal silicon, reactive ion etching process for microelectromechanical structures,” *Sens. Actuators A*, vol. 40, p. 63-70, 1994